Solef®

SOLVAY

asking more from chemistry®

Solef® PVDF Aqueous Dispersions

for Lithium Batteries

SPECIALTY POLYMERS

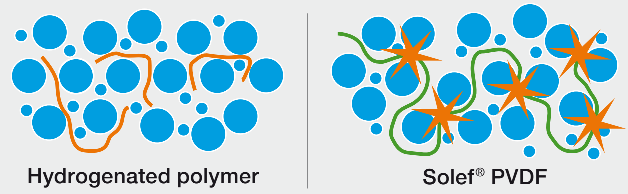
Innovative Polymerization Technology

Solef® PVDF is a partially fluorinated, semi-crystalline polymer with excellent thermo-mechanical and chemical properties. It is well-suited for use as the binder in Lithium Ion Batteries, offering many advantages in the formulation of the electrodes. PVDF is very stable and delivers reliable performance such as:

- Better cohesion between binder and active material
- Improved adhesion to metal collector
- Highly stable functional groups vs. SBR
- Lower binder content for improved energy density
- Higher capacity at high C-rate for improved power performance
- Higher flexibility of the electrodes for thick or conformable (shaped) electrodes
- Longer cycle life

Thanks to these exceptional characteristics, PVDF binders outperform the traditionally used hydrogenated binders.

PVDF for Improved Adhesion



Solef® PVDF Aqueous Dispersions

Solvay Specialty Polymers has developed a new generation of water-based PVDF dispersions with proprietary chemical modification (not blending materials), manufactured via emulsion polymerization.

These innovative materials enable the manufacturing of high performance electrodes through a sustainable process, without the use of NMP solvent, typically used for standard PVDF processing, which requires a solvent recycling system.

Key Advantages

- Environmental friendly technology
- No NMP solvent and related recycling system
- Lower processing temperature for reduced energy consumption
- Higher adhesion and better chemical resistance

Key Characteristics

Solef® PVDF water-based dispersions are stable and have the special feature of nano-size primary particle of PVDF in the shape of spheres:

- Latex viscosity: <5 cps [Brookfield, spindle #1, 60 rpm]
- Solid content of latex: 25–35 % w
- pH: 3–5 (stable to pH adjustment up to 13)
- Stable to shear stress

Solef® PVDF Aqueous Dispersions Grades

According to the specific design of the electrode and the manufacturing process, it is possible to select the most appropriate Solef® PVDF Aqueous Dispersion.

Products are available with processing temperatures between 60 °C and 170 °C.

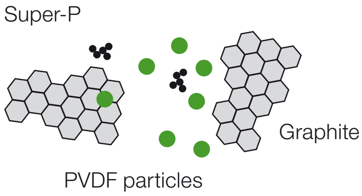
Grade	Crystallinity	Processing Temperature [°C]	Flexibility
Solef® XPH-838	High	> 170	Standard
Solef® XPH-882	Low	140	Good
Solef® XPH-859	None	60	Excellent
Solef® XPH-884	Low	150	Good

Water-based Binding Mechanism Through Film Formation Stage

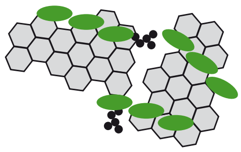
PVDF latex ensures the same type of continuous film binder between active material particles through the thermal process of film formation.

Moreover, the chemical modification in PVDF ensures improved and more stable adhesion in combination with flexibility of the final electrode.

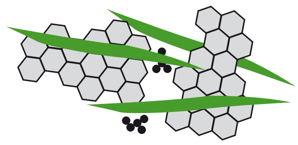
1. **Aqueous slurry**
   Dispersion of AM/binder



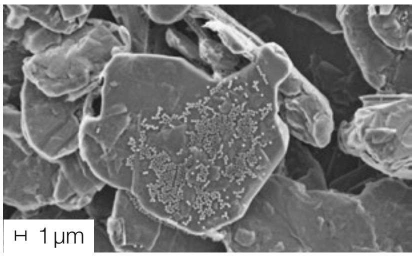
2. **Particles packing and deformation**
   Water evaporation, deformation of aggregated primary particles



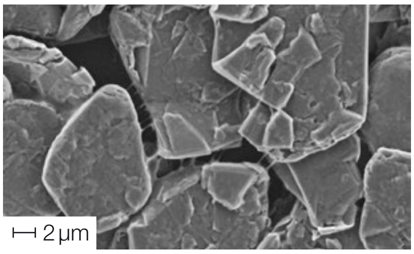
3. **Coalescence**
   Mechanically coherent dry film



Before coalescence
(below film formation temperature)



After coalescence
(above film formation temperature)



Adhesion and Cohesion

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

Solef® PVDF aqueous binders can selectively introduce chemical modification in the PVDF polymer chain to create special adhesion promoting sequences in the polymer. This results in localized higher polarity which in turn is more effective in creating adhesion to current collector and cohesion to active material particles.

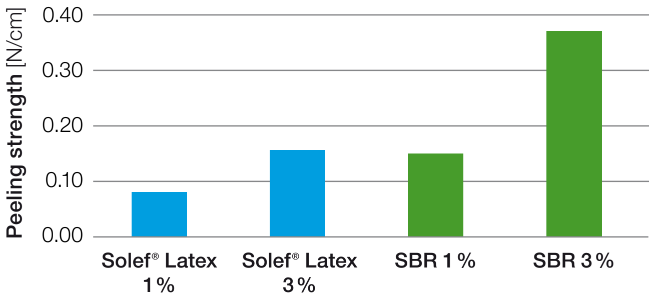
At the same binder weight, adhesion is lower for PVDF than Styrene Butadiene Rubber (SBR) due to difference in specific gravity between a partially fluorinated polymer and a fully hydrogenated polymer (PVDF 1.78, SBR 1.04).

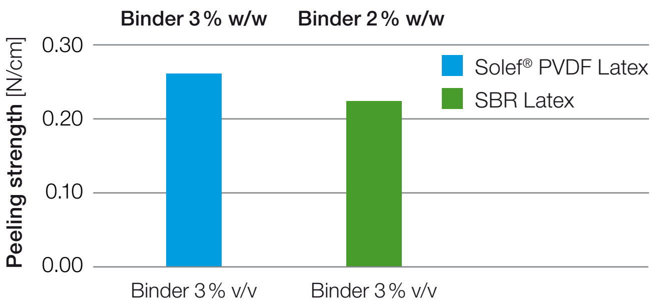
It must be noted that despite the different adhesion values, still electrode quality and appearance are the same and no peeling is observed.

When the same binder volume is considered, results in terms of adhesion are found to be more prositive for PVDF than for SBR.

Taking advantage of the PVDF binder's high adhesion and lower volume at equal weight compared to SBR, reduced amount of binder can be used in the formulation increasing the amount of active material (to exploit the theoretical capacity and energy density of the battery).

Peeling strength of Solef® PVDF Latex vs. SBR

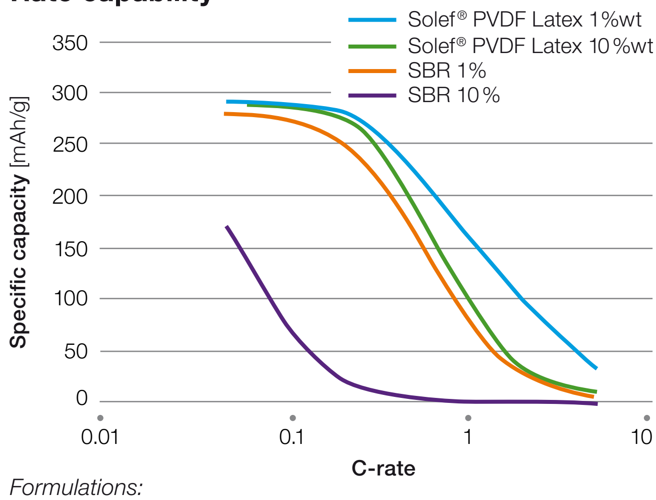




Electrochemical Performance

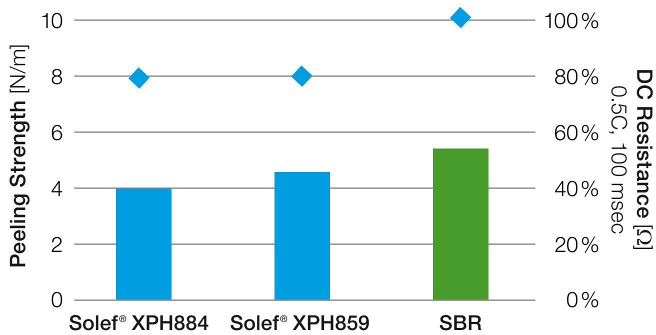
Electrochemical behavior is better than SBR at high C-rate (power density) due to lower internal resistance.

Rate capability



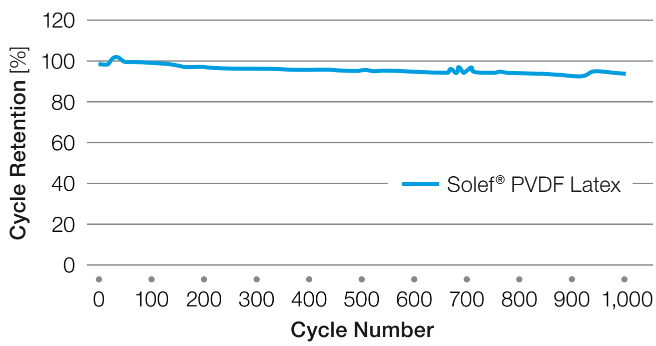
Formulations:
89/1/10 AM/CMC/Binder, 98/1/1 AM/CMC/Binder
Electrode thickness: 60–70 µm, Loading: 1.8 mAh/cm²,
Porosity: about 50 %, not calendered

Anode adhesion and DC resistance



Electrode formulation:
94 SCMG-AR: 3 SuperP: 1,8 CMC : 1,2 Binder
Electrode thickness: 95 µm

Cycle life in fuel cell – 1C – 1000 cycles at RT

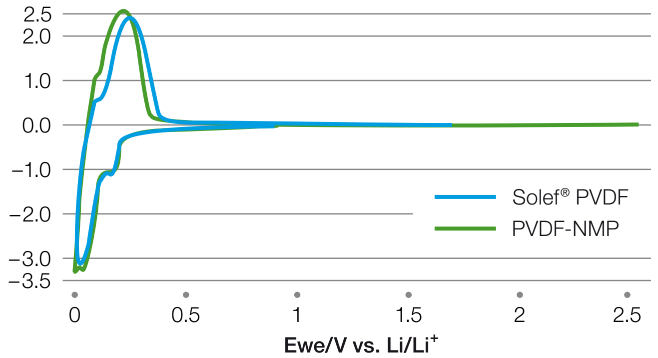


Anode formulation:
94 SCMG-AR: 3 SuperP: 1,8 CMC : 1,2 Binder
Electrode thickness: 95 µm

Electrochemical Stability at Low Voltage

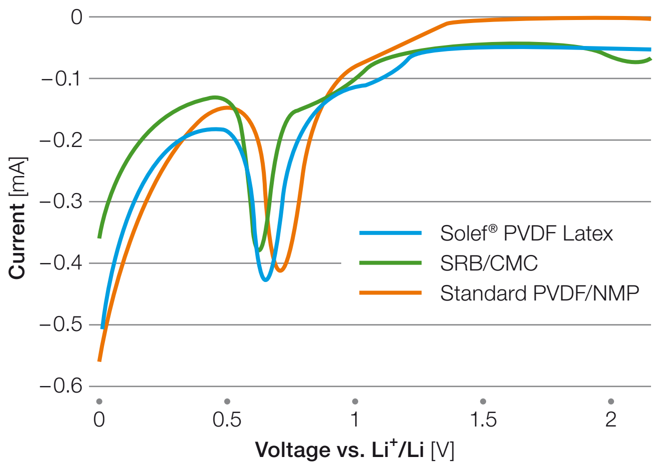
The electrochemical stability at low voltage of Solef® PVDF Latex in comparison to standard PVDF resin/NMP system was assessed by cycling voltammetry. Li metal was used as counter and reference electrode and graphite was used as working electrode, between 0–3 V.

Cyclic voltammetry
Solef® PVDF Latex vs. PVDF-NMP
(WE Graphite, RE and CE Li, 0–3V)



Electrode prepared by Solef® PVDF aqueous dispersion shows the same electrochemical behavior as PVDF-NMP (in terms of SEI formation and lithium intercalation mechanism).

Solef® PVDF aqueous dispersion vs. SBR

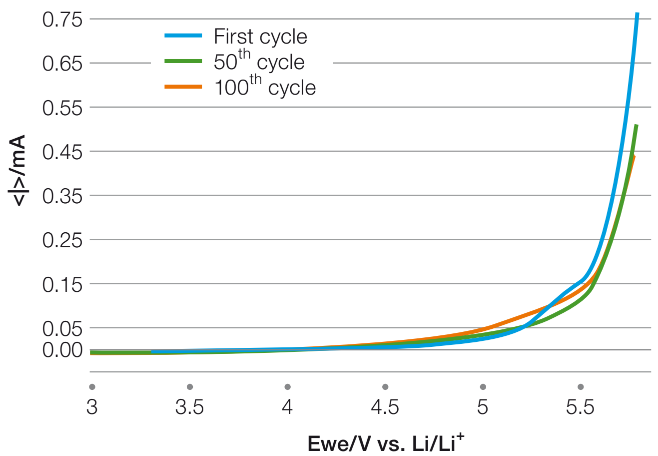


Electrochemical stability at low voltage was checked also for Solef® PVDF aqueous dispersion vs. SBR water-based binder, resulting equivalent for both materials; SEI formation with equivalent mechanisms observed as well.

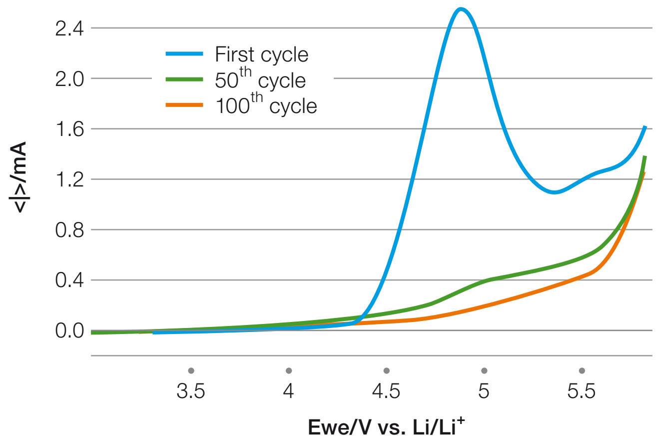
Electrochemical Stability at High Voltage

Electrochemical stability at high voltage was assessed by anodic stripping test between 0 and 6V using SuperP-Binder electrode vs. Li^+/Li.

Solef® PVDF Latex



SBR



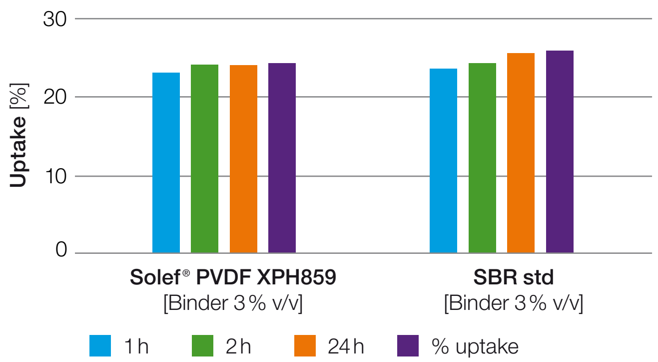
Solef® PVDF Latex shows excellent electrochemical stability up to 5.5V when electrolyte decomposition starts to happen, while extensive decomposition by oxidation at high voltage occurs in the case of hydrogenated binder like SBR.

Swelling in Electrolyte

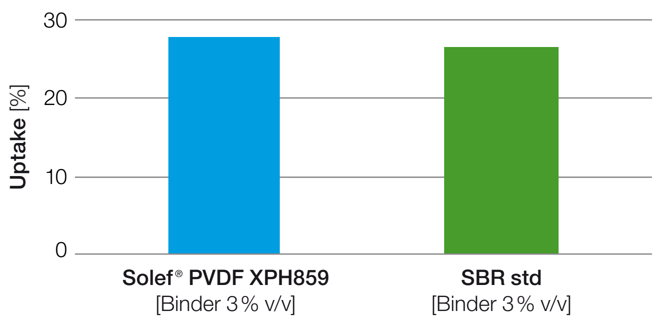
Swelling at different temperatures (24h at RT and 8h at 90°C) in EC/DMC 1/1 was measured on polymer film (obtained from latex by drying and pressing) as well as on electrodes.

The electrode from Solef® PVDF Latex is perfectly stable to both stressful treatments, showing very similar perfomance to SBR electrode, although pure PVDF polymer film is gelified at RT and is dissolved at 90°C.

Swelling at room temperature



Swelling at 90°C

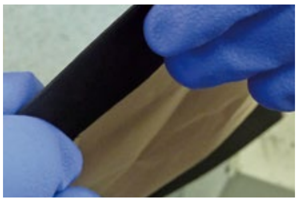


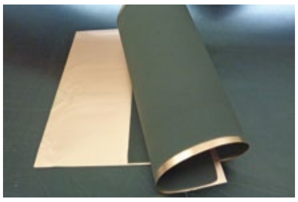
Flexibility

Flexibility is a key property that determines the final performance of batteries. A good binder allows the electrode to be bent in winding or z-fold configuration without cracks forming.

Tests were conducted by bending the electrode 360° around metal bars with 2 mm and 4 mm diameters, and then the bending point was checked for the presence of cracks.

Electrode (Binder: 3 %)	**□: 4 mm**	**□: 2 mm**
SBR	No cracks	No cracks
Solef® PVDF Latex	No cracks	No cracks





Lamination

Good interphase between electrodes and separator is a key factor to reduce internal resistance. Chemical affinity of PVDF with commercial polyolefin separators allows them to laminate together, ensuring a better interface. SBR does not provide this advantage, due to lower polarity, leading to a lack of continuous contact at the interface.

Lamination Polyolefin Separator with Electrode

Solef® PVDF latex	Lamination
SBR latex	No lamination

Processing

Correct processing is a key factor in achieving optimal performance of Solef® PVDF Aqueous Dispersions.

Extensive testing of PVDF Latex used as a binder for negative electrodes was performed using pilot scale equipment (mixing machine, coating machine, online drying, pressing) in EWHA Solvay R&I Center in Seoul, S. Korea to better understand the parameters needing to be controlled in order to optimize processing and performance.

Processing guidelines are available for different active materials.

Slurry Preparation

Thickener ▶ **Water** ▶ **Additive** ▶ **Active Material** ▶ **Binder** ▶

Slurry

Electrode Preparation

Coating ▶ [**Vacuum Dry** ▶ **Post Treatment** — *Low Temperature*] ▶ **Calendering** ▶ **Lamination** ▶

Electrode

1. Mixing Preparation

a) Mixing active materials

- AM + CMC + D.I. water (low speed impeller)
- D.I. water (low and high speed impeller)

b) Adding binder to solution

- Latex

c) D.I. water

- Added step by step to control and achieve viscosity target (v = 2,000 cPs), depending on coating machine in use.

d) Defoaming

- Bubbling occurs at low viscosity and high shear stress mixing conditions, and they can be removed via defoaming during processing.

e) Filtering (as needed)

2. Coating

- Line speed and comma roll gap are optimized to produce a homogeneous coating and the target loading thickness.

3. Drying After Coating

- Key parameters to achieve suitable drying temperature (70 °C) and line speed (exposure time).

4. Thermal Treatment

- Thermal process to generate film formation is a key step in processing. Processing temperatures are noted in technical data sheets.

5. Pressing

- After film formation, pressing is carried out to achieve the target electrode porosity.

Slurry Stability

The electrode preparation may be divided into different mixing steps in order to control slurry in terms of:

- Homogeneity
- Viscosity
- Temperature

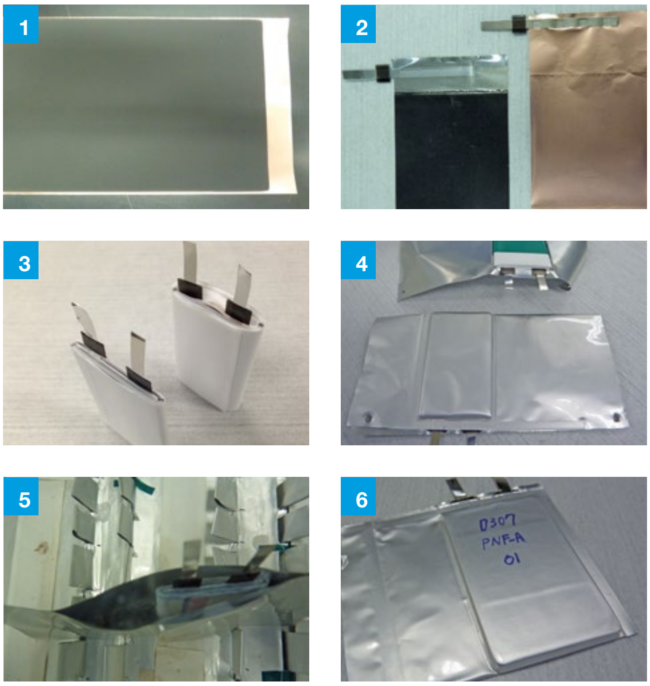
Properly controlling these parameters during processing will ensure slurry stability over a period of months after its preparation; moreover, proper processing is key to achieve good quality of the electrode, as well as highest adhesion and best overall performance of electrodes prepared with Solef® PVDF Latex.

Time = 0

Time = 2 weeks

Pouch Cell System – 500 mAh

Solef® PVDF Aqueous Dispersion as binder at anode was tested in full cell systems, with roll-on 383562 pouch cell configuration.



1. Double-side coated pattern
2. Electrodes contacts (tap-welding)
3. Jelly-rolls (before and after hot pressing)
4. Pouch cell forming
5. Electrolyte filling in vacuum system
6. Pouch cell with safety volume for degassing

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