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Fluoropolymers for the Chemical Processing Industry Applications

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Abstract

Fluoropolymers are very effective in corrosion protection applications due to their exceptional chemical resistance, low permeability to liquid and gases, and excellent strength and toughness at elevated temperatures. Fluoropolymer coatings and liners have been used successfully in a variety of industries for several years. This presentation reviews the performance of fluoropolymers in several chemical environments and describes the industrial case histories. The main focus of this work is the ECTFE resin; the liners manufactured from this resin performed very well for more than 20 years in several industrial applications.

Keywords: liners, plastic, protection, fluoropolymers, ECTFE.

Introduction

The U.S. Federal Highway Administration study (1), initiated by NACE International and released in 2002, shows that the direct cost associated with metallic corrosion in the U.S. is \$276 billion, approximately 3.1% of the nation's Gross Domestic Product. This study also shows that utilities, transportation, and production & manufacturing account for most of the annual industrial corrosion cost.

The use of proper materials can significantly lower the expenses caused by corrosion. Fluoropolymers are suitable for corrosion protection applications due to their excellent chemical resistance to a variety of chemicals over a wide range of concentrations and temperatures, as well as their low permeability, high temperature thermal stability, surface smoothness, high purity, and non-burning characteristics. They can successfully replace metals and in many cases, they are the only viable protection against highly corrosive and aggressive chemicals.

Fluoropolymers can be applied on metals, concrete, or FRP if high mechanical strength is required.

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Description of Fluoropolymers

The first fluoropolymer, polytetrafluoroethylene (PTFE) was discovered by Dr. Roy Plunkett from DuPont in 1938. This discovery was followed by the development of other fluoropolymers in late 40's. Initially, PTFE was used in military applications, but other industrial applications were developed in the late 40's. Most of the thermoplastic fluoropolymers were synthesized in the 50's and 60's, which triggered the development of the corrosion protection applications of these resins.

The fluoropolymers used for corrosion protection can be divided into two groups: fully fluorinated and partially fluorinated polymers. The first group of polymers, also called perfluoropolymers, consists of PTFE, FEP, and PFA. The partially fluorinated polymers, commonly used in the Chemical Processing Industry (CPI) applications, are PVDF, ECTFE, and ETFE. When compared to the partially fluorinated resins, the fully fluorinated polymers have higher upper service temperatures and better chemical resistance at higher temperatures, but lower mechanical properties. The structure of fluoropolymers are as follows:

Polymer	Monomer(s)
<i>Fully Fluorinated Polymers</i>	
PTFE	$\text{CF}_2=\text{CF}_2$
PFA	$\text{CF}_2=\text{CF}_2 + \text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_n-\text{F}$ $n = 1, 2, 3$
FEP	$\text{CF}_2=\text{CF}_2 + \text{CF}_2=\text{CF}-\text{CF}_3$
<i>Partially Fluorinated Polymers</i>	
PVDF	$\text{CF}_2=\text{CH}_2$
ETFE	$\text{CH}_2=\text{CH}_2 + \text{CF}_2=\text{CF}_2$
ECTFE	$\text{CH}_2=\text{CH}_2 + \text{CF}_2=\text{CFCl}$

Table 1: Chemical composition of fluoropolymers

Properties of Fluoropolymers

The C-F bond is the strongest in organic compounds, stronger than C-H or C-C bonds. Since more energy is required to break the C-F bond, fluoropolymers have a very good thermal stability and excellent chemical resistance.

The first fluoropolymer, PTFE, has an extremely high molecular weight and its' melt viscosity is about a million times higher when compared to the other polymers. Because of this extremely high melt viscosity and chain stiffness, the PTFE resin can not be processed using common melt-processable techniques.

The substitution of the fluorine atoms or the addition of side groups, allowed the synthesis of a variety of melt-processable fluoropolymers. These modifications improved the mechanical properties of fluoropolymers, but their chemical resistance and thermal stability were lowered.

There is no single material which will provide sufficient and cost effective corrosion protection. Fluoropolymers, due to their good chemical resistance and thermal stability, are one of the best choices in applications where good corrosion protection is required. In many cases, they are the only viable solution. The advantages of fluoropolymers as corrosion protection liners and coatings can be summarized as follows:

- good chemical resistance & low permeation
- low surface energy
- surface smoothness
 - low friction, excellent scaling and bio-film formation resistance
- high purity
- water repellent, anti-staining
- high temperature thermal stability
- excellent weathering resistance
- exceptional electrical properties
- non-burning & low smoke generation
- excellent UV and visible light resistance
- good light transparency

To choose the right fluoropolymer for a certain application, several performance criteria have to be considered. Table 2 lists the maximum service temperatures of fluoropolymers. This table shows that perfluoropolymers have a much higher temperature limit when compared to the partially fluorinated resins. However, the better mechanical properties of partially fluorinated resins (see table 3) give them a substantial advantage in free-standing structures, including piping systems.

Fluoropolymer	Max Temperature Rating [°C]
PTFE	260
PFA	260
MFA	235
FEP	210
ETFE	175
ECTFE	175
PVDF	150

Table 2: Maximum temperature ratings of fluoropolymers.

Fluoropolymer	T _m (°C)	Elastic Modulus (MPa)
PTFE	> 320	500
Hyflon® PFA	305	600-500
Hyflon MFA	265 - 275	500-400
Halar® ECTFE	240	2000-1500
Solef®/Hylar® PVDF	170	2200-1700

Table 3: Mechanical properties of Solvay Solexis fluoropolymers (2).

It is important to stress that there are substantial differences even between polymers which belong to the same group of resins. There are several grades of PVDF, ECTFE, and perfluoroalkoxy resins. Different grades of the same group of polymers were synthesized in order to get better performance for specific applications. In most cases, the modified grades were obtained by utilizing different co-monomers or by changing polymerization conditions. One of the examples showing the difference between polymers of the same fluoropolymer group is the surface smoothness of perfluoroalkoxy resins. Table 4 shows that the MFA resin has a much smoother surface when compared to the other PFA polymers. This makes this grade a good choice in applications where the elimination of scaling or biofouling is very important.

Material	Rms (Å)
Standard PFA	755
High-Purity PFA	290
MFA	161

Table 4: Surface smoothness of perfluoroalkoxy resins (3).

Chemical resistance & permeability

It is not a main goal of this paper to compare all performance data of fluoropolymers. However, since most of the CPI applications require using materials with very good chemical resistance and low permeation rate, a brief summary of the compatibility of fluoropolymers in different chemicals is included in this work. Table 5 summarizes the performance of fluoropolymers in acids, bases, and oxidizers. With few exceptions, mainly PVDF in strong acids and bases, fluoropolymers perform very well when exposed to these chemicals. Table 6 contains the chemical resistance of the ECTFE and MFA resins to several very aggressive chemical compounds at elevated temperatures. Both resins performed very well in these tests: their weight gain was negligible and the resins retained most of their mechanical properties. Please note that the color change of the Halar surface exposed to concentrated sulfuric and nitric acids did not affect the properties of the ECTFE resin.

	Temp. (°C)	MFA	PFA	PTFE	ECTFE	ETFE	PVDF
ACIDS							
98% Sulfuric	104		+		+	+	S
37% Hydrochloric	104		+		+	+	+
BASES							
50% Sodium Hydroxide	104		+		+	+	A
50% Sodium Hydrosulfide	104		+		+	S	A
OXIDIZERS							
100% Chlorine	93		+		S	S	S
60% Sodium Chlorate	93		+		+	S	S
65% Nitric Acid	93		+		S	A	A
OTHER FLUIDS							
Crude Oil	140		+		+	+	+
Ethanol	100		+		+	+	+

+: Unaffected, S: Slightly Affected, A: Attacked

Table 5: The effect of chemical exposure; 264 hours immersion test.

Chemical Name	ECTFE	MFA	Color After Exposure
37% HCl @100°C	0.2	0.0	ECTFE - light brown
65% HNO ₃ @ 65°C	0.2	0.0	ECTFE - yellow
65% HNO ₃ @ 100°C	0.8	0.0	No discoloration
98% H ₂ SO ₄ @ 140°C	0.2	0.0	ECTFE - black
Oleum - 20% SO ₃ @ 40°C	0.2	0.0	ECTFE - black
NaClO (5% chlorine)@ 100°C	0.0	0.0	No discoloration
NaClO (10-15%) @ 100°C	0.1	0.1	No discoloration
CH ₃ OH @ 65°C	0.6	0.1	No discoloration
CH ₃ OH @ 120°C	0.5	0.0	No discoloration

* The change in tensile modulus, tensile strength at break, yield stress, and elongation was insignificant in all cases

Table 6: 30 day chemical immersion test - Weight Gain [%] (4).

In most of the chemical resistance testing, polymers are exposed to pure reagents or to concentrated compounds. Based on this data, some resins might be excluded from the applications where they are exposed to dilute solutions of the same chemicals. Halar ECTFE performs poorly when exposed to methylene chloride at 40°C and it can not be recommended for corrosion protection in these conditions. However, the ECTFE resin can be successfully used when in contact with 2% CH₂Cl₂ at much higher, 100°C temperature (5).

Good chemical resistance does not always guarantee that parts made from the resin will perform well in specific applications. The other factor which has to be considered is the permeation resistance of the polymer. A high permeation rate through the coating or the liner can cause the chemical attack of the substrate and consequently the failure of the part.

Figure 1 compares the permeation resistance of ECTFE, ETFE, FEP, and MFA fluoropolymers in chlorine (6). This graph clearly shows that the ECTFE resin has the lowest permeation rate of all tested polymers.

The effect of permeation rate on the performance of dual laminate pipes was studied by the Swedish Corrosion Institute (7). The dual laminate pipes, having 1.5 mm thick ECTFE and FEP liners, were exposed to wet chlorine gas at 80-85°C for 2.5 years. These pipes were evaluated after the exposure and the amount of chlorine permeated through the liner was calculated. The SCI testing, summarized in Table 7, determined that the top 0.5 mm of the ECTFE liner was chemically attacked and the FEP resin was not chemically affected at all.

However, it was calculated that the amount of chlorine permeated through FEP was about 30 times higher when compared to the ECTFE resin. As a consequence of its poor permeability, the FEP liner developed blisters and delaminated from FRP. At the same time, the bond strength between the ECTFE liner and FRP was not affected.

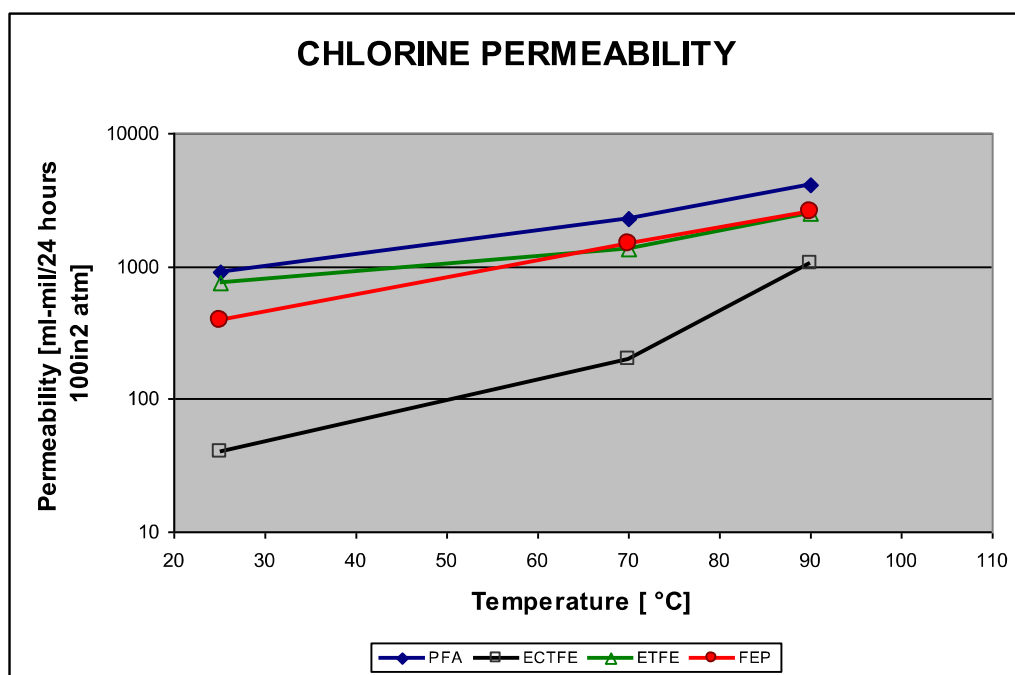


Figure 1: Fluoropolymer films - chlorine permeability.

	FEP/FRP	ECTFE/FRP
Melting Point (0-0.5 mm layer)	260°C	229°C
Melting Point (0.5-1 mm layer)	261°C	240°C
Visual Evaluation	Blister up to 5 mm in diameter, 0.5 - 0.8 mm of the liner depth	Whitening up to 0.5 mm of the liner depth
Total permeated chlorine through the liner	310 g/m ²	10 g/m ²
Bond strength between the liner and FRP after 2.5 years of exposure	Loss of adhesion	Not affected

Conditions: Wet chlorine gas; T=80-85°C, tested for 2.5 years; 1.5 mm thick liners of FEP & ECTFE

Table 7: The Swedish Corrosion Institute testing - evaluation of dual laminate pipes after 2.5 years of exposure to wet chlorine

The permeation resistance depends on the temperature to which the polymer is exposed. For example, PVDF has excellent permeation resistance to small molecules like nitrogen, oxygen, or hydrogen. However, the permeation rate of chemicals through PVDF increases significantly at elevated temperatures (8).

Fluoropolymers applications

There are several application methods and fabrication techniques of fluoropolymers that can be used in corrosion protection applications. The choice of the fabrication technique depends on the particular application and sometimes on the preference of the final user. These techniques include:

- Dispersion coating & solution casting
- Powder coating & rotolining
- Thick sheet structures
- Lined vessels, rail cars, and iso-containers
 - Sheet lining
 - Dual laminates
 - Loose lining
- Piping
 - Dual laminate piping
 - Metal lined piping
 - Thick wall, unsupported piping
 - Dual containment piping
- Tower packing
- Heat exchangers
 - Pumps (diaphragm & ball valve), valves, and fittings
 - Solid parts – injection molded or machined from thick stock shapes
 - Lined parts – transfer molding & fabric backed
- Internals for reactors & scrubbers

The fluoropolymer applications include the semiconductor & electronic, oil & gas, chemical processing, automotive, wire & cable, architecture & building, aerospace, and pharmaceutical industries. This paper focuses on the typical CPI applications where fluoropolymers are used in the production processes or in the storage and transport equipment. These applications include:

- General Corrosion Protection Equipment
- Corrosion Protection Equipment in Specific Industries:
 - Chlor-Alkali
 - Pulp & Paper
 - Sodium Chlorate
 - Mining
 - Sulfuric Acid Manufacturing
 - Power Industry
 - Bio-Fuel
 - UV and Photovoltaic
 - Geothermal Energy
 - Water Treatment
 - Mining

Case Histories

The performance data helps when selecting the right material for the particular application. However, performance in real life applications is always the best test. This paper focuses on the ECTFE resin, the fluoropolymer which has been successfully used in industrial applications for more than 20 years. The initial characterization of the ECTFE polymer performed in the 70's, confirmed by the testing performed later on, showed that this resin has excellent chemical and permeation resistance.

When combined with good mechanical properties, low brittleness temperature, exceptional surface smoothness, low notch sensitivity, excellent impact strength and abrasion resistance, this resin was quickly identified as the material of choice for the chemical processing industry. Several large industrial applications of ECTFE resin date back to the early 80's.

The industrial applications include reactors, scrubbers, electrolytic cell liners, transport and storage tanks, tower packing, pipe, and fittings, all exposed to very aggressive chemicals.

During the past few years, we have been working with end users and fabricators in order to identify the case histories where the ECTFE resin was used in industrial applications. We identified more than 40 such applications, not including powder coating. This presentation includes a summary of the most interesting applications.

A. Summary of the ECTFE case histories

The Halar ECTFE case histories identified by us and described in this work should help to confirm what type of chemistries ECTFE can be successfully used in. Examples of successful ECTFE applications include:

1. Transport and storage of aggressive chemicals such as HF, H₂SO₄, HCl, sodium hypochlorite, chlorine, and herbicides & pesticides. The sulfuric acid applications include:
 - 11 sheet-lined vessels exposed to different concentrations of acid at temperatures as high as 135°C. Several of these tanks and trailers, installed from 1989-1992, are still in use.
 - More than 100 ECTFE/FRP dual laminate plating tanks were installed since 1993. The liners are exposed to 20% sulfuric acid @ 105°C and all tanks are still in good condition.
 - 98% H₂SO₄, semiconductor grade sheet-lined tank container; installed in 1990, still in satisfactory condition.
2. Chlorine Scrubbers:
 - 3 ECTFE/FRP scrubbers were installed in the UK in 1985 and 1988. They performed very well after 10-15 years, when they were inspected. However, we were not able to obtain any information about the current status of these applications.
 - The scrubber installed in the USA in 1984 is still in use, but we did not get permission to publish this case history.
 - Vessels installed in Belgium and the Netherlands will be further described in this paper. Both applications were already published in the March and October 2009 issues of the MP magazine.
3. Chlorine Dioxide Bleaching Towers – the first Halar lined structure was installed in 1998. It performed very well for 7.5 years until the plant was shut down. Four other towers are still in service; they were installed from 5 to 9 years ago and did not require any maintenance.
4. Piping, Electrolytic Cell Covers, and Reactors in the sodium chlorate and chlor-alkali manufacturing processes.
5. Dual Laminate Chimney Stack in Denmark. This application was published in the December 2009 issue of POWER Magazine; it is also summarized in this paper.

B. Chlorine Scrubber at Monsanto, Belgium

Summary of the application:

- ECTFE/FRP vessel was installed in Belgium in 1987
- Conditions: 22% NaOH to scrub chlorinated solvents, HCl, and molecular chlorine; gas stream velocity = 9000 m³/hour; pH equal to or higher than 12, operating temperature = 40°C
- PVDF could not be used because of alkaline environment
- FRP structures were tried before installing ECTFE vessel, but they failed after a few years of service
- the ECTFE liner was in excellent condition after 14 years of continuous service when the plant was shut down

One of the reasons why the ECTFE resin was selected for this application was its excellent permeation resistance to chlorine and hydrochloric acid, the best of all fluoropolymers, at temperatures as high as 100°C. The two graphs below clearly show that the ECTFE resin has the lowest permeation rate at 45°C, slightly above the operating temperature in the Monsanto plant (6, 8).

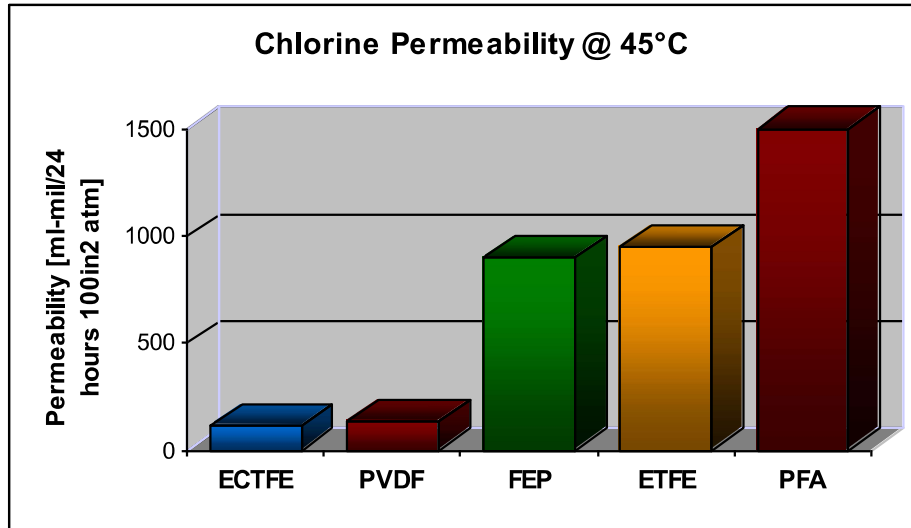


Figure 2: Chlorine gas permeability of 10 mil thick films

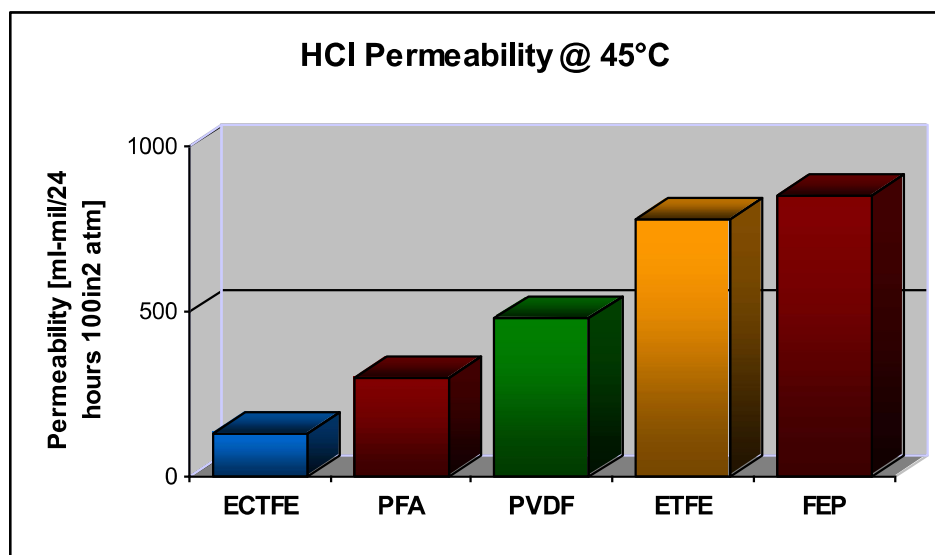


Figure 3: HCl gas permeability of 10 mil thick films

Before installing the liner, Monsanto exposed individual ECTFE coupons and ECTFE blind flanges for 6 to 12 months in-situ. When no color change or any noticeable degradation was observed after this test period, Monsanto decided to go ahead with an ECTFE lined FRP scrubber. More details of this case history was published in the March 2009 issue of the MP magazine, the NACE publication (9).

C. ECTFE/FRP Chimney Stack in Denmark

The power station in Nordjütlandwerk was designed to burn crude refinery residue with high sulfur content. In 1991 it was outfitted with a 112 m high concrete chimney stack, internally protected with acid resistant brick. However, shortly after going on stream, it appeared that the condensate of sulfuric acid quickly attacked the inner brick lining. During 1995, the decision was made to replace the failing brick lining with the ECTFE/FRP structure. The 2.3 mm thick liner was used to build a 4.3 m diameter, 92 m high chimney stack, prefabricated in 7 modular sections (10). The fabrication was performed by Tunetanken (Denmark) with help from PRP, Finland.



Figure 4: Installation of the chimney in 1995

		Start-up	Max. Service
O ₂	%	2 – 20	2 – 6
H ₂ O	%	0 – 3	6 – 9
SO ₂	ppm	0 – 200	50 - 200
SO ₃	ppm	0 – 40	5 – 15
No _x	ppm	0 – 100	20 - 50
HCl	ppm		max. 200
HF	ppm		max. 25
Temperature	°C	10 – 110	100 - 110
Temperature rise		0.7 °C/min. max.	
Temperature drop		0.7 °C/min. max.	
Fluegas flow			
Nm ³ /min.		1 - 9.10 ⁵	9 - 10.10 ⁵
Fluegas speed	m/s		28 max.
under pressure	Pa		175
over pressure	Pa		375

Table 9: Maximum Operating Conditions

The inspection performed by Tunetanken in September 2006 revealed that the ECTFE liner was in excellent condition and looked practically new.



Figure 5 – ECTFE liner after 10 years of service



Figure 6 – ECTFE liner after 10 years of service

The liner was also evaluated by the Danish Technological Institute in 2008. The results of the DTI evaluation showed that the liner was in excellent condition after approximately 13 years of service. The conclusions of the Danish Technological Institute were summarized in the May 2009 letter from Mr. Torben Martens Knudsen, the Project Manager of DTI's Plastics Technology:

“Samples taken from the ECTFE lining of the stack at Nordjyllandsvaerket Power Plant have been tested last year. Two drilled out samples were taken at level 24 and analyzed using IR-spectroscopy at test samples taken from inside surface and from the middle part of the lining. There were no sign of degradation of the polymer. Polished cross-sections of the samples were examined in microscope; a darker color was observed in a depth of 0.1 mm from inside surface. The joint between lining and glass fiber-polyester layer was fully intact. It was concluded that the ECTFE-lining was not influenced by the service conditions after approx. 13 years of service.”

More details of this case history can be found in the article published in the December 2009 issue of POWER magazine (11).

D. Chlorine Dioxide Bleaching Towers

The first ECTFE/FRP upflow tube was installed in the Muskegon mill in May 1998. It replaced the FRP structure which failed after less than 2 years of service. The total installation cost including equipment, labor, and material was US\$ 210,579,00. It was calculated that the return of investment was less than 2 months.



The Muskegon mill was shut down in 2005, which allows us to take samples for analysis. We also took pictures of the liner after more than 7 years of service. The photographs showed that the majority of the liner was in excellent condition.

The tensile properties measurement and DSC analysis of the liner showed that the properties of the ECTFE resin were not affected after 7.5 years of chlorine dioxide service. It was also determined that the total permeation of the chemicals through the portion of the liner, taken from the bottom of the column (the most affected part due to the highest concentration of chlorine dioxide), was about 50% of the liner thickness. This suggests the ECTFE liner would perform very well for at least 7 more years.

Figure 7 – Outside view of the Upflow Tube



Figure 8: Inside view of the ECTFE liner

Figure 9 - Inside view of the ECTFE liner after 7.5 years of service (bottom)

The second Halar/FRP bleaching tower was installed in the International Paper mill in France in 2000. It was inspected in 2009 and based on the statement of the plant engineer, no damage, no wear, and no discoloration of the liner was observed.

There are three other ECTFE/FRP bleaching towers installed in the USA. All of them are in service for more than 5 years; they perform very well and did not require any repair or maintenance.

E. ECTFE LINED TANK IN CAUSTIC SERVICE IN NETHERLANDS

This ECTFE lined vessel was a large holding tank which received a continuous flow of alkaline based fluids in addition to active chlorine. The liner was also exposed to sodium hypochlorite, the product of the reaction between chlorine and caustic soda. The design temperature of the vessel was 70°C with operating temperature between 40 and 50°C.

The 2m diameter and 3.5 m long steel vessel was lined with the ECTFE by Mainchem, UK and it was put in service in the vinyl chloride monomer plant in Botlek, Netherlands in June 1983. This vessel was in continuous service until February 2007 when it was replaced by the FRP/ECTFE dual laminate tank. It was discovered during the inspection in 2005 that, probably due to mechanical abuse, the liner was damaged around the flange and partially disbonded from the metal. Back in 1983, the VCM plant was owned by AKZO Zoutechemie, but since 2000 it has been a part of Shin-Etsu Chemicals Co. Ltd.

We received samples of the ECTFE after the vessel was replaced by the new FRP/ECTFE tank. Several tests were performed on the liner to determine the extent of chemical attack. This data showed that the properties of the ECTFE resin were only slightly affected or not affected at all after 23 years of service. The resin retained most of its tensile properties, which is illustrated on the graph presented below.

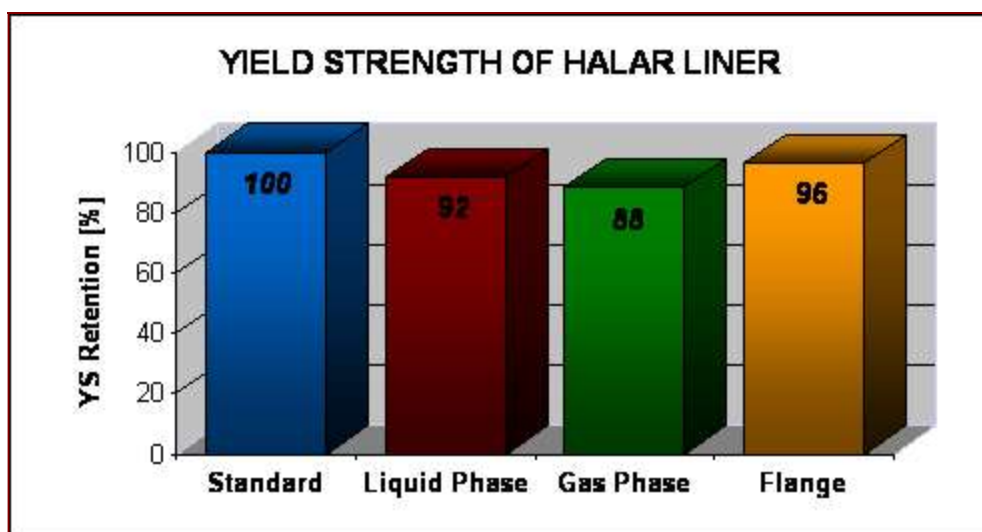


Figure 10: Yield Strength of the liner after 23 years of service. The samples were taken from four different parts of the vessel

The cross section of the liner, as illustrated on the microscopic picture below, shows no signs of chemical attack, with the permeation front reaching a maximum of 10% of the liner thickness.



Figure 11: The cross section of the liner after 23 years of service

This case history and more detailed results of the testing performed on the liner after 23 years of service was published in the October 2009 issue of the MP magazine (12).

F. OCEAN GOING TRANSPORT SHIPS

Steel and its alloys, based on their mechanical properties, are ideal materials of construction for large transport vessels. However, they have one major drawback which is well known - their limited chemical resistance. As a result, chemical shippers revert to suitable polymeric linings for transporting specialty chemicals. Seatrans, the Bergen, Norway based company, chose the ECTFE polymer to line large tanks to be installed on ocean-going chemical transport ships. As a result of the close collaboration between Seatrans and Ausimont, 636 chemicals, both organic and inorganic, were approved to be transported in the ECTFE lined vessels. These chemicals included: H_2SO_4 (up to 98%), HCl , NaOH , AlCl_3 , and FeCl_3 .

The first ship was equipped with two, 250m^3 ECTFE lined tanks in 1991. Since then, Seatrans added 3 other ships, containing more than 10 ECTFE lined tanks. These tanks have a total capacity of more than $6,000\text{ m}^3$. The sheet lining of the tanks was done by PRP in Finland. All ships are sailing 7 days a week and the owner of the fleet is satisfied with the performance of the ECTFE resin. Inspection of the tanks on the ship built in 1993 was performed in 2005 and no change of the ECTFE liner was observed.

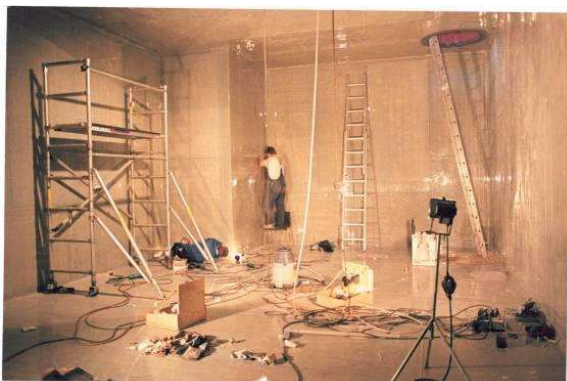


Figure 12: Sheet lining of the tank, to be installed on the ship



Figure 13: One of the ships containing the ECTFE lined tanks

Conclusions

Fluoropolymer has an excellent chemical resistance, very low permeability to liquid and gases, as well as very good strength and toughness at elevated temperatures. They have been widely used in chemical production, transport, and storage systems. Several case histories of the ECTFE polymer were identified during the last few years. These case histories, summarized above, show that the ECTFE pipes, liners and vessels performed very well in many industrial applications. It provided excellent corrosion protection from very aggressive chemicals for several years, and in many cases, for more than 20 years.

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Review

Recent Advances in Poly(vinylidene fluoride) and Its Copolymers for Lithium-Ion Battery Separators

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Abstract: The separator membrane is an essential component of lithium-ion batteries, separating the anode and cathode, and controlling the number and mobility of the lithium ions. Among the polymer matrices most commonly investigated for battery separators are poly(vinylidene fluoride) (PVDF) and its copolymers poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), due to their excellent properties such as high polarity and the possibility of controlling the porosity of the materials through binary and ternary polymer/solvent systems, among others. This review presents the recent advances on battery separators based on PVDF and its copolymers for lithium-ion batteries. It is divided into the following sections: single polymer and co-polymers, surface modification, composites, and polymer blends. Further, a critical comparison between those membranes and other separator membranes is presented, as well as the future trends on this area.

Keywords: PVDF; copolymers; battery separator; lithium-ion batteries

1. Introduction

In the field of mobile applications, the efficient storage of energy is one of the most critical issues, since there is a fundamental need to maximize the amount of energy stored. This issue can be accomplished by increasing the gravimetric and volumetric energy density of the batteries [1].

The electrochemical lithium ion battery is used to provide power to a large variety of mobile appliances, such as smartphones, tablets, and laptops, as well as an increasing number of sensors and actuators, which will have a fundamental role in the shaping of the Internet of Things and Industry 4.0 concepts, the main trend for current technological evolution [2]. Lithium ion batteries can also power electric and hybrid vehicles, and take part in the management of renewable energy production, being essential in a more sustainable energy paradigm. As some renewable resources, such as solar and wind, are intermittent over time, storing energy for their use during periods of lack of resources is a critical issue for lithium ion batteries [3,4].

Lithium ion batteries are very suitable for the aforementioned applications due to their advantages with respect to other battery types, as they are lighter, cheaper, have a higher energy density (250 Wh·kg⁻¹, 650 Wh·L⁻¹), lower charge lost, no memory effect, a prolonged service-life, and a higher number of charge/discharge cycles [5].

Furthermore, the global market of lithium ion batteries is currently growing, and it is expected that in 2022, the market value will reach \$46.21 billion, with an annual growth rate of 10.8% [6].

The first commercial lithium ion battery, which was by Sony, entered the market in 1991, with the fundamental contribution of John Goodenough in the development of LiCoO_2 as the active material for the cathode [7].

The main components of a battery are the anode, the cathode, and the separator, which are represented in Figure 1, together with the working principle of a lithium ion battery.

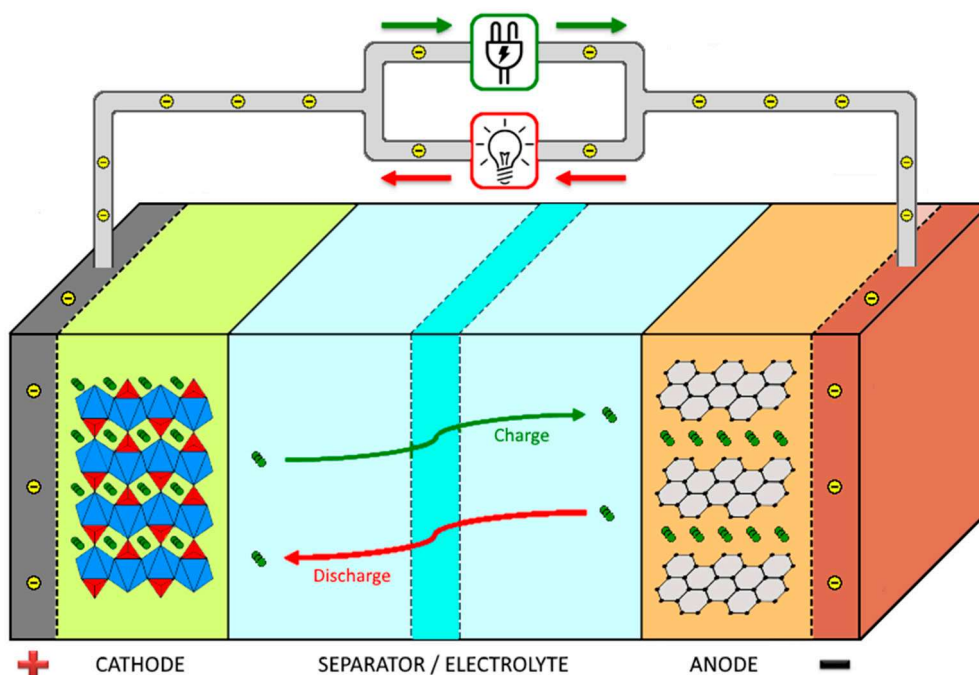


Figure 1. Schematic representation of a lithium ion battery and its working operation.

During the discharge process of the battery, the cathode acts as an oxidizing element, receiving electrons from the external electric circuit and being reduced. The anode is the reducing element, releasing electrons to the external electrical circuit, being oxidized during the electrochemical reaction [8].

2. Battery Separator: Function, Characteristics, and Types

Separators play a key role in the operation of electrochemical devices. The main purpose of the separator membranes is to separate the cathode from the anode, avoiding the occurrence of short circuits, and controlling to the mobility of lithium ions between electrodes. The performance of a separator in a lithium ion battery is determined by some requirements such as porosity, chemical and thermal stability, electrical insulator, wettability, dimensional stability, and resistance to degradation by chemical reagents and electrolytes (Figure 2) [9]. Figure 2 shows the ideal values for the main requirements of a separator membrane.

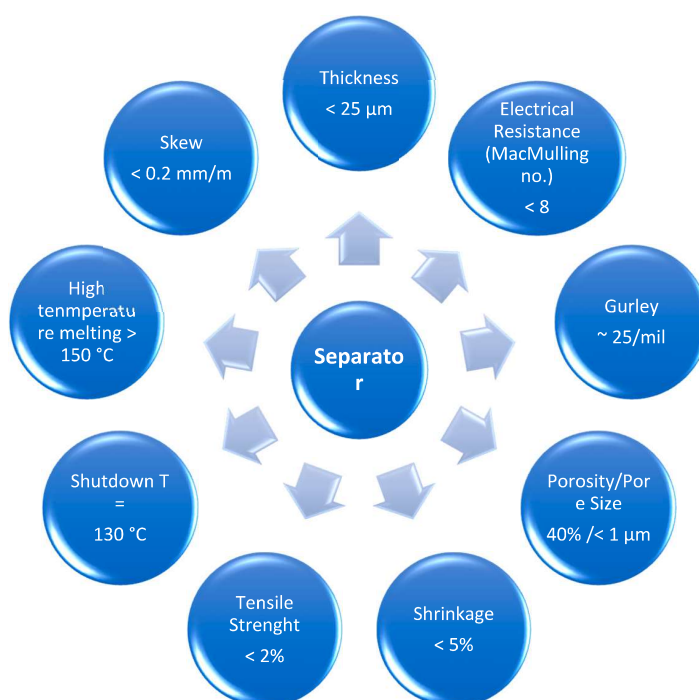


Figure 2. Ideal values for the main requirements of a separator membrane.

There are different types of separators, but the most widely used consist of a polymer matrix embedded by the electrolyte solution, i.e., a liquid electrolyte where salts are dissolved in solvents, water, or organic molecules. The main types of separators are shown in Table 1 [10].

Table 1. Types and characteristics of different separators adapted from [10].

Separator	Characteristics	Typical Materials
Microporous	Operates at low temperatures (<100 $^{\circ}\text{C}$); pore size = 50–100 $\text{\AA}$	Nonwoven fibers (cotton, nylon, polyester, glass), polymers (PP, PE, PVC, PTFE), rubber, asbestos, wood
Nonwoven	Resistance to degradation by electrolytes; thickness > 25 μm ; pore size = 1–100 μm	Polyolefins (PE, PP, PA, PTFE; PVDF; PVC)
Ion exchange membrane	High chemical resistance; impervious to electrolytes; pore size < 20 $\text{\AA}$	PE, PP, Teflon-based films
Supported liquid membrane	Solid matrix with a liquid phase; insolubility in electrolyte; high chemical stability	PP, PSU, PTFE, CA
Polymer electrolyte	Simultaneously separator and electrolyte; high chemical and mechanical integrity	Polyethers, PEO, PPO, lithium salts
Solid ion conductor	simultaneously separator and electrolyte	-

The most commonly used materials as matrix for lithium ion battery separators are polymers, or polymer composites. Some of the most commonly used polymers are poly(propylene) (PP), poly(ethylene) (PE), poly(vinylidene fluoride) (PVDF) and its copolymers, poly(ethylene oxide) (PEO), and poly(acrylonitrile) (PAN) [11]. Some separators are developed by blending two different polymers to improve the characteristics of the membrane. In some cases, nanoparticles are added to the matrix as fillers to increase its mechanical stability or ionic conductivity. In composites separators, the most widely used fillers are oxide ceramics (ZrO_2 [12,13], Al_2O_3 [14,15], SiO_2 [16,17]), carbonaceous fillers (graphene [18], carbon black [19], carbon nanofiber [20]), and ionic liquids [21], among others.

The solvents must possess some requirements to ensure proper battery operation. The properties of a good solvent are high dielectric constant, low viscosity, high chemical stability, and in liquid form over a wide temperature range. For this application, solvents of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) are the most commonly used [11].

3. Poly(vinylidene fluoride) and Its Copolymers

Considering the different polymer matrices used for battery separators, PVDF and its copolymers (poly(vinylidene fluoride-co-trifluoroethylene), poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and poly(vinylidene fluoride-cochlorotrifluoroethylene) (PVDF-CTFE)) show exceptional properties and characteristics for the development of battery separators, highlighting high polarity, excellent thermal and mechanical properties, wettability by organic solvents, being chemically inert and stable in the cathodic environment, and possessing tailorable porosity through binary and ternary solvent/non-solvent systems [22,23]. The main properties of these polymers are presented in Table 2 [11].

PVDF and its copolymers are partially fluorinated semi-crystalline polymers where the amorphous phase is located between the crystalline lamellae arranged in spherulites. It can crystallize in different crystalline phase, depending on the temperature and processing conditions [24,25]. In relation to the crystalline phases of PVDF and its copolymers, the most important phases are the β -phase, since it presents ferroelectric, piezoelectric, and pyroelectric properties, and the α -phase, which is the most stable thermodynamically, when material is obtained directly from the melt [24]. As illustrated in Table 2, PVDF and its polymers are characterized by excellent mechanical properties, good thermal stability up to 100 °C, and a high dielectric constant, which is essential for assisting the ionization of lithium salts.

Table 2. Main properties of PVDF and its copolymers [26–28].

Polymer	Melting Temp./°C	Degree of Crystallinity/%	Young Modulus/MPa	Dielectric Constant
PVDF	~170	40–60	1500–3000	6–12
PVDF-TrFE	~120	20–30	1600–2200	18
PVDF-HFP	130–140	15–35	500–1000	11
PVDF-CTFE	~165	15–25	155–200	13

PVDF copolymers have drawn increasing attention for battery separators, as the addition of other monomers to the VDF blocks increases the fluorine content and decreases the degree of crystallinity (Table 2), which is particularly relevant once the uptake of the electrode solution occurs in the amorphous region through a swelling process for accommodating the electrolyte and, as a result, increases the ionic conductivity [29]. The recent literature on PVDF and its battery separator copolymers is structured into four sections dedicated to single polymers, surface modification, composites, and polymer blends, respectively.

The main achievement for PVDF and co-polymers as battery separators was thoroughly reviewed in [11]. Since then, important contributions have been achieved, which are the subject of the present review.

3.1. Single Polymer and Co-Polymers

As already mentioned, one of the main characteristics of PVDF and its co-polymers is their high dielectric permittivity, providing a large affinity with polar electrolytes when compared to other polymers [11]. The main characteristics of the developed PVDF and the copolymer membranes are shown in Table 3.

Table 3. Separator membranes based on PVDF and co-polymers, indicating also the main properties, and the main goal/achievement of the investigation.

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Reference
PVDF	1 M (C ₂ H ₅) ₃ CH ₃ NBF ₄ + AN	-/-	-/-	Study of multistep electrospinning technique on the fabrication of PVDF composite membranes; High specific power.	[30]
PVDF	1 M LiPF ₆ in EC:DEC (1:1, w/w)	-/816	6.83 × 10 ⁻⁴ / 101.1 (0.5C)	Performance comparison with a PVDF-PDA separator; Enhanced cycling performance.	[31]
PVDF	1 M LiPF ₆ in EC:DEC (1:1, v/v)	7/-	-/-	Analysis of the migration mechanism of cation and anions through the separator; The separator allows the control of structural stability and ion mobility.	[32]
PVDF	1 M LiPF ₆ in EC/DMC/EMCC (1:1:1, w/w/w/w)	-/-	-/95 (0.2C)	Production of a PVDF membrane; Good capacity retention.	[33]
PVDF	1 M TEABF ₄ in AN/PC and 1 M LiPF ₆ in EC/DEC	80/-	1.8 × 10 ⁻² (25 °C)/-	Manufacturing of a PVDF separator; Favorable mechanical properties.	[34]
PVDF	1 M LiBF ₄ in EC/DMC (50:50 wt. %)	-/-	4.17 × 10 ⁻³ (20 °C)/-	Comparison of PVDF membrane performance with Nafgate separators.	[35]
PVDF	1 M LiPF ₆ in EC/DMC/DEC (1:1:1)	78.9/427	1.72 × 10 ⁻³ /164.3 (C/5)	Synthesis of dual asymmetric structure separators; Improved electrolyte uptake and ionic conductivity.	[36]
PVDF	1 M LiPF ₆ in EC/DMC/DEC (1:1:1)	-/-	-/447.36 (0.3C)	Production of a solid state SCPC with a PVDF separator; High storage capacity and stability.	[37]
PVDF	-	-/-	-/-	Assembly of a PVDF separator for air-cathode as application in microbial fuel cells; Improved electricity generation.	[38]
PVDF	PVA/H ₂ SO ₄	-/-	-/-	Production of a PVDF separator for piezoelectric supercapacitors; High mechanical strength and elevated capacitance.	[39]
PVDF	1 M NaClO ₄ in EC/DEC (1:1)	81/34	7.38 × 10 ⁻⁴ (29 °C)/153	Production of an electroactive electrospun PVDF separator for sodium ion batteries.	[40]

Table 3. Cont.

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Reference
PVDF	1 M LiPF ₆ in EC/DEC (1:1)	70/66	1.5 × 10 ⁻³ / 102 (2C)		
PVDF-TrFE	1 M LiPF ₆ in EC/DEC (1:1)	72/84	1.1 × 10 ⁻³ / 118 (2C)	Study of the effect of different PVDF copolymers as lithium ion battery separators.	[41]
PVDF-HFP	1 M LiPF ₆ in EC/DEC (1:1)	56/79	1.3 × 10 ⁻¹ / 107 (2C)	Demonstration of the relevance of β-phase content.	
PVDF-CTFE	1 M LiPF ₆ in EC/DEC (1:1)	59/80	1.5 × 10 ⁻³ / 85 (2C)		
PVDF	[C ₂ mim][NTf ₂]	20/98	2.3 × 10 ⁻⁴ (25 °C) / 74.6 (C/5)	Preparation of PVDF separators using a green solvent and ionic liquid as the electrolyte.	[9]
PVDF-HFP	LiTFSI	48/248	5.2 × 10 ⁻⁵ (20 °C) / -	Application of disiloxane-based electrolytes on PVDF-HFP for the production of gel electrolyte separators; Good thermal and mechanical stability.	[42]
PVDF-HFP	LiNfO/BMImNfO	-/-	2.61 × 10 ⁻² / (100 °C) 138.1 (C/4)	Production of ionic liquid gel polymer electrolytes; High ionic conductivity.	[43]
PVDF-HFP	1 M LiPF ₆ in EC/DMC (1:2)	70/247	3.2 × 10 ⁻³ (25 °C) / -	Evaluation of the performance of PVDF-HFP, as a single polymer membrane. Understanding of the method of avoiding the formation of beads in the nanofibers of PVDF-HFP; Good electrolyte uptake.	[44]
PVDF-HFP	1 M LiPF ₆ in EC:DMC (1:1)	78/86.2	1.03 × 10 ⁻³ / 145 (0.2C)	Development of a PVDF-HFP gel polymer electrolyte membrane with honeycomb type porous structure; Excellent electrochemical performance.	[45]
PVDF-HFP	1 M LiPF ₆ in EC/DEC/EMC (1:1:1)	-/-	-/-	Production of separators with controlled pore structure; Improved rates and cycling performances.	[46]
PVDF-CTFE	1 M LiPF ₆ in EC:DMC:EMC (1:1:1, v:v)	74/-	7.51 × 10 ⁻⁴ (25 °C) / 147 (0.2C)	Preparation of a nanofiber-coated composite separator by electrospinning; High discharge capacity and good cycling stability.	[47]

Table 3 shows that the electrospinning technique is widely used to produce functional membranes. Thus, electrospun separators have been developed for PVDF-PDA [31], PVDF-HFP [44], and PVDF-CTFE [47].

For the PVDF-CTFE membrane, the cell assembly considered for the battery performance tests is represented in Figure 3.

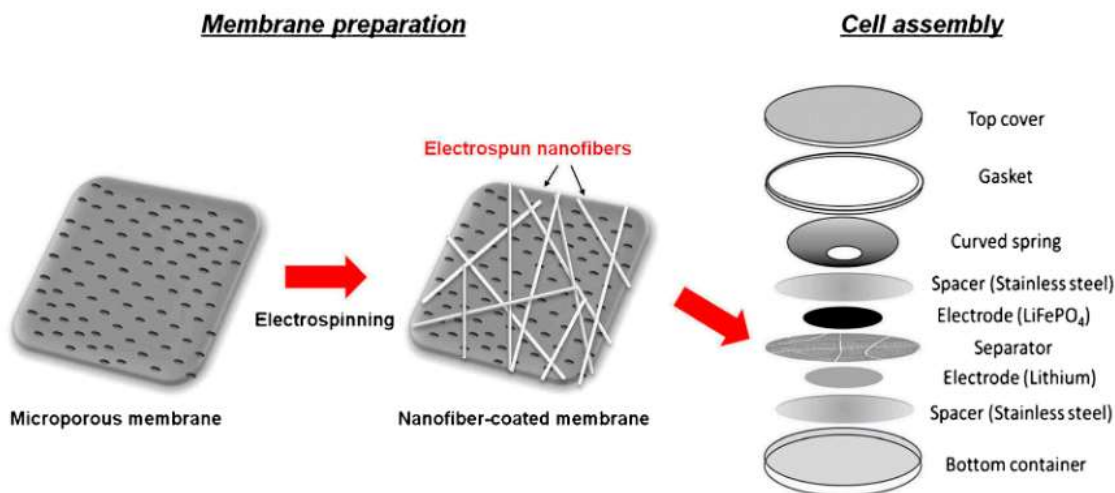


Figure 3. Manufacturing of a testing cell based on PVDF-CTFE separators [47], with copyright permission from Springer Nature.

For PVDF-HFP electrospun membranes, it has been demonstrated that a single layer membrane shows good porosity and uptake value, but that the mechanical stability is negatively affected, with the viscosity of the solution playing an important role [44]. Also, a novel gel electrolyte was developed based on PVDF-HFP by the addition of disiloxane into the electrolyte solution [42], leading to a thermally stable separator that is not flammable, thus contributing to safer lithium ion batteries [45]. In this sense, ionic liquids have also been used in electrolyte solutions, improving both safety and the ionic conductivity of the membranes [43].

A multistep electrospinning technique for the production of PVDF membranes for electrical double-layer capacitors has been proposed, allowing for the manufacture of thinner and more densely packed separators [30].

Further, membranes have been developed based on PVDF for air-cathode in microbial fuel cells [38] and piezo-supercapacitors [39]. Dual asymmetric PVDF separators were produced by a thermally-induced phase separation method, in which the large and interconnected pores in the bulk structure ensures an improved electrolyte uptake and ionic conductivity, while the small pores in the surfaces prevent the loss of electrolyte and the growth of lithium dendrites. It is indicated that those separators ensure safer batteries with high discharge capacity and longer cycle life [36].

A further step towards the development of more environmentally friendly PVDF separator membranes was proposed by using DMPU as a solvent for PVDF, and IL [C2mim][NTf2] as an electrolyte. The use of the IL increased the ionic conductivity and discharge capacity of the membrane when compared with separators using conventional electrolytes [9].

Porous PVDF-HFP membranes were prepared with non-solvents using the phase inversion technique. When selecting different types of non-solvents such as water, methanol, ethanol, and propanol, and their contents in acetone, it was possible to control the size of the pores (Figure 4) [46].

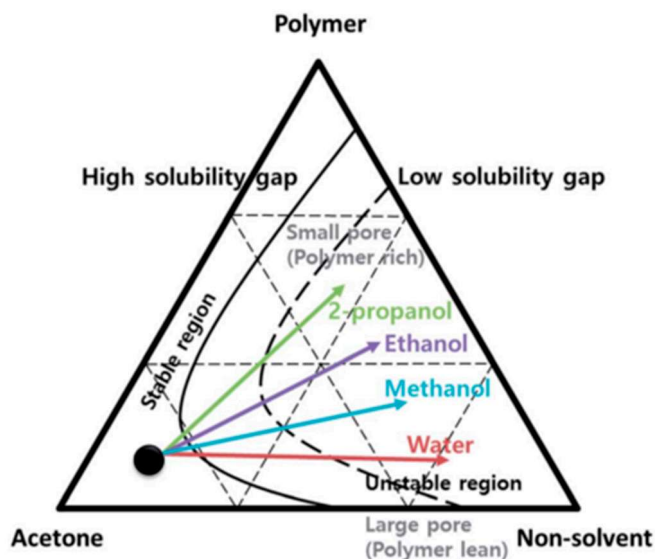


Figure 4. Phase diagram of the ternary mixture—PVDF–HFP, acetone, and non-solvent—in order to control PVDF–HFP membrane morphology [46], with copyright permission from the Royal Society of Chemistry.

Finally, a correlation between the β -phase content of the separators, and the rate capability and cyclability of the batteries was demonstrated for different PVDF co-polymers, showing that the PVDF-TrFE membrane has the best battery performance for the highest β -phase content (100%) [41].

Thus, it is observed that for single (co)polymer membranes, the main focus is to tailor the morphology to obtain good uptake without mechanical deterioration, and to improve the interaction between the electrolyte solution and the separator membrane.

3.2. Surface Modification of the Separator Membranes

Typically, surface modification of the membranes is carried out to improve specific properties such as wettability, and thermal and mechanical stability. PVDF membranes have been prepared after different surface modifications, but also have been used to modify the properties of other polymer membranes, as presented in Table 4.

Table 4. Surface modifications on PVDF and co-polymers, indicating also the main properties, goal and achievement.

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref
PVDF (plasma-treated)	1 M LiPF ₆ in EC/DMC (1:1)	-/1200	-/-	Study of the effect of plasma treatment in PVDF separators; Improved electrolyte uptake and mechanical properties.	[48]
PE/PVDF	1 M LiPF ₆ in EC:EMC:DEC (1:1:1, <i>w:w:w</i>)	-/-	0.89 × 10 ⁻³ (25 °C)/-	Investigation into the pore formation process in a coating layer for separators; Enhanced ionic conductivity.	[49]
PE/PVDF	1.10 M LiPF ₆ in EC/PC/EP (3:1:6, <i>w:w:w</i>)	-/-	-/1436 (0.2C)	Study of the electrochemical performance of PE/PVDF separators; Enhanced cycling performance.	[50]
PVDF/PP	1 M LiPF ₆ in EC/DMC (1:1)	58/140	5.9 × 10 ⁻⁴ /145 (0.5C)	Coating of PVDF particles in the surface of a PP membrane; Increased electrolyte uptake.	[51]
PET/PVDF	1 M LiPF ₆ in EC/DEC/DMC (1:1:1, <i>w/w/w</i>)	-/-	8.36 × 10 ⁻³ /-	Investigation of the performance of a hot-pressed PET/PVDF separator; Excellent mechanical behavior.	[52]
PVDF/HEC	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	-/135.4	8.8 × 10 ⁻⁴ (25 °C)/140	Preparation of a PVDF/HEC/PVDF membrane with a sandwich structure; High electrolyte uptake and ionic conductivity.	[53]
PVDF/PMMA	1 M LiTFSI in DME/DOL (1:1)	-/294	1.95 × 10 ⁻³ (25 °C)/1711.8	Preparation of a sandwiched GPE based on PVDF and PMMA for lithium-sulfur batteries; High discharge capacity and cycle stability.	[54]
PDA/PVDF	1 M LiPF ₆ in EC:DEC (1:1, <i>wt:wt</i>)	-/1160	9.62 × 10 ⁻⁴ /104.5 (0.5C)	Prove that the PDA coating can be promising for manufacturing electrospun nanofiber separators; Better cycling performance and elevated power capability.	[31]
PE/(PVDF/Al ₂ O ₃)	1 M LiPF ₆ in EC/DEC (1:1)	60.3/125, 314	1.14-1.23 × 10 ⁻³ /-	Development of a multilayer coating for separators; Improvement of thermal stability and electrolyte wetting.	[55]
PI/PVDF/PI	1 M LiPF ₆ in EC/DEC/DMC (1:1:1)	83/476	3.46 × 10 ⁻³ /114.8 (0.5C)	Production of an electrospun sandwich-type separator; Superior porosity, electrolyte uptake, and ionic conductivity.	[56]
PVDF-HFP	1 M NaClO ₄ in EC/PC (1:1)	-/-	3.8 × 10 ⁻³ /291.1 (0.2C)	Development of a PVDF-HFP-coated GF separator for sodium ion batteries; Good cycling performance.	[57]

Table 4. Cont.

Materials	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref
PVDF-HFP	1 M LiPF ₆ in DMC/EMC/EC (1:1:1)	53.5/106.9	8.34 × 10 ⁻⁴ / 131.33 (5C)	Study of the effect of the drying temperature on the performance of the separator.	[58]
PP/(PVDF-HFP/SiO ₂)	1 M LiPF ₆ in DEC/EC (1:1, v/v)	-/-	7.2 × 10 ⁻⁴ / -	Analysis on the effect of a PVDF-HFP/SiO ₂ coating layer for PP separators; Better electrolyte uptake and ionic conductivity.	[59]
PMMA/PVDF-HFP	1 M LiPF ₆ in EC:DMC (1:1)	-/342	1.31 × 10 ⁻³ / 143 (0.2C)	Investigation and analysis of a produced PMMA/PVDF-HFP electrolyte membrane; Exceptional thermal and electrochemical stability.	[60]
PVDF-HFP/PDA	LiPF ₆ in EC/DEC/DMC (1:1:1)	72.8/254	1.40 × 10 ⁻³ (20 °C) / -	Production of a PVDF-HFP/PDA separator by a dip-coating method.	[12]
PVDF-HFP/PET	1 M LiClO ₄ in DMSO	-/282	6.39 × 10 ⁻³ (25 °C) / 158 (0.1C)	Combination of PVDF-HFP with a SiO ₂ nanoparticle-modified PET matrix; Improved thermal stability, electrolyte uptake, and ionic conductivity.	[61]
PP/(AlO ₂ /PVDF-HFP)	1 M LiPF ₆ in EC/DEC (1:1, v/v)	-/-	7.95 × 10 ⁻⁴ / 98.6 (0.2C)	Inspection of the performance of a separator for PP membrane coating; Improved thermal stability.	[62]
γ-Al ₂ O ₃ /PVDF-HFP/TTT	1 M LiClO ₄ in EC/DEC (1:1)	-/157	1.3 × 10 ⁻³ / ~100 (0.5C)	Dip coating of a PE separator with γ-Al ₂ O ₃ /PVDF-HFP/TTT; Increased electrolyte uptake and ionic conductivity.	[13]
PP/PE/PP/PVDF-co-CTFE	1 M LiPF ₆ in EC/DMC/DEC (1:1:1, v:v:v)	-/-	-/-	Fabrication of PVDF-co-CTFE nanofiber coatings for improving the performance of polyolefin separators; High electrolyte uptake and good wettability.	[63]

The most commonly used surface modification is the use of PVDF and its copolymers for the coating of other polymers such as polyethylene porous separators. Thus, the coating of PE with a Al_2O_3 ceramic layer and a PVDF electrospun nanofiber layer leads to enhanced electrolyte uptake, improved capacity discharge, and cycle life [55]. Similarly, a PDA coating on PVDF improves hydrophilicity, enhancing electrolyte uptake and ionic conductivity of the separator [31].

A typical surface modification technique, such as plasma treatment, allows significant improvement of the electrolyte uptake of PVDF electrospun membranes [48].

A hot-pressing technique was proposed to develop PET/PVDF separators, with improved mechanical behavior properties [52].

The preparation of a PVDF/PMMA/PVDF separator showed great potential for its use in lithium-sulfur batteries, showing high initial discharge capacity and cycle stability, also reducing cell polarization and suppressing the shuttle effect, which is described as the transport of soluble polysulfides between both electrodes and the associated charge [54].

A composite membrane with a PVDF/HEC/PVDF sandwich structure was developed, leading to higher electrolyte uptake, ionic conductivity, and cycling performance. It is also greener and safer because of the fire-retardant behavior of its components [58].

For PVDF-HFP membranes, several coatings have been applied, such as ZrO_2 nanoparticles [64], PP polymer [59], PMMA polymer [60], PDA layer [12], and SiO_2 -modified PET [61], leading mainly to improved electrolyte uptake.

Surface modifications are also achieved by modifying the drying temperature of PVDF-HFP/PET separators prepared by dip-coating, with a drying temperature of 80 °C improving cycle and rate performances with respect to batteries with a conventional PP separator [58].

The dip-coating of a PE separator with $\gamma\text{-Al}_2\text{O}_3$ /PVDF-HFP/TTT, proved to increase electrolyte uptake and ionic conductivity when compared with conventional membranes, as shown in Figure 5 where its microstructure and cycling performance are presented. The discharge performance was also enhanced as well as the thermal resistance [13].

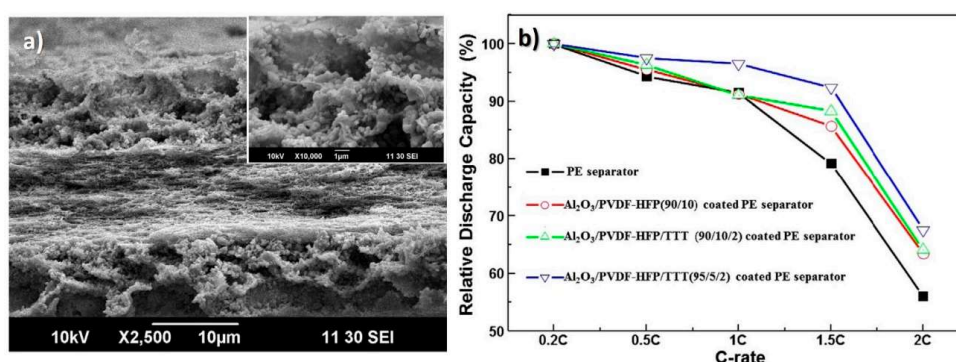


Figure 5. (a) Cross-section scanning electron microscopy (SEM) images of the $\gamma\text{-Al}_2\text{O}_3$ /PVDF-HFP/TTT(95/5/2)-coated PE separator and (b) relative discharge capacities as a function of the C-rate [13], with copyright permission from Elsevier.

Basically, surface modifications are essential for improve the electrolyte wettability of the separators, and are realized in several polymer membranes of single and multiple layers with many polymers (PP, PET, PMMA, etc.) and filler nanoparticles.

3.3. Composite Membranes

Polymer composites are used to improve battery performance by incorporating suitable fillers, such as oxides ceramic, zeolites, and carbon nanotubes, among others, with the objective of increasing ionic conductivity, mechanical strength, and thermal stability. The main properties of composite separator membranes based on PVDF and its copolymers are presented in Table 5.

Table 5. Polymer composites based on PVDF and co-polymers with main properties, goal, and achievement.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF	Al ₂ O ₃	1 M LiPF ₆ in EC/DEC/DMC (1:1:1)	55.8/153.5	2.23 × 10 ⁻³ (25 °C)/114.2	Production of a composite PVDF/Al ₂ O ₃ ; High thermal stability and ionic conductivity, low discharge capacity decay.	[15]
PVDF	Al ₂ O ₃	EC/DMC (1:1)	-/230	1.24 × 10 ⁻³ /151.97 (C)	Core-shell composite nonwoven separator of PVDF-HFP@Al ₂ O ₃ ; high heat resistance up to 200 °C without any shrinkage.	[65]
PVDF	Al ₂ O ₃	1 M LiPF ₆ in EC/DEC (<i>w:w</i>)	67/230	1.49 × 10 ⁻³ /146.3 (0.2C)	Separator-cathode assembly with PVDF/Al ₂ O ₃ ; Good electrochemical performance.	[66]
PVDF	AlO(OH) nanoparticles	1 M LiPF ₆ in EC/DEC (3:7)	-/65	-/-	Ceramic separator based on boehmite nanoparticles; Improved safety and wettability.	[67]
PVDF	BC	1 M LiTFSI in EC/DEC (1:1)	-/-	4.2 × 10 ⁻³ (30 °C)/-	Preparation of GPEs based on cross-linkers; High ionic conductivity and thermal stability.	[68]
PVDF	Carbon	1 M LiTFSI and 0.1 M LiNO ₃ in DOL/DMC (1:1)	-/-	-/827 (0.5C)	PVDF-C separator by phase inversion technique; Superior rate performance and stability.	[69]
PVDF	CNF	1 M LiTFSI in DOL/DMC (1:1)	-/119	-/1739.2 (C)	Production of CNF/PVDF separators for Li-S batteries Great battery discharge capacity and cycling stability.	[20]
PVDF	Cellulose acetate/Al(OH) ₃	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	68.6/403.9	2.85 × 10 ⁻³ /151.97 (C)	Environmental friendly materials in a separator; High electrolyte uptake, ionic conductivity and cycling performance.	[70]
PVDF	DNA-CTMA	LiAsF ₆ in EC/EMC/DMC	-/-	-/-	PVDF/DNA-CTMA membrane as a solid polymer/gel electrolyte separator; Improved thermal and mechanical properties.	[71]
PVDF	LiPVAOB	1 M LiPF ₆ in EC/DMC/EMCC (1:1:1, <i>w:w:w</i>)	-/88.5	2.6 × 10 ⁻⁴ /120 (0.2C)	Composite gel polymer electrolyte PVDF/LiPVAOB membrane; Good ionic conductivity.	[33]
PVDF	Nanoclays/PVP	1 M LiPF ₆ in EC/DMC (1:1)	87.4/553.3	-/-	Study of the influence of solvents in the separator High porosity and uptake.	[72]

Table 5. Cont.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF	NCC	1 M LiPF ₆ in EC/DMC (1:1)	-/-	3.73 × 10 ⁻³ (25 °C)/-	Preparation of NCC-PVDF separators by phase inversion; Improved wettability and mechanical properties.	[73]
PVDF	MA groups	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	67.4/-	1.48 × 10 ⁻³ /136 (0.2C)	Study of the addition of MA groups to the PVDF structure; High ionic conductivity.	[74]
PVDF	MMT	1 M LiPF ₆ in EC/EMC/DEC (1:1:1)	84.08/333	4.20 × 10 ⁻³ (25 °C)/144	Effect of different contents of MMT filler in PVDF separators; High ionic conductivity and porosity.	[75]
PVDF	MOF-808	-	-/-	1.56 × 10 ⁻⁴ (65 °C)/-	Production of a MOF/polymer membrane; Good mechanical properties and durability.	[76]
PVDF	Octaphenyl-POSS	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	66.1/912	4.2 × 10 ⁻³ /145.8 (0.5C)	Electrospun membrane with octaphenyl-POSS particles; Increased uptake and porosity, high ionic conductivity.	[77]
PVDF	Polyether (PEGDA+PEGMEA)	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	-/230	~1.4 × 10 ⁻³ (25 °C)/93 (0.5C)	Preparation of GPEs with PVDF and polyethers.	[78]
PVDF	PMIA	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, <i>w:w:w</i>)	-/-	8.1 × 10 ⁻⁴ /135.29 (0.2C)	Composite sandwich type separator, by electrospinning; High capacity retention and good rate performance.	[79]
PVDF	P-PAEK	1 M LiPF ₆ in EC/DMC (1:1)	71.7/123.7	/141.6 (C/2)	Development of a P-PAEK/PVDF separator High wettability and electrolyte uptake.	[80]
PVDF	PFSA	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	-/-	1.53 × 10 ⁻³ /137.9 (C)	PVDF/PFSA blend membrane; High stability and discharge capacity.	[81]
PVDF	rGO	1 M LiTFSI + 0.1 M LiNO ₃ in DME/DOL (1:1)	71/380	/646	Double-layer PVDF/rGO membrane by electrospinning; High safety and cycling stability.	[82]
PVDF	SiO ₂	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	54.1/279.5	-/175.7	Synthesis of a composite separator with SiO ₂ ; High wettability, uptake and thermal/mechanical stability.	[17]
PVDF	SiO ₂	1 M LiPF ₆ in EC/EMC (1:1 in volume)	70/370	2.6 × 10 ⁻³ /132 (C)	Addition of SiO ₂ nanoparticles on PVDF membranes; Improvement of wettability and ionic conductivity.	[83]
PVDF	SiO ₂	1 M LiPF ₆ in EC/DEC (1:1, <i>w:w</i>)	85/646	7.47 × 10 ⁻³ /159 (0.2C)	Electrospun PVDF/SiO ₂ composite separator; Excellent thermal stability and high ionic conductivity.	[84]
PVDF	SnO ₂	1 M LiPF ₆ in EC/DMC (1:1 <i>w:w:w</i>)	-/-	-/-	Use of SnO ₂ nanoparticles in a PVDF electrospun separator; Good cycling performance.	[85]

Table 5. Cont.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF	ZnO	1 M LiPF ₆ in EC/EMC (1:2)	-/-	-/-	Piezo-separator for integration on a self-charging power cell; Enhanced electrochemical performance.	[86]
PVDF	ZnO	1 M LiPF ₆ in EC/DEC (1:1)	-/-	-/-	Piezo-separator for self-charging power cells; Stable and efficient performance.	[87]
PVDF	ZrO ₂ /PEO	1 M LiTFSI in DOL/DME (1:1)	-/147.3	3.2×10^{-4} (25 °C)/1429 (0.2C)	GPE for lithium-sulfur batteries; High discharge capacity and rate performance.	[88]
PVDF-HFP	Al ₂ O ₃	0.5 M NaTf/EMITf	-/-	$6.3\text{--}6.8 \times 10^{-3}$ (25 °C)/-	Introduction of Al ₂ O ₃ in a gel polymer electrolyte; Improved mechanical properties.	[14]
PVDF-HFP	Al ₂ O ₃	1 M LiPF ₆ in EC/DEC +2% VC	-/372	1.3×10^{-3} /155 (0.5C)	Colloidal Al ₂ O ₃ composite separator; enhancement of the mechanical strength of the PVDF-HFP separator.	[89]
PVDF-HFP	Al ₂ O ₃	1 M LiPF ₆ in EC/DMC/EMC (v:v:v = 1:1:1)	-/420	4.7×10^{-4} /109 (4C)	Production of a low cost membrane, with a simple and easy scalable manufacturing process; High electrolyte uptake and good electrochemical stability and performance.	[90]
PVDF-HFP	Al(OH) ₃	1.15 M LiPF ₆ in EC/EMC (3:7, v:v)	84/127	10^{-3} /81 (C/2)	Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; Suitable electrolyte uptake.	[91]
PVDF-HFP	Al ₂ O ₃ /CMC	1 M LiPF ₆ in EC/DEC/PC/EMC (2:3:1:3)	42.7/-	9.3×10^{-4} (25 °C)/-	Composite separator with Al ₂ O ₃ /CMC; Safer and more stable separators.	[92]
PVDF-HFP	BN	1 M LiPF ₆ in EC/DEC (1:1)	-/-	-/150 (0.2C)	3D separator; improved cycling stability with lower voltage polarization	[93]
PVDF-HFP	CA	1 M LiPF ₆ in EC/DMC	85/310	1.89×10^{-3} /136 (8C)	Porous and honeycomb-structured membrane; higher lithium-ion transference number and improved rate performance	[94]
PVDF-HFP	Clay	1 M LiPF ₆ in EC/DEC/EMC (1:1:1, v:v:v)	-/-	1.49×10^{-3} /-	New technique to incorporate clay sheets in a PVDF-HFP matrix, as separator; Thermal stability and higher ionic conductivity.	[95]
PVDF-HFP	EMImNO-LiNfO	-	-/-	3.92×10^{-4} /(20 °C) 57 (C)	Introduction of anion-based IL and lithium salt in a GPE; High thermal stability, good electrochemical properties.	[96]
PVDF-HFP	GO	1 M LiPF ₆ in EC/DEC/EMC (1:1:1)	-/71	1.115×10^{-3} (25 °C)/-	Addition of GO in separators to increase thermal properties; improved electrochemical and mechanical properties.	[97]

Table 5. Cont.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF-HFP	Graphene	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	88/470	3.61 × 10 ⁻³ /149 (C)	PVDF-HFP/graphene GPE by NIPS; Increased porosity, uptake and ionic conductivity.	[18]
PVDF-HFP	HMSS	1 M LiPF ₆ in EC/DEC (1:1)	~70/285	2.57 × 10 ⁻³ (25 °C)/-	Development of PVDF-HFP with HMSS separators; Increased wettability and porosity.	[98]
PVDF-HFP	Li _{1.3} Al _{0.3} Ti _{1.7} (PO ₄) ₃	1 M LiTFSI + 0.25 M LiNO ₃ in DME/DOL (1:1)	34/143.9	8.8 × 10 ⁻⁴ (25 °C)/1614	Ceramic/polymer membrane for lithium-sulfur cells; High ionic conductivity and discharge capacity.	[99]
PVDF-HFP	LiTFSI/SN	-	-/-	1.97 × 10 ⁻³ (20 °C)/-	Production of supercapacitors with GO electrodes and GPE; High ionic conductivity.	[100]
PVDF-HFP	LLTO	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	69.8/497	13.897 × 10 ⁻³ (25 °C)/155.56	Incorporation of LLTO in a PVDF-HFP separator; Improved ionic conductivity.	[101]
PVDF-HFP	PI	1 M LiPF ₆ in EC/DMC (1:1)	73/350	1.46 × 10 ⁻³ /-	Evaluation of a bicomponent electrospinning method to produce the separator, Good physical properties and improved electrochemical stability.	[102]
PVDF-HFP	PET/SiO ₂	1 M LiPF ₆ in EC/DEC (1:1)	60/-	9.3 × 10 ⁻⁴ /-	Separator with an organized porous structure, with benefits for cell operation at high C-rates; Excellent cell performance.	[103]
PVDF-HFP	MgAl ₂ O ₄	1 M LiPF ₆ in EC:DEC (1:1, <i>v/v</i>)	-/-	2.80 × 10 ⁻³ /140 (0.1C)	Influence of different quantities of the MgAl ₂ O ₄ filler in the membrane; Good ionic conductivity.	[104]
PVDF-HFP	MgAl ₂ O ₄	1 M LiPF ₆ in EC/DEC (1:1, <i>w/w</i>)	60/81	10 ⁻³ (30 °C)/140 (C/10)	MgAl ₂ O ₄ as filler of thin and flexible separator; Good thermal stability and stable cycling performance.	[105]
PVDF-HFP	Mg(OH) ₂	1.15 M LiPF ₆ in EC/EMC (3:7, <i>v/v</i>)	64/115	8.08 × 10 ⁻⁴ /105 (C/2)	Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; High thermal stability and good capacity retention.	[106]
PVDF-HFP	MMT	1 M LiPF ₆ in EC/DEC (1:1, <i>v/v</i>)	40/251	9.01 × 10 ⁻⁴ /105 (0.1C)	Use of montmorillonite as filler; High thermal stability and stable cycling performance.	[107]
PVDF-HFP	NaA	1 M LiPF ₆ in EC/DEC (1:1, <i>v/v</i>)	65/194	2.1 × 10 ⁻³ /-	Separator with incorporation of NaA zeolite; Excellent thermal stability and wettability.	[108]

Table 5. Cont.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF-HFP	NaAlO ₂	0.5 M NaTf/EMITf	-/-	5.5–6.5 × 10 ⁻³ (25 °C)/-	Introduction of NaAlO ₂ in a gel polymer electrolyte; Improved ionic conductivity.	[14]
PVDF-HFP	m-SBA15	1 M LiPF ₆ in EC/DEC (1:1)	-/82.83	3.23 × 10 ⁻³ /156 (0.1C)	A PVDF-HFP composite membrane with m-SBA15 as filler; High coulomb efficiency.	[109]
PVDF-HFP	m-SBA15	1 M LiPF ₆ in EC/DEC (1:1)	-/85.36	3.78 × 10 ⁻³ /198.6 (0.1C)	Effect of the addition of a silica filler on a PVDF-HFP composite matrix separator; High coulomb efficiency.	[110]
PVDF-HFP	OIL	1 M LiPF ₆ in EC/DEC (1:1)	-/13	2 × 10 ⁻³ (25 °C)/141 (C)	Synthesis of OIL from a phenolic epoxy resin; Non-flammability, good cell performance.	[111]
PVDF-HFP	SiO ₂	1 M LiPF ₆ in EC/DMC (1:2)	65.41/217	-/124.5 (C)	Synthesis of dual asymmetric structure separators with SiO ₂ particles; High thermal stability and electrolyte uptake.	[16]
PVDF-HFP	SiO ₂	1 M LiPF ₆ in DMC/EMC/DC/VC (46.08:22.91:27.22:3.79)	26.7/202	8.47 × 10 ⁻⁴ (25 °C)/154.4	Composite separator with SiO ₂ ; Improved thermal stability and cycling performance.	[112]
PVDF-HFP	TiO ₂	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, <i>vvv</i>)	58/330	3.45 × 10 ⁻³ /122 (10C)	Evaluation of the performance of a nanocomposite polymer membrane with addition of TiO ₂ ; Excellent electrochemical performance.	[85]
PVDF-HFP	ZrO ₂	1 M LiPF ₆ in EC/DEC (1:1)	71/182	1.48 × 10 ⁻³ S·cm ⁻¹ (25 °C)/126.8 mAhg ⁻¹ (0.5C)	Preparation of ZrO ₂ /PVDF-HFP by the dip-coating method; High wettability, ionic conductivity, and thermal resistance.	[113]
PVDF-HFP	ZrO ₂	1 M LiPF ₆ in EC/EMC (1:3)	-/-	2.06 × 10 ⁻³ (25 °C)/149.7	Improvement of the electrochemical properties of a electrospun membrane; High uptake and ionic conductivity.	[114]
PVDF-HFP	ZrO ₂	1 M LiPF ₆ in EC/DEC/DMC (1:1:1)	87.53/351.2	3.2 × 10 ⁻⁴ /646 (0.2C)	Inorganic fibers as substrates to separators; High thermal stability and good mechanical properties.	[115]
PVDF-HFP	ZrO ₂	1 M LiPF ₆ in EC/DMC (1:1)	60/160	10 ⁻³ (25 °C)/75 (C)	Development of thin and flexible ZrO ₂ separators; High porosity and thermal stability.	[116]

Table 5. Cont.

Materials	Fillers	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref.
PVDF-HFP	ZrO ₂	1 M LiPF ₆ in EC/DMC (1:1)	95.7/481	2.695 × 10 ⁻³ (25 °C)/-	Incorporation of ZrO ₂ in PVDF-HFP electrospun membranes; High ionic conductivity and cycling stability.	[117]
PVP/PVDF	Black carbon nanoparticles	6 M KOH	-/-	-/-	Production of separators for supercapacitor applications Improved thermal and mechanical properties.	[19]
PP/PVDF-HFP	PMMA	1 M LiPF ₆ in EC/DMC (1:1, <i>vvv</i>)	77.9/212	1.57 × 10 ⁻³ /138 (0.2C)	Physical and electrochemical performances of a PP/PVDF-HFP/PMMA composite separator; Enhanced thermal stability and electrolyte uptake.	[52]
PP/PVDF-HFP	SiO ₂	1 M LiPF ₆ in EC/DEC (1:1, <i>vvv</i>)	-/290	1.76 × 10 ⁻³ /150 (0.2C)	PP/PVDF-HFP separator, with the inclusion of SiO ₂ nanoparticles; Favorable chemical stability and discharge capacity.	[118]
PI/PVDF-HFP	TiO ₂	1 M LiPF ₆ in EC/DEC (1:1, <i>vvv</i>)	-/-	1.88 × 10 ⁻³ /161 (0.5C)	Electrospun PI/PVDF-HFP membrane, with addition of TiO ₂ nanoparticles; Excellent electrochemical properties.	[119]

Several fillers such as n-butanol [90], SiO₂ [103], ZnO [86] MgAl₂O₄ [105], and MMT [107] particles were used with PVDF and its copolymer composites in order to improve thermal and mechanical stability as well as the ionic conductivity value.

Mechanical improvement of separators has been achieved by developing sandwich-type composite separators, by a successive electrospinning method and based on PMIA [79].

The addition of DNA-CTMA in a PVDF matrix allows the development of flexible membranes, with interesting mechanical properties, highlighting its favorable stretch properties, allowing foldable separators with elevated elasticity [71].

The addition of cellulose nanoparticles in the separator structure proved to significantly increase the mechanical strength of the membrane. It also improves the wettability and induces the β -phase formation in PVDF. However, the presence of NCC reduces the ionic conductivity of the membrane [73].

The use of SiO₂ nanoparticles in a PVDF electrospun separator can raise the mechanical strength of the membrane, thus leading to a more tough and durable battery [106].

Improved security operation for lithium ion batteries, due to suitable flammability resistance, has been addressed by developing PVDF/LiPVAOB composites membranes [33].

The direct application of a ceramic suspension of PVDF/Al₂O₃ in the electrode, resulting in a separator-cathode assembly, enhances the adhesion between these structures, and improves electrochemical cell performance [66].

PVP/PVDF membranes incorporated with carbon black nanoparticles were produced for supercapacitor applications. The separators showed improvements in mechanical properties and dielectric constant values [19].

GPEs based on boron-containing cross-linker proved to have high thermal resistance, maintaining their dimensional stability up to 150 °C, due to their stable PVDF matrix. Also, ionic conductivity and electrochemical stability were improved when compared to commercial separators [68].

Studies on the influence of solvents in nanoclay/PVDF separators showed that using DMAc as a solvent improves the porosity and electrolyte uptake of the membrane when compared with most used solvents such as NMP or DMF. Furthermore, the addition of PVP to the separator structure contributed to increase the pore size and to reduce the degree of crystallinity [72].

The addition of a metal-organic framework to a polymer structure proved to increase the conductivity of the produced membrane without needing an electrolyte. The membrane also showed high durability and good mechanical properties [76].

The dipping of PVDF nanofiber membranes into Al₂O₃ proved to improve the thermal stability of the produced separator and its ionic conductivity. It also shows a low discharge capacity decay, even at high discharge rates [111].

A double-layer separator was prepared with PVDF and reduced graphene oxide, for lithium-sulfur batteries. It is shown that the two layers combined their properties to enhance the thermal stability of the membrane and the cycling performance of the cells [82].

The use of inorganic fibers as substrate for separators lead to improved thermal and mechanical stability when compared to commercial membranes. It was also proven that it enhanced the electrochemical performance of lithium ion cells [115].

CNF/PVDF composite membranes showed greater performance when applied in Li-S batteries, with enhanced cycling stability. The produced batteries retained a capacity of 768.6 mAhg⁻¹ after 200 cycles at a 0.5 C rate [20]. The development of PVDF-C separators by the phase-inversion method for Li-S batteries also leads to outstanding electrochemical performance results, associated with the presence of the conductive carbon network in the polymer matrix [69].

In the search for more environmental friendly materials, a separator with PVDF, cellulose acetate and Al(OH)₃ particles was developed by non-solvent induced phase separation (NIPS), the microstructure being presented in Figure 6a. This membrane exhibited high porosity, electrolyte uptake, and ionic conductivity, as well as good cycling capacity, even at high C-rates, as demonstrated in Figure 6b [70].

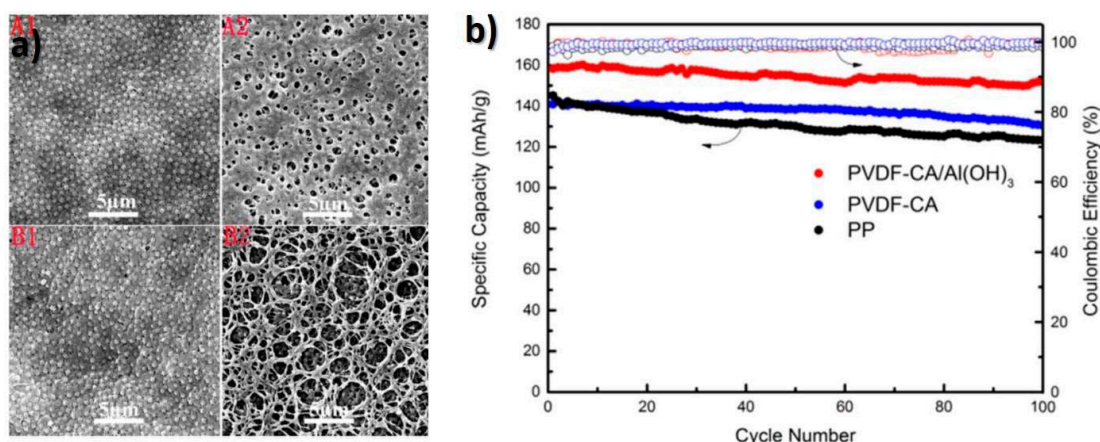


Figure 6. (a) SEM images of separators microstructure and (b) cycle performance of cells assembled [70], with copyright permission from Elsevier.

PVDF was also used in the study of the potential of zeolitic imidazolate framework-4 in separators. The prepared membranes showed high thermal stability, porosity, ionic conductivity, and cycling performance when compared with conventional separators [120].

The incorporation of Meldrum's acid groups in the PVDF structure proved to increase the ionic conductivity of the membrane, as well as the cycling performance, in particular at high C-rates [74].

PVDF/PFSA electrospun nanofibers allow the development of membrane with high mechanical stability and ionic conductivity with high discharge capacity and cycling stability [81].

A GPE membrane was developed by blending PVDF with PEO and ZrO₂. This membrane showed high electrolyte uptake, and excellent rate performance and discharge capacity for application in lithium-sulfur batteries [88].

Electrospun membranes with Octaphenyl-POSS nanoparticles showed a significant improvement in porosity and electrolyte uptake. For a ratio of 2:100 (*w:w*), the separator proved to have high mechanical stability, ionic conductivity, and thermal stability [77].

A nonaflate anion-based IL and lithium salt was introduced on a GPE, allowing the development of a membrane with high thermal stability and electrochemical properties. When used alongside with a LiCoO₂ cathode, this separator also showed good discharge capacity and capacity of retention [96].

The addition of MgAl₂O₄ as filler in electrospun fibrous PVDF-HFP separators contributes to improving electrochemical performance, with high discharge capacity and excellent cycle life results [104].

The integration of m-SBA15 as filler in a polymer matrix, on the other hand, is advantageous as it decreases the degree of crystallinity of PVDF-HFP, increasing electrolyte uptake and enhancing the ionic conductivity [109,110].

The enhancement of the electrochemical performance has been extensively addressed by composites membranes with TiO₂ nanoparticles [119], and clay nanosheets [95], the latter improving the interfacial areal connection between the polymer structure and clay, facilitating ion transport.

The NaA zeolite is considered to be a very interesting material for incorporation as filler in lithium ion battery separators. It allows the formation of voids in the composite separator structure, which are filled with electrolyte, substantially increasing the ionic conductivity [108].

The safety operation of lithium ion batteries can be upgraded by the addition of metal hydroxides such as Al(OH)₃ and Mg(OH)₂, in PVDF-HFP composite separators. These metal hydroxides endow a fire-retardant behavior to the cells, due to their natural thermal stability [91].

Kuo et al. synthesized an oligomeric ionic liquid from a phenolic epoxy resin. By blending this ionic liquid with PVDF-HFP, a high performance, non-flammable gel polymer membrane was

obtained. This membrane exhibits high ionic conductivity, although with a low liquid electrolyte uptake (<50%) [111].

The addition of ZrO_2 filler increases the porosity, ionic conductivity, and thermal resistance of the PVDF membranes. The presence of polar constituents and high connected interstitial voids facilitate electrolyte absorption, increasing the ionic conductivity and the performance of the membranes [113]. When a layer of ZrO_2 was added between two layers of PVDF-HFP, the obtained separator presented even better electrochemical properties [114].

Graphene oxide nanosheets incorporated during the phase inversion of PVDF-HFP improve electrochemical battery performances of the produced separators, as well as thermal stability and the mechanical properties of the membrane [97].

HMSS/PVDF-HFP composite separators with improved porosity were developed; the presence of SiO_2 spheres created a well-developed microporous structure, leading to higher wettability and ionic conductivity [98].

The incorporation of a superfine LLTO in a PVDF-HFP separator enhanced the ionic conductivity of the membrane. It was also been shown that a cell with a this type of separator presents improved discharge capacity and rate performance [101].

Bohemite composite separators were produced, exhibiting cycling performances comparable to the conventional ones. These membranes are also safer because of the limitation to Li dendrite formation, preventing the occurrence of short circuits [67].

A comparative study of Al_2O_3 and NaAlO_2 particles in a gel polymer electrolyte proved that NaAlO_2 membranes present higher ionic conductivity than Al_2O_3 , as well as improved mechanical properties [14].

ZrO_2 membranes with PVDF-HFP as a binder were produced by solvent casting methods. These separators present high porosity and thermal stability, but show lower mechanical strength than commercially available membranes [116].

A GPE produced by thermal crosslinking of PEGDA and PEGMEA proved to be compatible with lithium ion batteries, with a high coulombic efficiency of 94% after 100 cycles [78].

Liu et al. produced a GPE with PVDF-HFP and graphene via NIPS. The addition of a small concentration of graphene (0.002 wt. %) proved to significantly improve the properties of the membrane by increasing porosity, electrolyte uptake, ionic conductivity, and cycling performance, when compared to commercial separators [18].

Regardless of the fillers type used, Table 5 shows that most of the work is devoted to increasing ionic conductivity and electrochemical performance compared to the pure matrix. In particular, inert oxide ceramics (Al_2O_3 , TiO_2 , SiO_2 , ZrO_2) reduce the degree of crystallinity, and enhance mechanical properties and ionic conductivity value. Carbon materials (CNF, Graphene, rGO) improve safety and interfacial stability between electrodes and separator membranes, and lithium fillers such as $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, LiTSFI, and LLTO increase ionic conductivity value of the separators.

In addition, there are other fillers types such as zeolites and clays that are being intensely used for the development of separators, allowing the improvement of electrochemical behavior.

3.4. Polymer Blend Separator Membranes

Finally, another type of separator membrane are polymer blends where two different polymers with complementary properties are used; for example one showing excellent mechanical properties and the other with a hydrophilic character. The main properties of polymer blends based on PVDF and its copolymer are presented in Table 6.

Table 6. Polymer blends based on PVDF and co-polymers with main properties, goal, and achievement.

Materials	Blends	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref
PVDF	HDPE	1 M LiPF ₆ in EC/DEC/DMC (1:1:1)	58/260	2.54 × 10 ⁻³ S·cm ⁻¹ (25 °C)/156.1 mAhg ⁻¹ (0.1C)	Production of a sponge-like PVDF/HDPE film; High ionic conductivity and cycling performance.	[121]
PVDF	HTPB-g-MPEG	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	56/350	3.1 × 10 ⁻³ /116 (C)	Enhancement of the stability of entrapped liquid electrolyte and corresponding ion conductivity.	[122]
PVDF	MC	1 M LiPF ₆ in EC/DEM/EMC (1:1:1, <i>w:w:w</i>)	-/138.6	1.5 × 10 ⁻³ /110 (C)	PVDF composite separator with cellulose material; Excellent electrochemical performance.	[123]
PVDF	MEP	1 M TEABF ₄ in AN/PC and 1 M LiPF ₆ in EC/DEC	77/-	1.3 × 10 ⁻² /-	Manufacturing by phase inversion, with MEP as a cross-linking agent; Good mechanical strength.	[34]
PVDF	NCC	1 M LiFAP in EC/DMC (1:1)	-/-	-/-	Separators with applications in hybrid electric vehicles; Favorable performance at high-voltage cells.	[124]
PVDF	NCC	1 M LiPF ₆ in EC/DMC (1:1)	-/-	-/108 (1C)	Separators with applications in hybrid electric vehicles; Influence on high-rate cell operation.	[125]
PVDF	PAN	1 M LiPF ₆ in EC/DMC/DEC (1:1:1)	77.7/414.5	2.9 × 10 ⁻³ (25 °C)/-	Improved thermal and mechanical properties; High cycling stability.	[126]
PVDF	PAN	1 M LiPF ₆ in EC/DMC/EMC (1:1:1)	-/320	1.45 × 10 ⁻³ /145.71 (0.2C)	Production of an electrospun blended membrane; High thermal and mechanical stability.	[127]
PVDF	PBA	1 M LiPF ₆ in EC/DEC/DMC (1:1:1)	-/120	8.1 × 10 ⁻⁴ (25 °C)/95 (0.1C)	Preparation of cross-linked PBA/PVDF GPE; Good cycling stability.	[128]
PVDF	PDMS-g-(PPO-PEO)	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, <i>w:w:w</i>)	80.1/512	4.5 × 10 ⁻³ /120 (1C)	Porous separator; Good electrochemical stability.	[129]
PVDF	PEGDA	1 M LiPF ₆ in EC/DMC (1:1)	-/-	3.3 × 10 ⁻³ /117 (0.1C)	Separator produced by thermal polymerization; High capacity retention.	[130]
PVDF	PEO	1 M LiPF ₆ in EC/DMC (1:1)	/530	-/-	Production of blended membranes by electrospinning; improved conductivity and uptake.	[131]

Table 6. Cont.

Materials	Blends	Electrolyte Solution	Porosity and Uptake (%)	Conductivity (S·cm ⁻¹) and Capacity (mAh·g ⁻¹)	Main Goal/Achievement	Ref
PVDF	PEO	1 M LiPF ₆ in EC/DMC (1:1)	-/527	-/-	Development of electrospun membranes; High electrolyte uptake, low shutdown temperature.	[132]
PVDF	PET	-	80/270	-/-	Synthesis of a hybrid separator; High wettability and electrolyte uptake.	[133]
PVDF	PI	1 M LiPF ₆ in EC/PC/DEC/VC (35.4:17.2:45.1:2.3)	-/-	1.3×10^{-3} /141	Preparation of the separator by electrospinning; Improved thermal stability and mechanical properties.	[134]
PVDF	PMMA/CA	1 M LiPF ₆ in EC/DMC (1:1, <i>w:w</i>)	99.1/323	-/-	Elevated porosity and electrolyte uptake.	[135]
PVDF	P(MMA-co-PEGMA)	1 M LiPF ₆ in EC/EMC/DMC (1:1:1, <i>w:w:w</i>)	-/372	3.01×10^{-3} /-	Porous separator; Improved capacity retention.	[136]
PVDF	PMMA/SiO ₂	-	80.1/293.2	1.97×10^{-3} /-	Evaluation of the effect of a PMMA and SiO ₂ blend on a PVDF electrospun membrane as a separator; High electrolyte uptake and improved ionic conductivity.	[137]
PVDF	PVP	1 M Et ₄ N-BF ₄ /PC	-/360	1.8×10^{-3} (25 °C) /-	Separators for supercapacitors; High uptake and power density.	[138]
PVDF	TAIC	1 M TEABF ₄ in AN/PC and 1 M LiPF ₆ in EC/DEC	75/-	1.4×10^{-2} /-	Manufacturing of separator by phase inversion, with TAIC as cross-linking agent. High ionic conductivity.	[34]
PVDF-TrFE	PEO	1 M LiTFSI in PC	44.5/107	5.4×10^{-4} /124 (C/5)	Research on the physical and chemical properties of a PVDF-TrFE/PEO blend Favorable cycling performance.	[139]
PVDF-HFP	CA	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, <i>v:v:v</i>)	66.36/355	6.16×10^{-3} /138 (0.2C)	Investigation of the use of CA from waste cigarette filters, in PVDF-HFP membranes; Good electrochemical performance and excellent thermal stability.	[140]
PVDF-HFP	HDPE	-	71/300	2.97×10^{-3} (25 °C) /140.5 (C)	Preparation of the separator by non-solvent-induced phase separation; High ionic conductivity.	[141]
PVDF-HFP	PANI	1 M LiPF ₆ in EC/DMC (1:1)	83/270	1.96×10^{-3} /-	High thermal stability, electrolyte uptake, and ionic conductivity	[142]

Table 6. Cont.

Materials	Blends	Electrolyte Solution	Porosity and Uptake (%)	Conductivity ($S \cdot cm^{-1}$) and Capacity ($mAh \cdot g^{-1}$)	Main Goal/Achievement	Ref
PVDF-HFP	PEG/PEGDMA	1 M $LiClO_4$ in EC/DEC (1:1, <i>v:v</i>)	71/212	1.70×10^{-3} / -	Investigation into a strengthened electrospun nanofiber membrane separator; High porosity and electrolyte uptake.	[143]
PVDF-HFP	PLTB	1 M $LiPF_6$ in EC/DMC (1:1, <i>v:v</i>)	70/260	1.78×10^{-3} / 138 (0.5C)	Excellent electrochemical performance.	[144]
PVDF-HFP	PSx-PEO3	1 M LiTFSI in EC/DMC (1:1, <i>w:w</i>)	-/520	4.2×10^{-4} (20 °C) / 123 (C)	Production of a safe PVDF-HFP blended membrane, which can be sprayed; Elevated electrolyte uptake.	[145]
PVDF-HFP	PVSK	1 M LiTFSI + 0.25 M $LiNO_3$ in DME/DOL (1:1)	27 / -	- / 1220	Improved cycling performance.	[146]
PVDF-HFP	PVC	1 M $LiPF_6$ in EC/DMC (1:2)	62/230	1.58×10^{-3} / 125 (0.1 C)	Tri-layer polymer membrane; Good mechanical and thermal stability.	[44]
PEI/PVDF	x-PEGDA	1 M $LiPF_6$ in EC/DMC/EMC (1:1:1)	64.6/235.6	1.38×10^{-3} (25 °C) / 160.3 (0.2C)	Production of x-PEGDA-coated PEI/PVDF membranes; high wettability, porosity, and ionic conductivity.	[147]

PVDF composite separators with methyl cellulose as host of gel polymer electrolyte allows the development of low cost and environmentally friendlier separators with excellent mechanical, thermal, and electrochemical performances [123].

A trilayer porous membrane of PVDF-HFP with PVC as the middle layer was developed. It was shown that a good porosity and uptake value can be achieved, though the mechanical stability was negatively affected [44].

Cells produced with PVDF-NCC separators presented good battery performance at high C-rates, which is very critical for meeting the minimum and maximum power-assist requirements for integration in hybrid electric vehicles [124,125].

A mechanically strengthened electrospun composite PVDF-HFP/PEG/PEGDMA separator was developed. PEG and PEGDMA allow the improvement of the mechanical strength of the composite membrane, which is confirmed by the existence of physical bonded structures [143].

P(MMA-co-PEGMA) and PDMS-g-(PPO-PEO) copolymers within PVDF allow the reduction of the crystallinity of the PVDF matrix, and gently improve the electrolyte uptake, thus leading to an enhanced ionic conductivity [129,136].

PLTB can be successfully used in a PVDF-HFP composite separator. In comparison with a typical PP separator, it is more safe and efficient, due to its thermal and electrochemical stability. This separator is very promising in terms of security operation, because of flame retardant characteristics [144].

An eco-friendly technique to recover cellulose acetate from wasted cigarette filters (Figure 7) was developed, and the material can be integrated in a PVDF/CA membrane for lithium ion batteries, which presents a good performance [140].

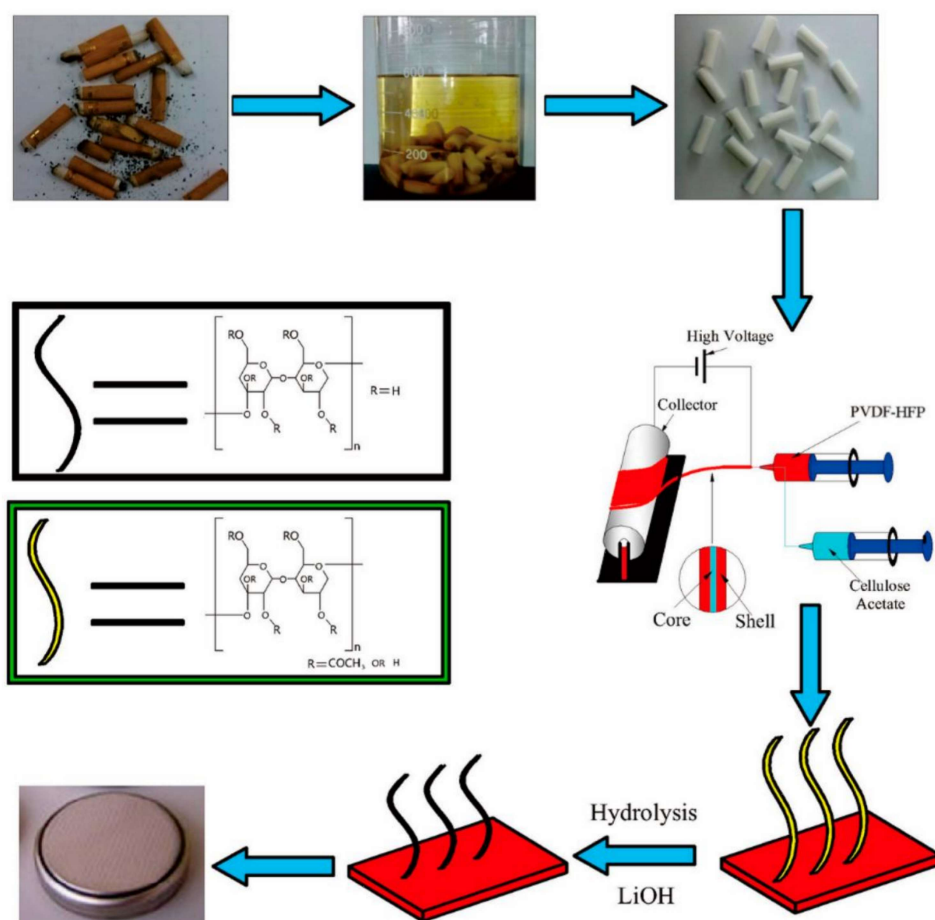


Figure 7. Preparation of PVDF-HFP/CA nanofiber separators for lithium ion batteries [140], with copyright permission from the American Chemical Society.

PVDF separators were manufactured by a phase inversion technique, with two different cross-linking agents (TAIC and MEP) and with the application of gamma radiation. The produced membranes are characterized by good mechanical behavior and low electrical resistance [34].

Electrospun PVDF membranes blended with PMMA/SiO₂ showed good porosity and elevated electrolyte uptake [137]. Blending with PI further enhanced their thermal and mechanical properties, ensuring a better battery performance than commercial PE separators [134].

PVDF/PEO blend membranes show an increase of the ionic conductivity and electrolyte uptake when compared with PVDF membranes. The improved wettability and porosity in x-PEGDA-coated PEI/PVDF membranes has been also reported [147].

PVDF-HFP/HDPE membranes were prepared by non-solvent induced phase separation. This separator presents good cycling performance in lithium ion batteries and a high ionic conductivity [141]. Further studies showed an increased discharge capacity of these membranes, by decreasing the size of the HDPE fillers [121].

PVDF/PAN blend separators were produced by TIPS [126] and electrospinning [127], with improved thermal and mechanical properties. The best PVDF/PAN ratio was 90:10. Despite the lower ionic conductivity when compared with conventional separators, these membranes showed higher cycle and C-rate performance [126].

PVDF/PAN electrospun membrane have excellent dimensional stability even at high temperatures, high electrolyte uptake and ionic conductivity, and superior discharge capacity [127].

The blending of PVDF and PEO in an electrospun membrane proved to increase significantly the electrolyte uptake of the separator, while decreasing the shutdown temperature [132].

Cross-linked PBA/PVDF GPE were prepared by soaking semi-interpenetrating polymer networks with liquid electrolyte. For a PBA/PVDF ratio of 1:0.5, the best results of electrolyte uptake, ionic conductivity, and cycling stability were obtained [128].

A PVDF/PET hybrid separator was produced via a mechanical pressing process. The obtained membrane presented high wettability and electrolyte uptake, while maintaining good thermal stability [133].

The introduction of PANI in a PVDF separator by the breath figure method proved to increase the electrolyte uptake and ionic conductivity of the membrane. The best results were obtained for 30% of PANI, with a uniform pore structure and excellent thermal stability [142].

The use of PVDF-HFP/PVSK membranes in lithium-sulfur batteries has been reported. It has been proved that even small amounts of PVSK (5 wt. %) increase the discharge capacity of the cell and reduce the capacity decay [146].

An increase of the use of natural polymers and biopolymers is observed for the preparation of PVDF and copolymer blends, considering the environmental issues. It is demonstrated in Table 6 that they allow to improve mechanical properties and wettability, and consequently the battery performance. In addition, the use of conductive polymers such as PANI in polymer blends has acquired special attention in recent years, considering that the electrical properties are improved without mechanical deterioration. Typically, the most commonly used PVDF and PVDF-HFP blends are developed with PAN and PEO polymers, allowing the improve thermal and mechanical stability, as well as wettability and ionic conductivity value, respectively.

4. Conclusions and Future Trends

In this review, the latest advances in PVDF-based battery separators for lithium-ion battery applications are presented.

Considering the excellent properties of PVDF and its copolymers as a separation membrane and the importance of the role of the battery separator in battery applications, this review was divided into four different sections—single polymers, surface modification, polymer composites, and blends, where, for each category, the improvement of the main properties of the separators' degree of porosity,

uptake value, mechanical and thermal properties, ionic conductivity, and cycling performance, as well as safety and environmental impacts,- for the different developed materials was presented.

In the single polymer category, PVDF and PVDF-HFP stand out as the most commonly applied polymers produced by various processing techniques, with TIPS and electrospinning methods being the most commonly used to tailor microstructure (degree of porosity and pore size) to improve battery performance.

The number of research papers on surface modifications of the membranes has increased in recent years, as the surface of the polymer membrane strongly affects the uptake process. Surface modification is accomplished by coating hydrophilic polymers or plasma treatment to increase the interaction between the polymer membrane and the electrolytic solution.

Generally, the addition of fillers increases battery performance through the improvement of ionic conductivity in polymer composites, but has not yet demonstrated the best filler for PVDF and its copolymer membranes. The most commonly used fillers are inert oxide ceramics, carbon materials, and lithium fillers. The most improved properties are mechanical properties, interfacial stability, between electrodes and separator membranes and ionic conductivity value, respectively.

In relation to the polymer blends, the appearance of new blends based on natural and conductive polymers within PVDF for battery separators has been observed.

The blends of PVDF and its copolymers widely used are with PAN and PEO polymers, allowing the improvement of mechanical properties and wettability and electric properties, respectively.

The future trends for single polymer separators are to obtain single polymers with a porosity above 50% but a smaller pore size below 500 nm to prevent dendrite growth. Further, it is expected an increase in the use of ionic liquids as electrolytic solution. In relation to surface modifications, the use of poly (ionic liquids) and natural polymers as a surface modification coating of PVDF polymer membranes will be interesting, considering environmental issues.

With respect to polymer composites, future perspectives are related to improving the interaction between polymer matrix and fillers, in order to optimize filler content without decreasing electrical properties or hindering mechanical stability. Also, the use of more than one filler with complementary properties may be the way for improving cycling performance.

The progress with respect to polymer blends is related to the scalability of the fabrication process, increasing the interaction and compatibilization of the two polymers.

In summary, PVDF-based battery separators allow the tailoring of all the properties/characteristics required for a new generation of separator membranes for lithium-ion batteries with high power and excellent cycling performance.

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List of Symbols and Abbreviations

$(C_2H_5)_3CH_3NBF_4$	Triethylmethylammonium tetrafluoroborate
[C2mim][NTf2]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
Al(OH) ₃	Aluminum hydroxide
Al ₂ O ₃	Aluminum oxide
AlO(OH)	Bohemite
AN	Acetonitrile
BC	Boron-containing cross-linker
CA	Cellulose acetate
CMC	carboxymethyl cellulose
CNF	Carbon nanofiber
DEC	Diethyl carbonate

DEM	Diethoxymethane
DMAc	Dimethyl acetamide
DMC	Dimethyl carbonate
DME	1,2-dimethoxyethane
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DNA-CTMA	Deoxyribonucleic acid-cetyltrimethylammonium
DOL	1,3-dioxolane
EC	Ethylene carbonate
EMC	Ethyl methyl carbonate
EMImNfO-LiNfO	1-ethyl-3-methylimidazolium nonafluoro-1-butanesulfonate/lithium nonafluoro-1-butanesulfonate
EMITf	1-ethyl 3-methyl imidazolium trifluoromethane sulfonate
EMITFSI	1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide
EP	Ethyl propionate
Et ₄ N-BF ₄	Tetraethylammonium tetrafluoroboratein
GF	Glass fiber
GO	Graphene oxides
GPE	Gel polymer electrolyte
H ₂ SO ₄	Sulfuric acid
HDPE	High density polyethylene
HEC	Hydroxyethyl cellulose
HMSS	Hollow mesoporous silica spheres
HTPB-g-MPEG	Hydroxyl-terminated polybutadiene-grafted-methoxyl polyethylene glycol
KOH	Potassium hydroxide
LiClO ₄	Lithium perchlorate
LiCoO ₂	Lithium cobalt oxide
LiFAP	Lithium Tris(pentafluoroethane)-trifluorophosphate
LiNfO/BMImNfO	Lithium nonafluorobutanesulfonate/1-butyl-3-methylimidazolium nonafluorobutanesulfonate
LiNO ₃	Lithium nitrate
LiPF ₆	Lithium hexafluorophosphate
LiPVAOB	Lithium polyvinyl alcohol oxalate borate
Li-S	Lithium-sulfur
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
LLTO	Li _{0.33} La _{0.557} TiO ₃
MA	Meldrum's acid
MC	Methyl cellulose
MEP	Ethylene oxide-propylene oxide
Mg(OH) ₂	Magnesium hydroxide
MgAl ₂ O ₄	Magnesium aluminate
MMT	Montmorillonite
MOF-808	Zirconium (IV) metal-organic framework
m-SBA 15	Mesoporous silica
NaA	NaA zeolite
NaClO ₄	Sodium perchlorate
NaTf	Sodium trifluoromethane sulfonate
NCC	Nanocrystalline cellulose
NIPS	Non-solvent induced phase separation
NMP	N-methyl-2-pyrrolidone
OIL	Oligomeric ionic liquid (bromide bis(tri-fluoromethane)sulfonimide)
P(MMA-co-PEGMA)	Poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate)
PAN	Polyacrylonitrile
PANI	Polyaniline
PBA	Poly(butyl acrylate)
PC	Propylene carbonate
PDA	Polydopamine
PDMS-g-(PPO-PEO)	Poly(dimethylsiloxane)-graft-poly(propylene oxide)-block-poly(ethylene oxide)
PE	Polyethylene

PEG	Polyethylene glycol
PEGDA	Poly(ethylene glycol)diacrylate
PEGDMA	Polyethylene glycol dimethacrylate
PEGMEA	Poly(ethylene glycol) methyl ether acrylate
PEI	Polyetherimide
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PFSA	Perfluorosulfonic acid
PI	Polyimide
PLTB	Polimeric lithium tartaric acid borate
PMIA	Poly(m-phenylene isophthalamide)
PMMA	Polymethyl methacrylate
POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
P-PAEK	Phenolphthaleine-poly(aryl ether ketone)
PSx-PEO3	Polysiloxane-comb-propyl(triethylene oxide)
PSU	Poly(sulfone)
PTFE	Poly(tetrafluoroethylene)
PVA	Polyvinyl alcohol
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVDF-co-CTFE	Polyvinylidene fluoride-co-chlorotrifluoroethylene
PVDF-co-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropene)Poly(vinylidene fluoride-hexafluoropropylene)
PVDF-PE	Polyvinylidene difluoride-coated polyethylene
PVDF-TrFE	Poly(vinylidene fluoride-trifluoroethylene)
PVP	Polyvinylpyrrolidone
PVSK	Polyvinylsulfate potassium salt
rGO	Reduced graphene oxide
SCPC	Self-charging power cell
SiO ₂	Silicon dioxide
SN	Succinonitrile
SnO ₂	Tin oxide
TAIC	Triallyl isocyanurate
TEABF ₄	Tetraethyl ammonium tetrafluoroborate
TiO ₂	Titanium dioxide
TIPS	Thermal-induced phase separation
TTT	1,3,5-triallyl-1,3,5-triazine-2,4,6(1 H,3 H,5 H)-trione
VC	Vinylene carbonate
x-PEGDA	x-polyethylene glycol diacrylate
ZnO	Zinc oxide
ZrO ₂	Zirconium dioxide

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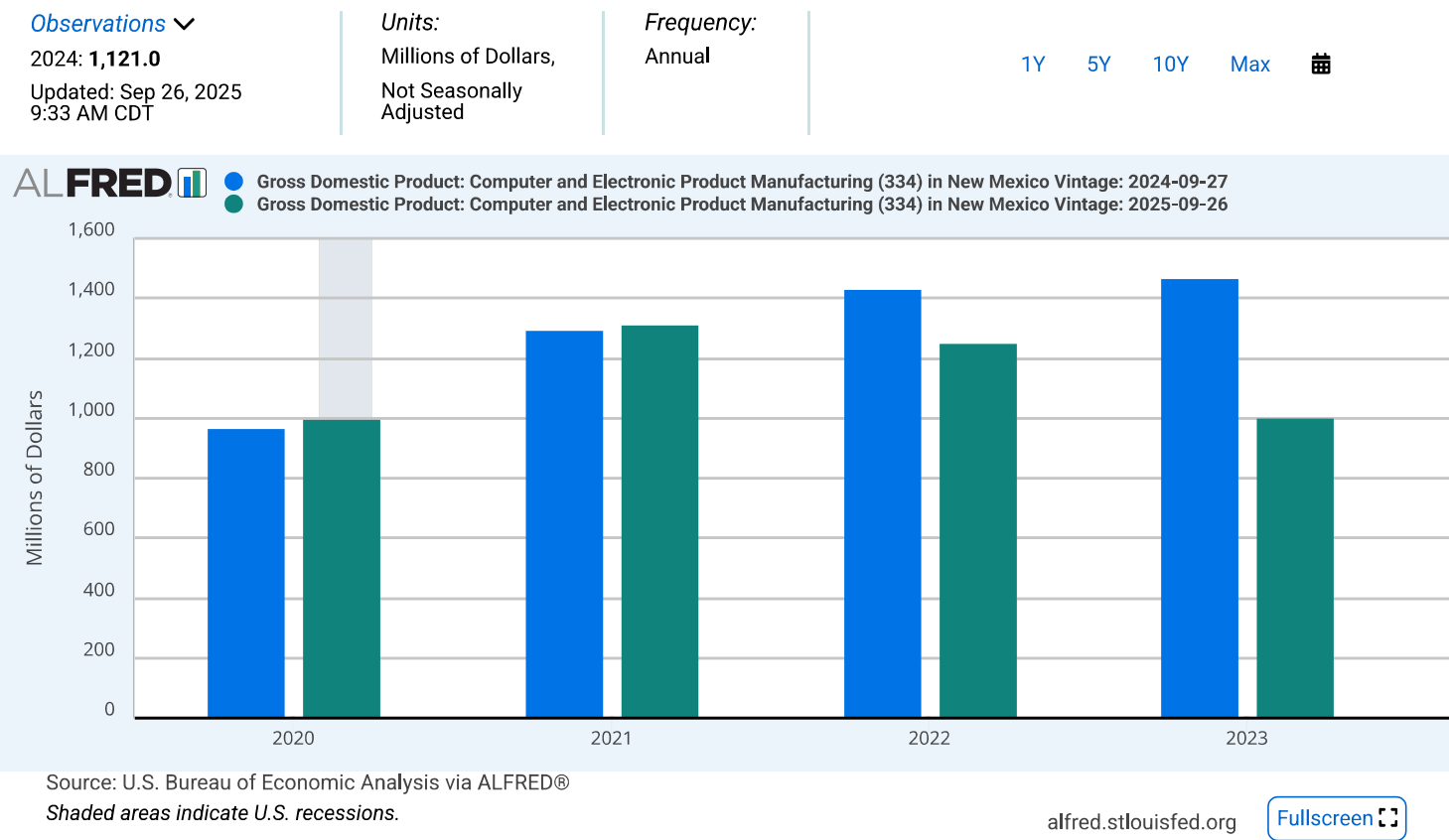


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Gross Domestic Product: Computer and Electronic Product Manufacturing (334) in New Mexico

(NMCPUELCPMANNNGSP)



ALFRED

Gross Domestic Product: Computer and Electronic Product Manufacturing (334) in New Mexico Vintage: 2024-09-27

Gross Domestic Product: Computer and Electronic Product Manufacturing (334) in New Mexico Vintage: 2025-09-26

Year	2024 Vintage (Millions of Dollars)	2025 Vintage (Millions of Dollars)
2020	~940	~970
2021	~1270	~1290
2022	~1400	~1220
2023	~1440	~970

Source: U.S. Bureau of Economic Analysis via ALFRED®
Shaded areas indicate U.S. recessions.

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Notes

Title	Release Dates
Gross Domestic Product by Industry: Private Industries: Manufacturing: Durable Goods Manufacturing: Computer and Electronic Products Manufacturing for New Mexico	2016-07-27 2021-06-21
Gross Domestic Product: Computer and Electronic Product Manufacturing (NAICS 334) in New Mexico	2021-06-22 2023-09-28
Gross Domestic Product: Computer and Electronic Product Manufacturing (334) in New Mexico	2023-09-29 2025-09-26

Source

Release

Gross Domestic Product (GDP) by State	2016-07-27	2021-02-15
Gross Domestic Product by State	2021-02-16	2025-09-26

Units

Millions of Dollars	2016-07-27	2025-09-26
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Frequency

Annual	2016-07-27	2025-09-26
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Seasonal Adjustment

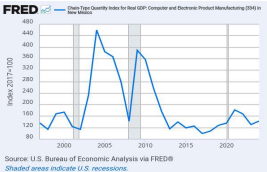
Not Seasonally Adjusted	2016-07-27	2025-09-26
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Notes

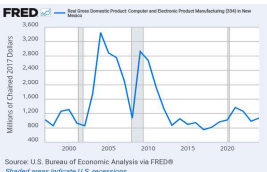
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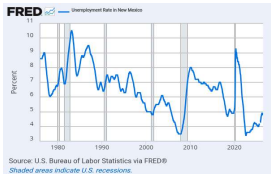
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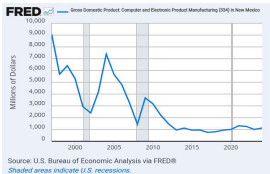
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