Solef®


SOLVAY

asking more from chemistry®

# Solef® PVDF

## for Li-Ion Batteries

SPECIALTY POLYMERS

# Solef® PVDF for Binders to Improve Battery Performance

Lithium batteries are a challenging application for most polymeric materials, as they demand long-term reliability as well as chemical and electrochemical resistance in the specific chemical environment of Li-ion cells. In the case of automotive applications, higher temperature performance is also required.

Solef® PVDF is a partially-fluorinated, semi-crystalline polymer with excellent thermo-mechanical and chemical properties. It brings many advantages to the lithium battery industry when used as a binder in the formulation of electrodes as well as in the design of the separator.

Solef® PVDF is already well assessed in many specialty applications such as oil and gas, semiconductors, membranes for water filtration, plumbing, architectural coatings and photovoltaics.

- Solef® PVDF is electrochemically stable in the full range of voltage between 0 and 5 V vs Li+/Li, which guarantees its safe use in the electrochemical environment of the lithium cell.
- Thermogravimetric analysis shows that Solef® PVDF resins are stable at high temperature: no thermal degradation occurs below 420 °C for short-term treatments.
- The shelf life of Solef® PVDF is infinite. In accordance with ISO 9080 extrapolation standards, Solef® PVDF pipes are stable for more than 50 years under 25 MPa at room temperature.

## Solef® PVDF Grades

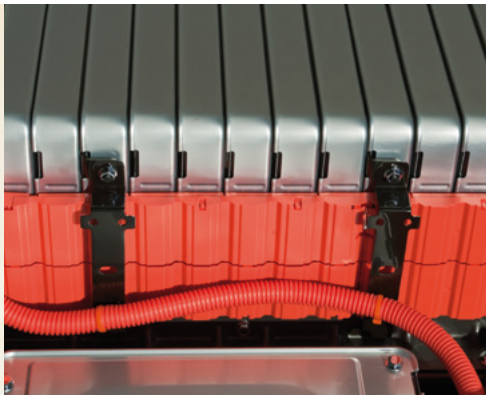
In order to achieve targeted chemical resistance it is important to choose the right Solef® PVDF grade. Thanks to its high crystallinity levels, homopolymer PVDF offers high resistance in typical electrolytes used in lithium batteries. PVDF copolymers, characterized by lower crystallinity, are soluble in a wider range of solvents and show different levels of swelling in organic carbonates. This property makes them suitable for manufacturing the separator in gel polymer type batteries.

## High Purity

The high purity of Solef® PVDF is a guarantee for enhanced safety. Solef® PVDF has been used for more than 15 years in the high purity industry, including many semiconductor applications. Therefore, Solvay Specialty Polymers has consolidated its experience in guaranteeing a very low level of contamination in Solef® PVDF resins. Strict production conditions and quality control rules enable Solvay Specialty Polymers to reach a strong position among today's semiconductor industry leaders.

## Innovation from Solvay

The R&I expertise of Solvay Specialty Polymers in fluorinated chemistry and polymerization technology is continuously focused on the development of new tailored solutions in order to fulfill increasing requirements for safety and performance in the growing lithium batteries market.

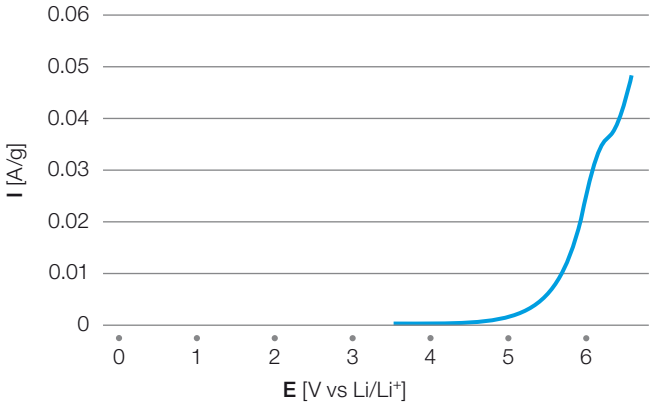


# Portfolio of Grades – General Properties

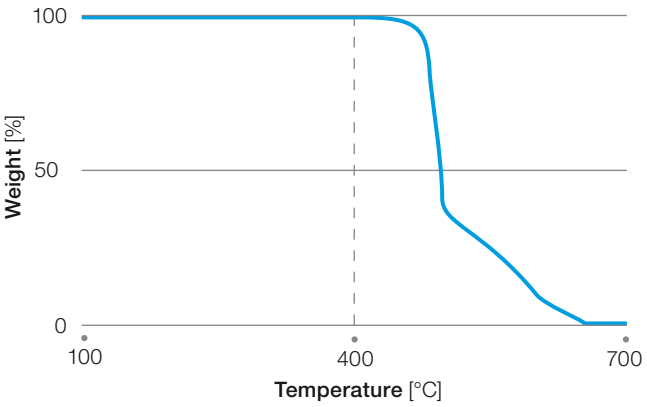
| | | PVDF Homopolymer | Modified PVDF | | | |
|---|---|---|---|---|---|---|
| | | **Solef® 6020** | **Solef® 5120** | **Solef® 5130** | **Solef® 5140** | |
| **Typical properties** | **Units** | 2nd generation binder | 3rd generation binder for automotive application (or for high adhesion) | 3rd generation binder for cathode and anode with highest performances | New grade for higher specific energy electrodes | **Test Method** |
| Molecular weight | Da | 670,000 – 700,000 | 570,000 – 600,000 | 1,000,000 – 1,100,000 | > 1.2 M | GPC* |
| Melting point | °C | 170 – 175 | 158 – 166 | 158 – 166 | 158 – 166 | STM D3418 |
| Glass transition ($T_g$) | °C | – 40 | – 40 | – 40 | – 40 | DMTA |

** Molecular weight data were obtained by gel permeation chromatography in dimethylacetamide (DMAC), calibrated using a polystyrene standard. The results are useful for a relative comparison.*
*Typical property values are reported in this document. They should not be interpreted as material specifications.*

### Electrochemical stability of Solef® PVDF homopolymer




### Thermogravimetric analysis of Solef® PVDF homopolymer





# Binders for Stable Electrodes

Among other polymers, Solef® PVDF is one of the preferred choices as binder material for electrodes thanks to its stable and reliable performance.

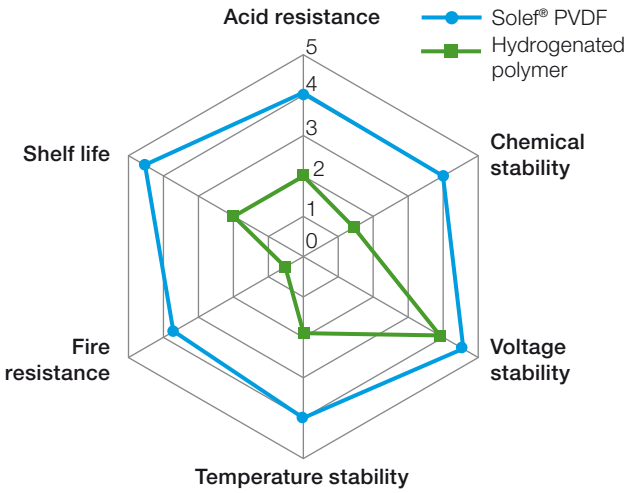
In particular Solef® PVDF guarantees:

- Electrochemical stability from 0 to 5 V vs $Li^+/Li$
- Solubility in NMP for easy processing
- Chemical resistance in the electrolyte
- Suitable cohesion between active materials
- Durable adhesion to the current collector

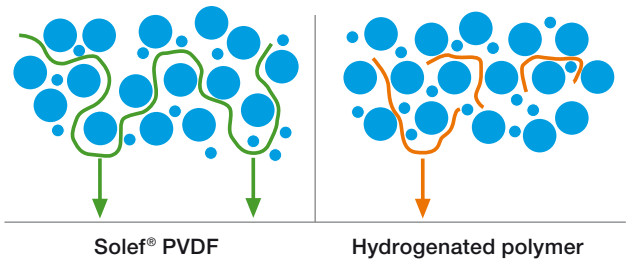
Adhesion is a key property which determines final performance of batteries, especially in the long term. A good binder guarantees the homogeneous dispersion of active materials and conductive carbon together with stable bonding to the metallic collector.

Various tests have been conducted to evaluate the binder effect. Cathodes have been prepared from NMP slurry in standard conditions ($LiCoO_2$ as active component, 5 % carbon black and a fixed amount of Solef® PVDF), then coated onto an aluminum foil and dried in oven at 130 °C. Adhesion has been measured by peeling test following ASTM D903.

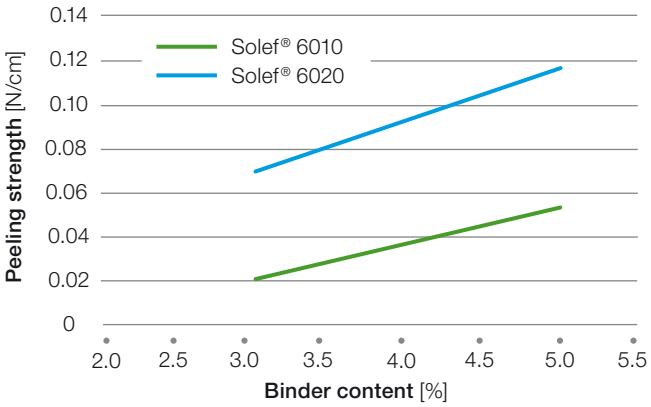
It is possible to notice the effect of molecular weight and binder content on the mechanical consistency of electrodes. The temperature of drying, the chemistry and quantity of active material as well as post-treatments all play a role in the determination of adhesion performance and may be optimized for improving electrodes quality.




## Adhesion comparison




## Adhesion to cathode with $LiCoO_2$



# Solef® PVDF Grades for xEV Traction Batteries

Solvay Specialty Polymers has taken advantage of its expertise in fluorine chemistry and polymerization technologies for designing a new generation of fluoropolymers, Solef® 5000 series. This high-performance fluoropolymer class is designed for use as binder and is especially tailored for high-demanding xEV battery applications, where it is necessary to guarantee best performance during battery operation.

## Solef® 5130

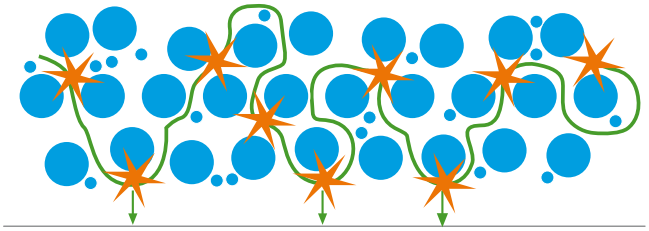
Solef® 5130 combines the effect of ultra-high molecular weight with the benefit of the polar functional groups distributed in the polymer chain.

The reinforced intermolecular interactions between polymer, active materials and current collector result in increased performance in terms of adhesion and chemical resistance in the electrolyte. These effects are especially translated for xEV batteries into:

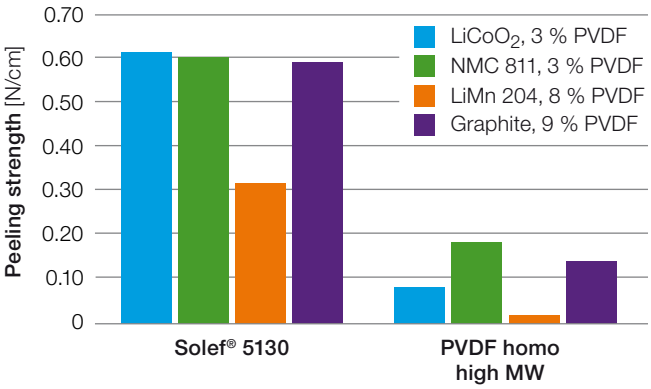
- higher energy density
- better power performance
- longer cycle life

The polymer has been tested in combination with different active materials (LCO, LFP, NMC, NCA, etc.), and graphite for anode has been considered. In all cases Solef® 5130 shows superior adhesion properties compared with PVDF standard homopolymer, with high MW. It is therefore possible to significantly reduce binder content, giving access to higher energy density as well as lower internal resistance.

### Reinforced intermolecular interactions



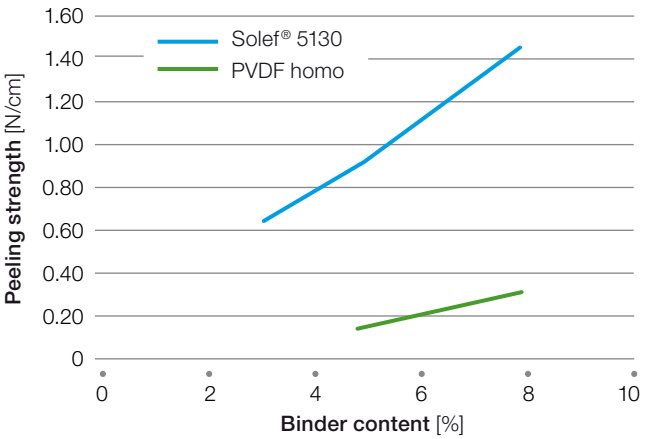

### Adhesion to electrodes

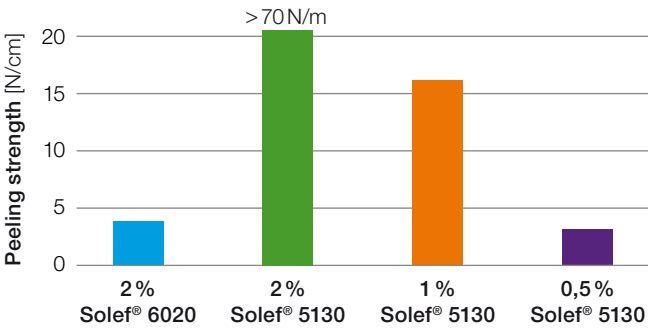



Electrodes have been prepared with standard conditions from NMP solutions, then coated onto a metal foil and dried in an oven at 130 °C. Adhesion has been measured by peeling test following ASTM D903.

Examples obtained by reducing binder content with $LiFePO_4$ and $LiCoO_2$ as active materials are reported.

### Adhesion to cathode with $LiFePO_4$




## Formulation [%wt]

| PVDF | Super C65 | LCO |
|---|---|---|
| 2 | 2 | 96 |
| 1 | 2 | 97 |
| 0,5 | 2 | 97,5 |

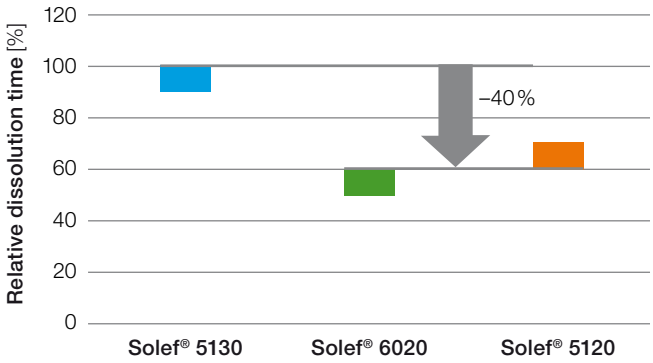
*Slurry TSC 70 %, electrode porosity 30 %, thickness 70–80 µm*

## Solef® 5120

Solef® 5120's underlying concept is based upon the technology of Solef® 5130. It is especially designed for customers with very high demand for such higher processibility as is given by short and rapid dissolution time as well as fast coating. Within the polymer chain Solef® 5120 features the unique combination of a well-distributed polar functional group, with a tuned molecular weight which ensures fast dissolution and medium solution viscosity.

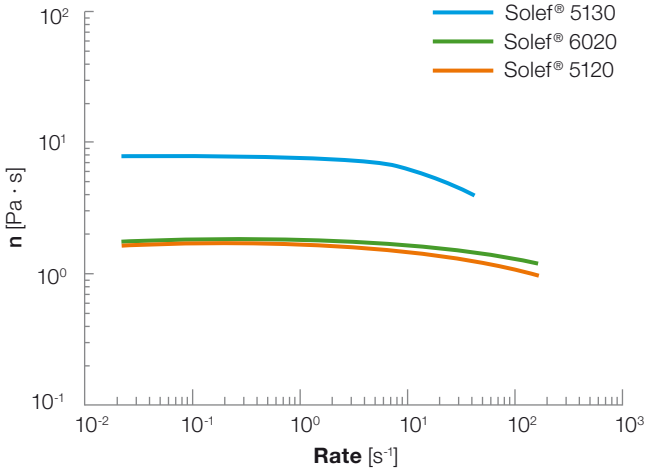
- Fast Dissolution: compared to Solef® 5130, the dissolution time of Solef® 5120 is significantly reduced by up to 40 %
- Apart from fast dissolution, Solef® 5120's medium rheological property supports for easy slurry preparation, high coating speed, etc.
- A higher solid content can be achieved by using Solef® 5120, which can reduce the usage (cost) of NMP and, more importantly, enhance adhesion of the electrode.

## Dissolution time




*8 % PVDF (weight) in NMP. Relative dissolution time uses dissolution time of Solef® 5130 as reference.*

## Solef® PVDF grades in NMP



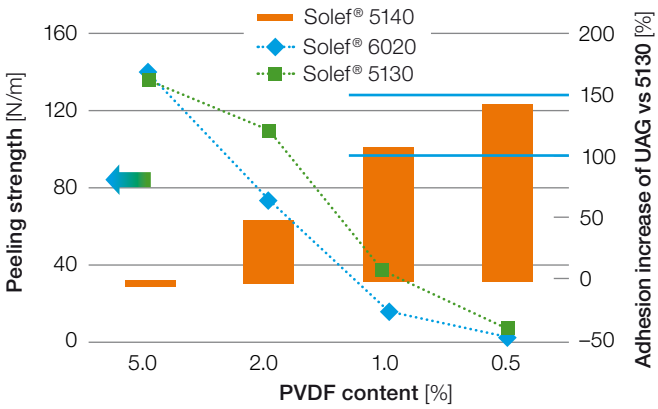

*NMP solutions: 8 % PVDF (weight), 25 °C*

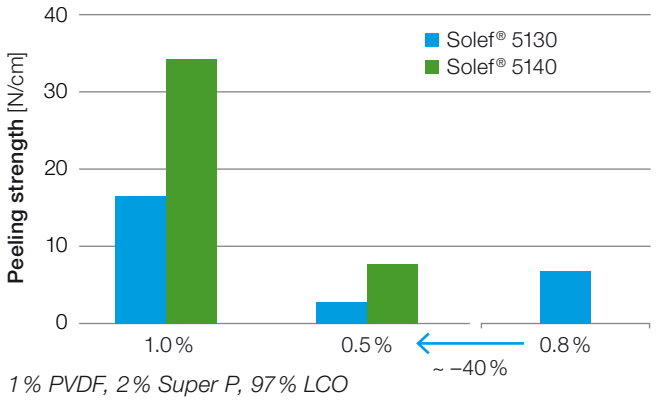
## Solef® 5140

Solef® 5140 is the new binder, prepared using a unique proprietary polymerization technology that allows Solvay to chemically modify the PVDF polymer and achieve ultra-high molecular weight in a tightly controlled process. These features result in enhanced adhesion and cohesion properties required in high energy electrode binder formulations for xEV battery applications.

New Solef® 5140 offers the greatest cohesion between the active material particles as well as the conductive agents to ensure longer life cycle and achieve higher energy density with an even lower binder addition than ever before.

- Highest adhesion: compared to Solef® 5130, adhesion (peeling strength) of cathodes prepared with Solef® 5140 is appreciably increased, especially at low binder content. As a result, much lower content is needed to reach the same adhesion level as Solef® 5130




*1 % PVDF, 2 % Super P, 97 % LCO*
*0.5 % PVDF, 2 % Super P, 97.5 % LCo*

## Battery Performance

PVDF standard grades such as Solef® 6020 are recognized on the market and already offer stable performance when utilized as binders for consumer application cathode and anodes.

For the automotive industry it is necessary to assure better performance especially at high discharge depth in the case of electric vehicles (EV), while stability at higher current rates for short cycles and lower depth of discharge is requested for hybrid electrical vehicles (HEV).

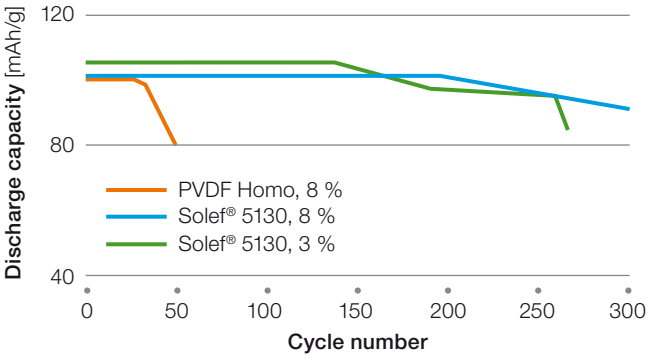
All advantages of Solef® 5130 may be appreciated when reduced binder content is utilized for high energy applications: cells are characterized by higher capacity and, at the same, time long life is guaranteed.

It can be noted that the initial capacity is increased by more than 5 % with a lower binder content. In our testing this percentage increases significantly after 50 cycles.

When high power performance is needed Solef® 5130 provides still more stable performance with time. An example of life cycle improvement obtained with the new polymer is shown on the following page.

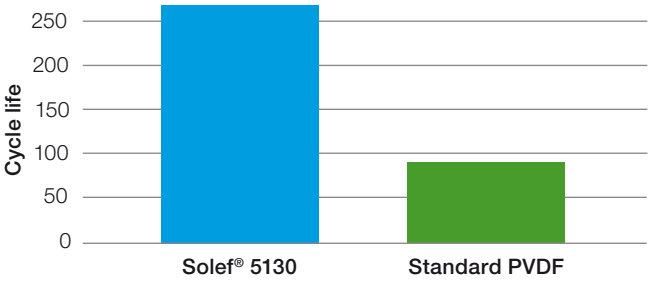
*Electrodes and coin cells*

### Cycle life for energy applications



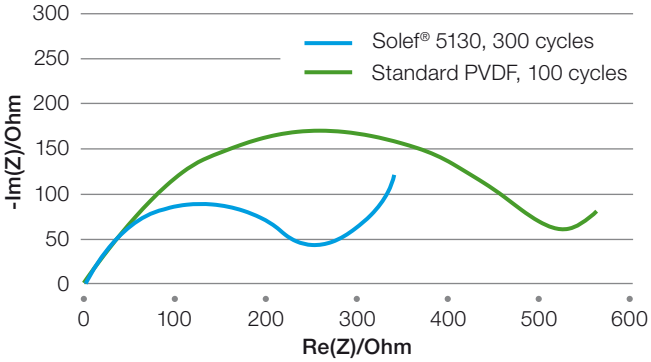

*Galvanostatic cycles on coin cell test samples 1C, 2.5 – 4.0 V; 80 % DoD at RT; electrode composition: PVDF binder, 10 % super P, $LiFePO_4$; discharge capacity is normalized for electrodes weight.*

### Cycle life for power applications




*Galvanostatic cycles on coin cell test samples 2C, 2.5 – 4.0 V; 40 % DoD at RT; electrode composition: 8 % PVDF binder, 10 % super P, 82 % $LiFePO_4$; cycle life: cycle number when cell capacity reaches 80 % of the initial capacity.*

### Impedance after cycling



## The Longer Life Obtained with Solef® 5130

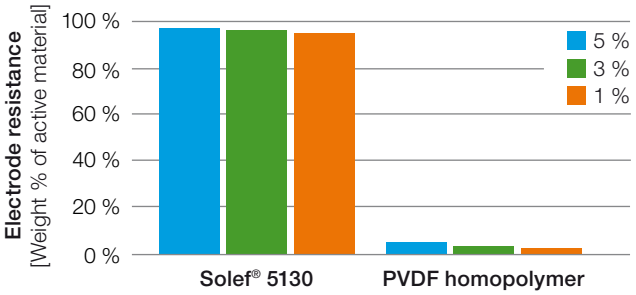
How can Solef® 5130 guarantee the constancy of its improved performance?

An important aspect linked to long-term stability is the chemical resistance in the aggressive environment of a lithium-ion cell, which contains organic carbonates and lithium salt. Especially at high temperature the weight uptake of Solef® 5130 is very low, as reported in the following paragraph. Molecular weight plays an important role in determining this property.

The breakthrough in term of adhesion properties in harsh conditions is linked to the chemical nature of the polymer. In order to demonstrate this aspect, a stability test following immersion in the electrolyte was conducted. Cathodes prepared with differing homopolymer PVDF and Solef® 5130 binder content s were dipped in the electrolyte mixture (EC/DMC 1:1) at 90 °C for 5 days. The resistance of electrodes once immersion was determined by comparing the weight of the active material retained on the metal collector before and after the test.

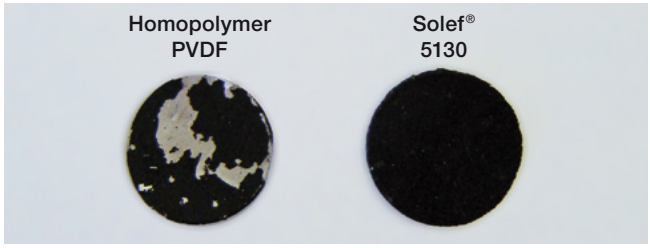
Although the test conditions (free electrode film dipped into an excess of electrolyte) are much more severe than those in a real battery, this can be taken as an indicator of the stability given by the binder. Solef® 5130 demonstrates excellent performance, ensuring long-term battery stability where other binder grades do not.

### Cathode – $LiCoO_2$ – active material




### Binder stability in electrolyte immersion

*after treatment of coin cells at 85 °C for 2 days*




*For example, coin cell test samples have been stored at 85 °C for 2 days. The visual appearance of electrodes is reported in the picture. This result can be easily scaled-up on pouch or prismatic cells.*

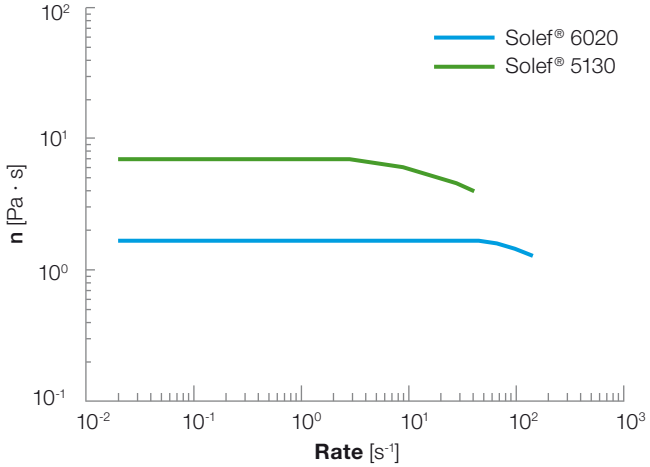
# Processing Information

Processing is a key factor for the lithium battery industry. Some evaluations have been performed for better understanding the parameters to be controlled as well as to optimize processing and performance of PVDF.

The first step of electrodes manufacturing is the dissolution of PVDF in an organic solvent such as NMP. Certain guidelines may be taken into consideration for improving the efficiency of this process.

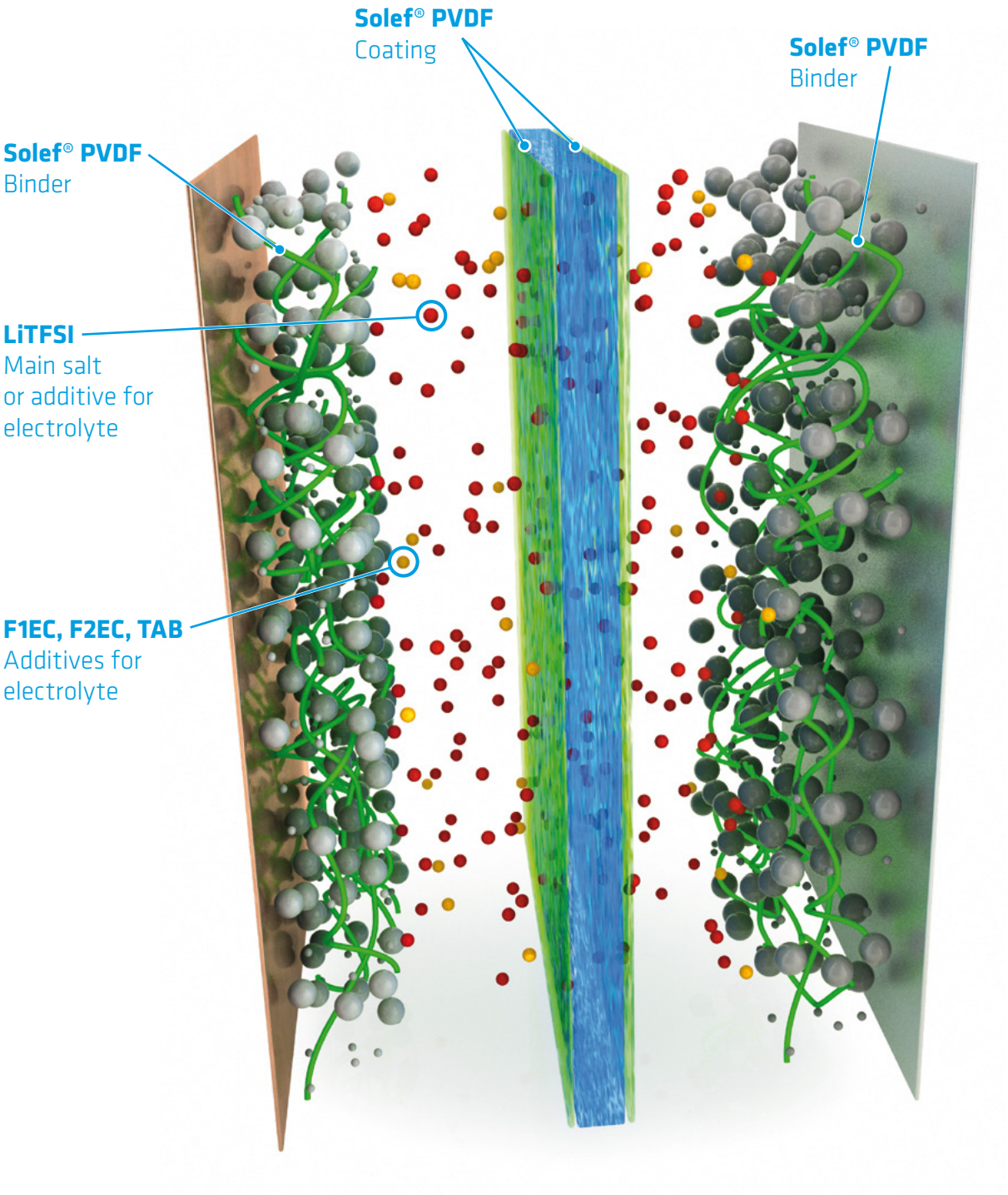
- The method for adding the powder to the solution plays a major role in dissolution ease and duration: in particular, it is advised to that the powder be slowly added to the solution during stirring.
- Mixing speed, geometry of the stirrer and temperature of the solution play key roles in kinetics dissolution. It is advised to give enough time to the polymer to dissolve completely in the solvent; a slight heating of the solution can improve dissolution time.
- It is important to use dry materials and solvents and to operate in a dry environment so as to improve the dissolution process.

**Solef® PVDF grades in NMP**




*Flow curves measured by rheometer RFS III; T = 25 °C, concentration 8 % w/w*

# Solvay High Performance Materials for Batteries



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