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 are 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 before 420 °C for short term treatments.
- The shelf life of Solef® PVDF is infinite. According to ISO 9080 extrapolation standard, Solef® PVDF pipes are stable for more than 50 years under 25 MPa at room temperature.

Solef® PVDF Grades

It is important to choose the right Solef® PVDF grade in order to achieve the targeted chemical resistance. 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 make them suitable for manufacturing the separator in gel polymer type batteries.

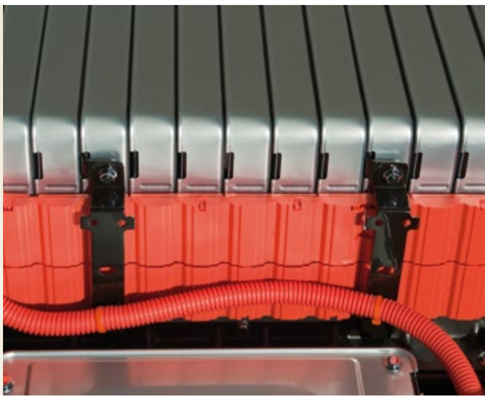
High Purity

The high purity of Solef® PVDF is a guarantee for more safety. The 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 on how to guarantee a very low level of contaminations in Solef® PVDF resins. Strict production conditions and quality control rules enable Solvay Specialty Polymers to reach a strong position among the leaders in the semiconductor industry.

Innovation from Solvay

The R&D 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.



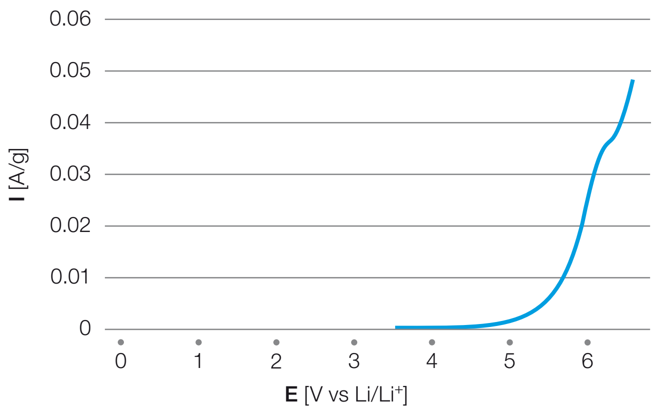


Portfolio of Grades – General Properties

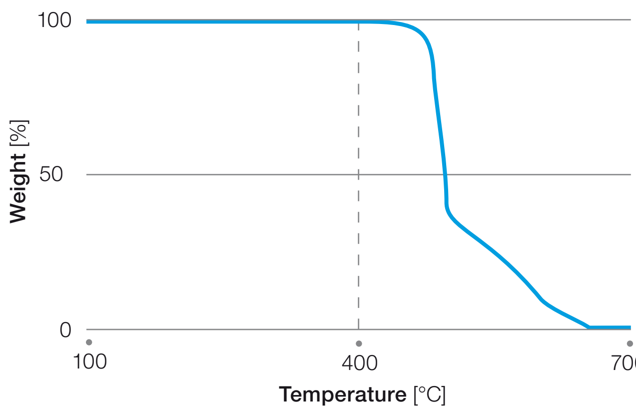
Properties	Units	PVDF Homopolymer		Modified PVDF	PVDF Copolymer	Test Method
		Solef® 6010	**Solef® 6020**	**Solef® 5130**	**Solef® 21216**	
		1st generation binder	2nd generation binder and porous separator	3rd generation binder for automotive application (or for high adhesion)	Flexible binder and gel polymer separator	
Typical properties						
Molecular weight	Da	300,000 – 330,000	670,000 – 700,000	1,000,000 – 1,200,000	570,000 – 600,000	GPC*
Thermal properties						
Melting point	°C	170 – 175	170 – 175	158 – 166	130 – 136	ASTM D3418
Heat of fusion (ΔHf)	J/g	58 – 66	55 – 65	40 – 48	20 – 28	ASTM D3418
Glass transition (Tg)	°C	– 40	– 40	– 40	– 40	DMTA
Tensile properties at 23 °C						
Modulus	MPa	1,700 – 2,500	1,300 – 2,000	1,000 – 1,500	400 – 600	ASTM D638 1 mm/min
Electrical properties						
Volume resistivity	Ohm · cm	$\geq 1 \cdot 10^{14}$	$\geq 1 \cdot 10^{14}$	$\geq 1 \cdot 10^{14}$	$\geq 1 \cdot 10^{14}$	ASTM D257 DIN 53483

** 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.

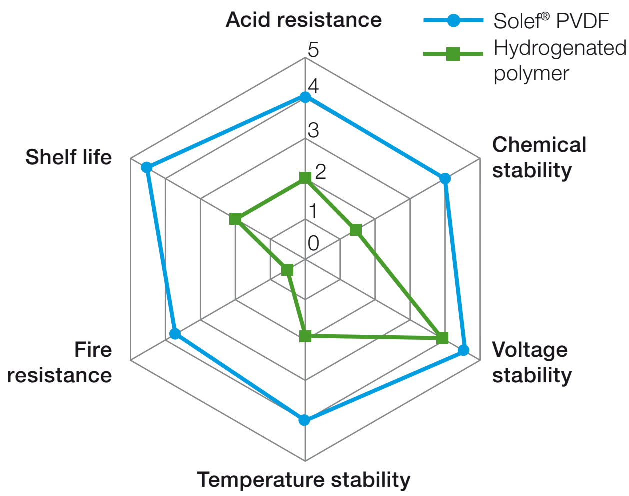
In particular Solef® PVDF guarantees:

- 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

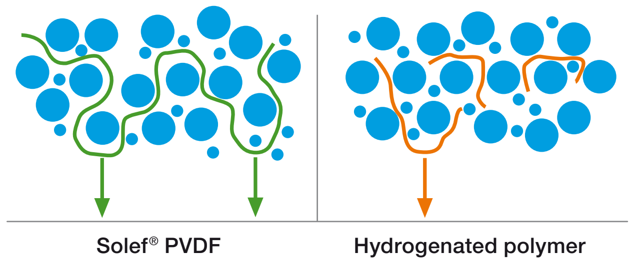
Adhesion is a key property which determines final performance of batteries especially at long term. A good binder guarantees the homogeneous dispersion of active materials and conductive carbon together with stable bonding to the metallic collector.

In order to evaluate the binder effect, some tests have been performed. Cathodes have been prepared from NMP slurry in standard conditions ($LiCoO_2$ as active component, 5 % of 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.

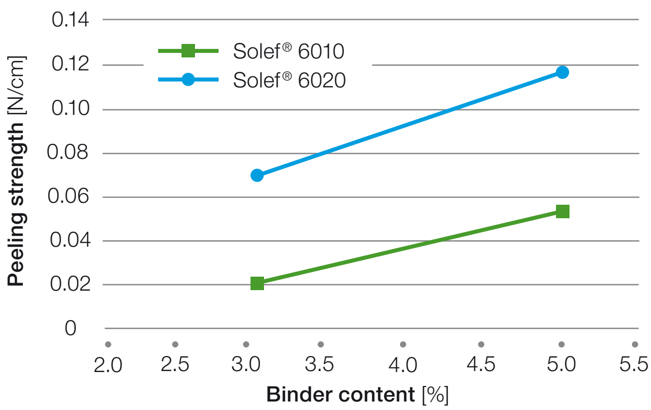
It is possible to notice the effect of molecular weight and binder content on mechanical consistency of electrodes. The temperature of drying, the chemistry and quantity of active material as well as post-treatments play also a role in the determination of adhesion performance and may be optimized for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



Adhesion comparison



Adhesion to cathode with $LiCoO_2$



New Solef® 5130 for High Energy and Large Format Cells

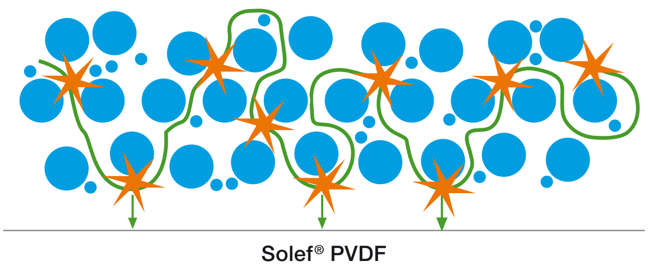
Solvay Specialty Polymers has taken advantage of its expertise in fluorine chemistry and polymerization technologies for designing a new generation of fluoropolymers, Solef® 5130. This high-performance fluoropolymer is designed for use as a binder and is especially tailored for high-demanding applications, where it is necessary to guarantee best performance during battery operation.

As result, the new 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 metal collector result in increased performance in terms of adhesion and chemical resistance in electrolyte. These effects are translated into higher energy density, better power performance and longer cycle life of batteries for the automotive industry.

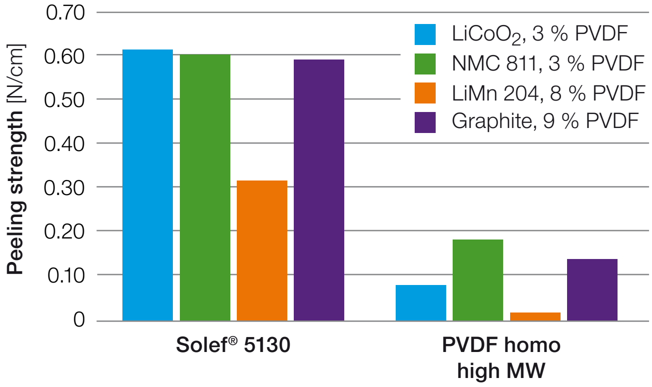
The polymer has been tested in combination with different active materials. Especially new oxides, which find an increasing interest in large battery applications, and graphite for anode have been considered. Electrodes have been prepared with standard conditions from NMP solutions, then coated onto a metal foil and dried in an oven at 130 °C. Adhesion has been measured by peeling test following ASTM D903. In all cases Solef® 5130 shows superior adhesion properties compared with PVDF standard homopolymer with high MW.

Therefore it is possible to significantly reduce binder content, giving access to higher energy density as well as lower internal resistance. An example obtained by reducing binder content with $LiFePO_4$ as active material is reported.

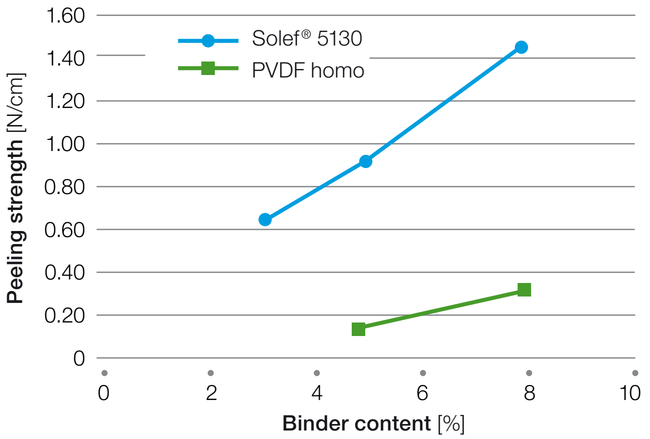
Reinforced intermolecular interactions



Adhesion to electrodes



Adhesion to cathode with $LiFePO_4$



Battery Performance

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

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

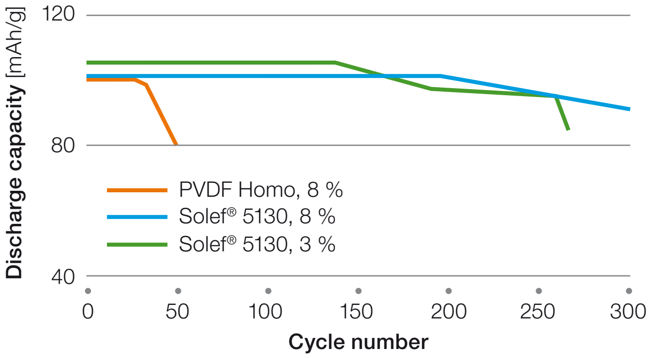
All advantages of Solef® 5130 may be appreciated when reduced binder content is utilized for high energy applications: cells are characterized by higher capacity and at the same time long life is guaranteed.

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

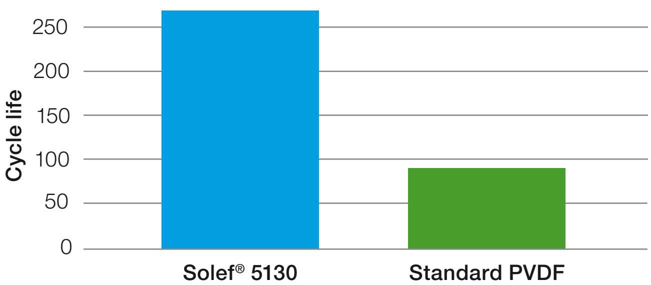
Electrodes and coin cells

Cycle life for energy applications



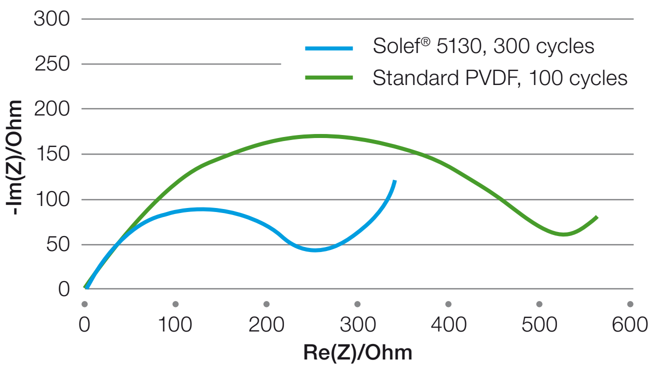
Galvanostatic cycles on coin cell test samples 1C, 2.5 – 4.0 V; 80 % DoD at RT; electrode composition: PVDF binder, 10 % super P, $LiFePO_4$; discharge capacity is normalized for electrodes weight.

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

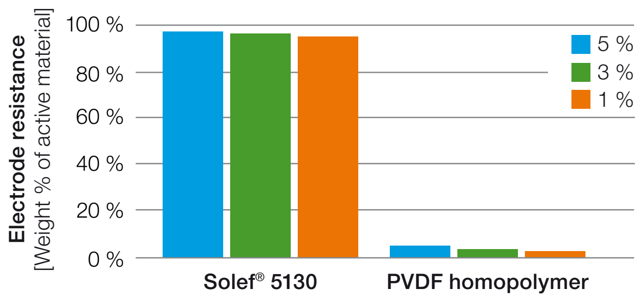
How can Solef® 5130 guarantee the constancy of its improved performance?

An important aspect which is linked to the 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 test of stability after immersion in the electrolyte was performed. Cathodes prepared with different binder content of homopolymer PVDF and Solef® 5130 were dipped in the electrolyte mixture (EC/DMC 1:1) at 90 °C for 5 days. The resistance of electrodes after immersion was determined by comparing the weight of the active material retained on the metal collector before and after the test.

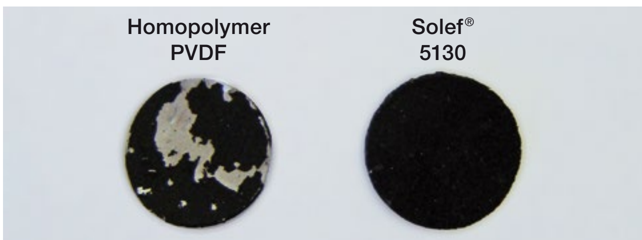
Although the test conditions (free electrode film dipped in an excess of electrolyte) are much more severe than those in a real battery, it can be taken as an indicator of the stability given by the binder. Solef® 5130 demonstrates excellent performance, ensuring long-term battery stability, where other 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 and the visual appearance of electrodes is reported in the picture. This result can be easily scaled-up on pouch or prismatic cells.

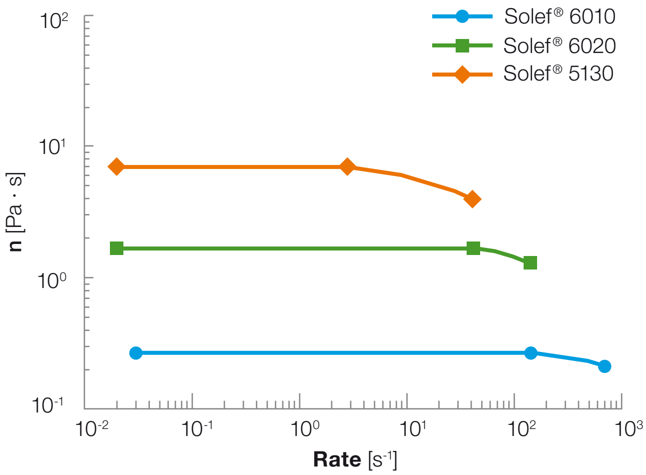
Processing Information

Processing is a key factor for the lithium battery industry. Some evaluations have been performed for a better understanding of the parameters to be controlled in order 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. Some guidelines may be taken into consideration for improving the efficiency of this process.

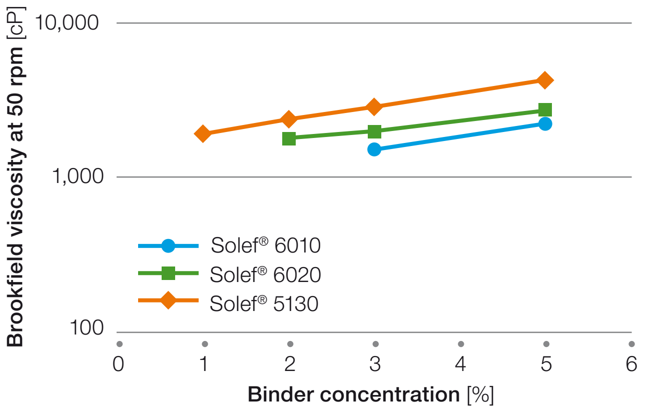
- The method for adding the powder to the solution plays a major role in dissolution ease and duration: in particular it is advised to slowly add the powder to the solution while stirring.
- Mixing speed, geometry of the stirrer and temperature of the solution play key roles in the kinetics of dissolution.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

Solef® PVDF grades in NMP



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

Slurry viscosity – $LiCoO_2$



PVDF grade, concentration of the solution and temperature are key factors in determining the solution viscosity. Slurry viscosity is furthermore affected by the chemical nature and the concentration of active materials, as well as slurry viscosity. It is therefore recommended to optimize PVDF concentration and slurry formulation in order to reach suitable processing conditions. For example, some results of slurry viscosity are reported, where slurries have been prepared with the same active material ($LiCoO_2$) but with different polymer content. It may be also necessary to optimize the total solid content of the slurry in order to obtain the targeted slurry viscosity for the coating process. Besides, the nature of active materials and its particle size also play an important role in the determination of slurry viscosity.

Slurry for electrodes coating

Specialty Polymers

Worldwide Headquarters
SpecialtyPolymers.EMEA@solvay.com
Viale Lombardia, 20
20021 Bollate (MI), Italy

Americas Headquarters
SpecialtyPolymers.Americas@solvay.com
4500 McGinnis Ferry Road
Alpharetta, GA 30005, USA

Asia Headquarters
SpecialtyPolymers.Asia@solvay.com
No.3966 Jindu Road
Shanghai, China 201108

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www.solvay.com

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