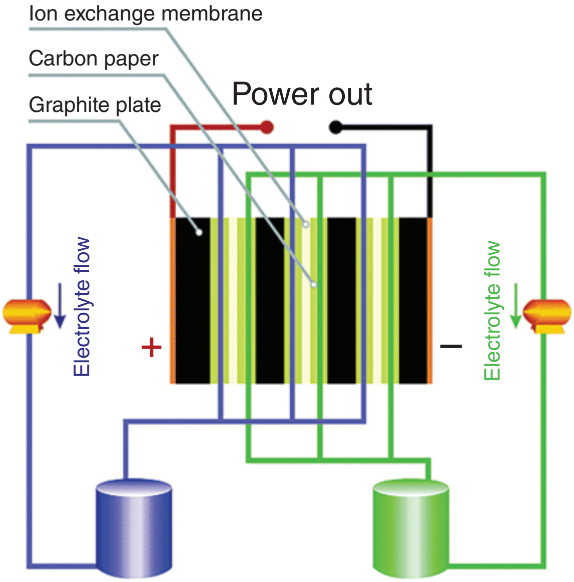


Figure 1.5 Schematic illustration of a vanadium redox flow battery. Source: Reproduced from Xuanli Luo et al. [91]./with permission of American Chemical Society.

methods include radiation grafting, which can be divided into co-irradiation and pre-irradiation, BPO-initiated grafting and ATRP grafting. The most common synthesis method is radiation grafting.

PVDF-g-PSSA is widely used in vanadium redox flow batteries (VRBs) (Schematic illustration of a VRB is shown in Figure 1.5) [91]. The PVDF-g-PSSA membrane prepared by solution grafting has a high conductivity of $3.22 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$ at 30 °C. ICP studies show that compared with Nafion 117, the vanadium ion permeability of PVDF-g-PSSA membrane is greatly reduced. Of all these membranes, pentavalent vanadium ions have the lowest permeability and trivalent vanadium ions the highest. With a low-cost PVDF-g-PSSA membrane, VRB outperforms Nafion 117 under the same operating conditions, and its energy efficiency reaches 75.8% at $30\ \mathrm{mA\,cm^{-2}}$. After more than 200 cycles, the VRB with PVDF-g-PSSA membrane can continue to function at a current density of $60\ \mathrm{mA\,cm^{-2}}$.

1.3.6 Poly(Vinylidene Fluoride-Trifluoroethylene) (P(VDF-TrFE))

VDF can be copolymerized with trifluoroethylene (TrFE) [92, 93] in various proportions to form random semi-crystalline thermoplastic copolymers. In contrast to PVDF, which requires mechanical stretching or poling to create net dipoles (β-phase) in the material, P(VDF-TrFE) can form a crystal structure with dipoles that permanently polarize the polymer without the need for these treatments [94]. It could be a useful starting material for tissue engineering applications, modifying cell behavior, and cell proliferation in a three-dimensional matrix [94].

P(VDF-TrFE) microporous membrane separators for LIBs can be prepared using the solvent-cast approach (chemical structure described in Table 1.3) [95], and Figure 1.6 shows porous P(VDF-TrFE) structures obtained by solvent evaporation

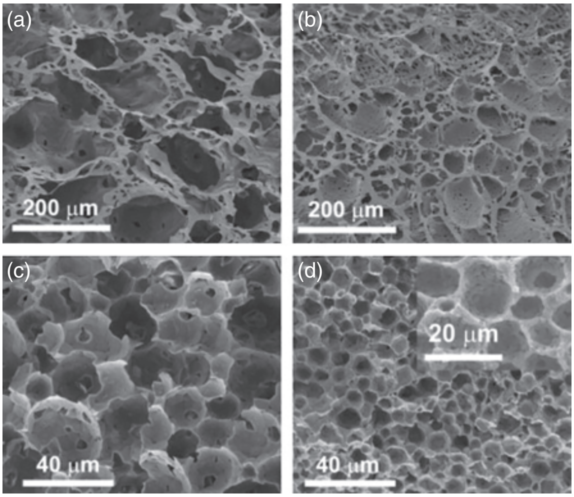


Figure 1.6 SEM microphotographs of the surface and cross-section (a, b) of 5/95 P(VDF-TrFE)/DMF and (c, d) 20/80 P(VDF-TrFE)/DMF samples obtained by solvent evaporation at room temperature. Source: California et al. [96]/with permission of Elsevier.

at room temperature [96]. Additionally, electrospinning can produce P(VDF-TrFE) copolymer membranes with low dielectric constant and good flexibility [97].

In a tissue engineering application known as directed tissue regeneration, a membrane is crucial to isolating periodontal abnormalities of the gingival connective and epithelial tissues and achieving the regeneration of bone, periodontal ligament, and cementum from their own cells. An excellent material should have acceptable electromechanical capabilities as well as biocompatibility to promote periodontal tissue regeneration. *In vitro* biocompatibility of a composite membrane of poly(vinylidene-trifluoroethylene)/barium titanate (P(VDF-TrFE)/BT was superior to that of ordinary expanded PTFE (ePTFE) [98].

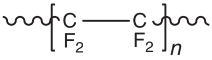
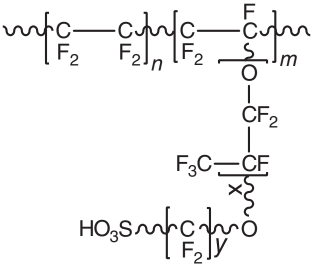
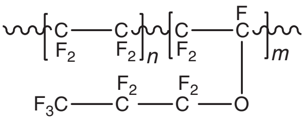
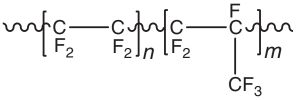
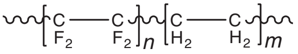
1.4 PTFE and Its Copolymer

Porous polytetrafluoroethylene (PTFE) membranes exhibit chemical inertness and have found extensive applications in many membrane separation processes, such as MD, oil–water separation, and gas–solid separation. The prevalent types of Teflon membranes are plates and hollow fibers. PTFE membranes are primarily manufactured using drawing, spinning, and pore-forming techniques. To enhance the performance of PTFE membranes and achieve enhanced results in the target application, several modification techniques were employed. These techniques included wet chemistry, plasma treatment, radiation exposure, atomic layer deposition, and high-temperature melting. Table 1.9 presents the chemical structures of homopolymeric and copolymer PTFE.

1.4.1 Homopolymeric PTFE

PTFE (chemical structure is shown in Table 1.9) is a perfluoropolymer material in which all hydrogen atoms in PE are replaced with fluorine atoms. The structural

Table 1.9 Chemical structures of homopolymeric and copolymer PTFE.

Polymer		**Chemical structure**
Poly(tetrafluoroethylene) homopolymer	PTFE	
PTFE copolymer	Perfluorosulfonic acid (PFSA)	
	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA)	
	Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)	
	Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE)	

formula is: $-[CF_2-CF_2]_n-$. PTFE is a white, hydrophobic solid whose properties depend strongly on its molecular weight. PTFE surface free energy is very low and almost does not adhere to any substance, due to its strong C—C and C—F bonds and carbon skeleton, has excellent high-temperature resistance, chemical resistance, environmental resistance, electrical insulation, oxidation resistance, strong hydrophobicity, and high fracture toughness, which is protected by a uniform spiral sheath formed by the electron cloud of fluorine atoms [28]. Table 1.10 lists the salient properties of PTFE.

These characteristics make it suitable for a variety of applications, such as exhaust-gas treatment [100], MD [101, 102], osmotic distillation (OD) [103, 104], and oil–water separation [105].

Specific membrane qualities are required depending on the application. Different membrane applications can benefit from a custom-made PTFE membrane. The most essential properties of porous membranes in gas–solid separation are solid phase rejection and gas permeability. A high pore size of about 5 μm, a narrow pore size distribution, and a thickness of less than 50 μm are necessary for effective membrane separation performance. Furthermore, for gas–solid separation, PTFE

Table 1.10 Physical and chemical properties of PTFE.

Property (standard)	PTFE	Criterion
as-polymerized PTFE	335	
Melting point (°C)		D3418
Glass transition (°C)	−103	—
Decomposition point (°C)	590	—
Phase transition (°C)	19	—
Processed PTFE		
Theoretical density/g cm^{-3} (at 23 °C)	2.16	ASTM D4895
Tensile strength/MPa (at 23 °C)	31	ASTM D4894
Compressive strength/MPa (at 23 °C)	4.4	ASTM D695
Hardness/shore D	55	ASTM D2240

Source: Reproduced from Puts et al. [99]/with permission of American Chemical Society.

membranes with high porosity and specific surface area are required [106]. PTFE nanofibers are usually prepared by biaxial stretching and electrospinning to achieve a higher specific surface area, allowing for a larger contact area between particles and fibers while maintaining adequate particle retention and breathability. This is done to meet the requirements of the gas–solid separation process. MD is a thermally driven technique for separating molecules across hydrophobic membranes by taking advantage of the temperature differential. The mass transfer coefficient and heat transfer coefficient are the two main factors that determine how effective the MD process is [107]. The structure and chemical characteristics of the membrane influence mass and heat transfer optimization in MD. Because of its low thermal conductivity and hydrophobicity, PTFE membrane is employed in the MD process to minimize heat loss. Furthermore, PTFE has a pore structure suitable for MD and a low inlet pressure. The pore diameters of PTFE membranes employed in MD are usually around 0.5 μm. Additionally, the membrane in the oil–water separation process needs to be either oleophobic (also oleophilic and hydrophobic) or hydrophobic (also oleophilic and hydrophobic) [108–110], depending on the water–oil supply (oil-in-water emulsion or water-in-oil emulsion).

The biaxial stretching method used to prepare PTFE membranes was originally developed by Stein [111] and has been used for several years in the preparation of porous PTFE membranes. In the following decades, the biaxial stretching method was adopted and modified by many researchers. Bukchon, etc. [112] prepared porous PTFE membrane by mechanical operation, and the formation mechanism of the porous structure in PTFE was proposed. The fibril is formed in the crack by tensile action and oriented in the direction of tensile action. The spatial unit size of the periodic structure depends on the amount of PTFE, the average molecular weight, and the stretching conditions. The schematic of the various stages of

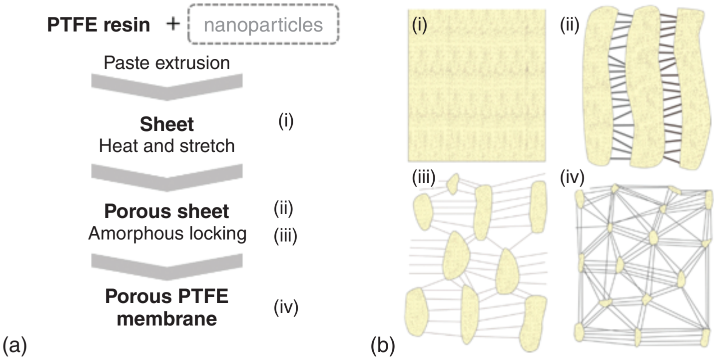


Figure 1.7 (a) Preparation process of porous PTFE membrane [113] and (b) schematic of PTFE stretching process in different stages: (i) raw PTFE sheet, (ii) early-stage stretching or strip crack process, (iii) node-forming stage or uniaxial tension process, and (iv) uniform node connection or biaxial tension process. Source: Wikol et al. / W. L. Gore & Associates, Inc.

the PTFE stretching process and the preparation procedure for the porous PTFE membrane [113] are shown in Figure 1.7.

Due to its perfect fiber shape and great productivity, electrospinning has garnered a lot of attention as a process for creating nano-/submicron fibers. After the polymer fluid is exposed to a high-voltage electric field via a micro-nozzle, it hardens into a fiber membrane. Since PTFE has a high viscoelasticity, spinning molten PTFE into fibrils is challenging [114]. Consequently, in order to facilitate the electrospinning process of creating PTFE membranes, additives are added to the PTFE emulsion. Xiong et al. blended various quantities of poly(vinylalcohol) (PVA) into a PTFE emulsion in order to electrospun a porous PTFE membrane [115]. The PVA mass ratio and emulsion concentration both have significant impacts on the membrane shape. Electrospun composite fibers with varying PVA to PTFE mass ratios are shown in Figure 1.8 as scanning electron microscopy (SEM) images: (i) 10 : 90, (ii) 20 : 80, (iii) 30 : 70, (iv) 40 : 60, and (v) 50 : 50. The surfactant tends to be more stable at high emulsion concentrations, which causes the fiber's diameter to increase. The fibers are comparatively uniform when the PVA mass ratio exceeds 3 : 7.

1.4.2 Perfluorosulfonic Acid-PFSA

The structure of perfluorosulfonic acid (PFSA) polymers is divided into two parts (seen in Table 1.9): one is a hydrophobic PTFE backbone and the other is a branched chain with a hydrophilic ion exchange group (sulfonic acid group) at the end. In the PFSA structure, the sulfonic acid group ($-SO_3^-$) is fixed on the polymer molecular chain through a covalent bond, and the sulfonic acid group formed by combining with H^+ can dissociate in a protic solvent (H_2O) and can move freely.

Generally, the proton conductivity of such proton exchange membranes under high humidity conditions can reach $0.1\,S\,cm^{-1}$ or more. The sulfonic acid group in

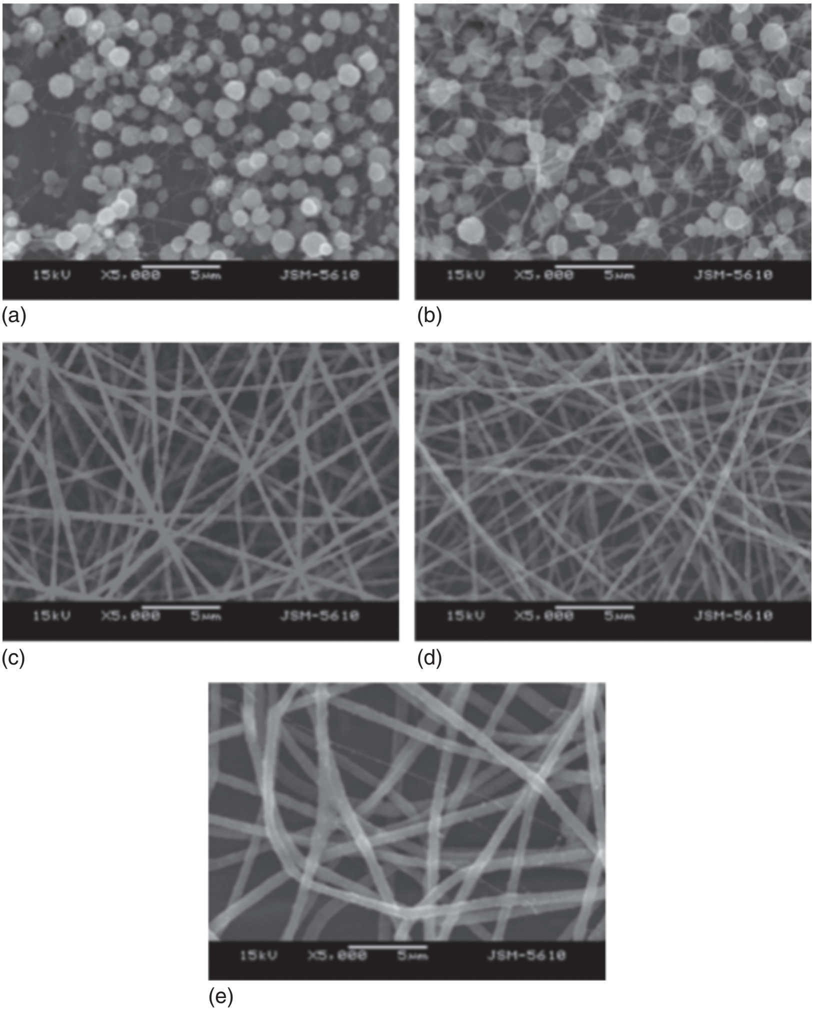


Figure 1.8 Scanning-electron-microscopy (SEM) images of electrospun composite fibers with different mass ratios of PVA to PTFE: (a) 10 : 90, (b) 20 : 80, (c) 30 : 70, (d) 40 : 60, and (e) 50 : 50. Source: Xiong et al. [115]/with permission of Cambridge University Press.

the PFSA resin is connected with the perfluoroalkyl group, and the fluorine atom has a strong electron-attracting property, which significantly improves the acidity of the sulfonic acid group. Trifluoromethanesulfonic acid (CF_3SO_3H) is 1000 times stronger than sulfuric acid, so it is called super acid. This property makes the PFSA resin have better proton conductivity. On the other hand, the molecular chain backbone of PFSA resin uses fluorocarbon chains while the C—F bond has a high bond energy ($4.85 \times 10^5\ \mathrm{J\,mol^{-1}}$) and a large fluorine atom radius (0.64×10^{-10} m). A protective barrier can be formed near the C—C bond. So, the tetrafluoroethylene segment of the PFSA resin has good hydrophobicity, and the polymer membrane has high chemical stability and strong mechanical strength [116].

PFSAs have found widespread application as solid electrolytes in electrochemical technologies, notably as proton-exchange membranes (PEMs) in polymer-electrolyte fuel cells (PEFCs) and as sodium-ion conductors in the chlor-alkali industry. These particular applications have been pivotal in driving research efforts focused on PFSAs since the 1970s when DuPont successfully developed the first commercially available PFSA ionomer known as Nafion [117]. The Nafion membrane, which is a PFSA-based membrane, is widely utilized in fuel cell applications and is readily accessible in the commercial market. Despite extensive research spanning several decades, Nafion continues to be the predominant solid electrolyte utilized in a wide range of energy storage and conversion devices. This is primarily attributed to its inherent electrochemical properties, which enable efficient ion and solvent transportation within chemically inert and mechanically resilient substrates. Consequently, Nafion effectively restricts the movement of electrons as well as reactants and products. The lifespan of PFSA membranes varies significantly, spanning from several thousand to tens of thousands of hours. This variability is influenced by various factors, including the specific end groups of the resin, the membrane's inherent features, and the operating circumstances during fuel cell testing.

Nafion is a random copolymer composed of an electrically neutral semicrystalline polymer backbone (PTFE) and a randomly tethered side-chain (polysulfonyl fluoride vinyl ether) with a pendant ionic group, SO_3^-, that is associated with a specific counterion (e.g., $–SO_3^- + H^+ \rightarrow –SO_3H$). The inherent disparity between the covalently bound pendant group and backbone leads to spontaneous phase separation, which is further intensified by solvation (when water or solvent molecules are introduced). The distinctive capability of transporting ions and solvents is attributed to the phase separation form of PFSA. PFSA, in essence, can be described as a flexible polymer that is influenced by its structure through electrostatic contact transmission and mechanical functions. Nonetheless, the morphology of the system is contingent upon a multitude of interactions and equilibriums between the mechanical energy linked to the hydrophobic backbone's deformation and the chemical/entropic energy connected to the hydration of hydrophilic ionic groups and their respective side chains. The equilibrium of this balance is regulated and influenced by a diverse array of environmental and material characteristics that dictate the relationship between the structure and properties of PFSAs, as outlined in Figure 1.9.

1.4.3 Poly(Tetrafluoroethylene-*co*-Perfluoropropyl Vinylether) (PFA)

Similar to other fluorocarbons like PTFE and fluorinated ethylene propylene, PFA has a similar coefficient of friction, dielectric properties, and chemical resistance. Its wear resistance, shore hardness, and mechanical strength are better than PTFE and equivalent to PTFE at temperatures over 150 °C. Similar to PTFE, PFA exhibits good heat resistance between −200 and 260 °C, but it also has a higher creep resistance.

PFA, whose chemical structure is displayed in Table 1.9, has a strong mix of physicochemical, structural, and thermal properties, making it a viable material for

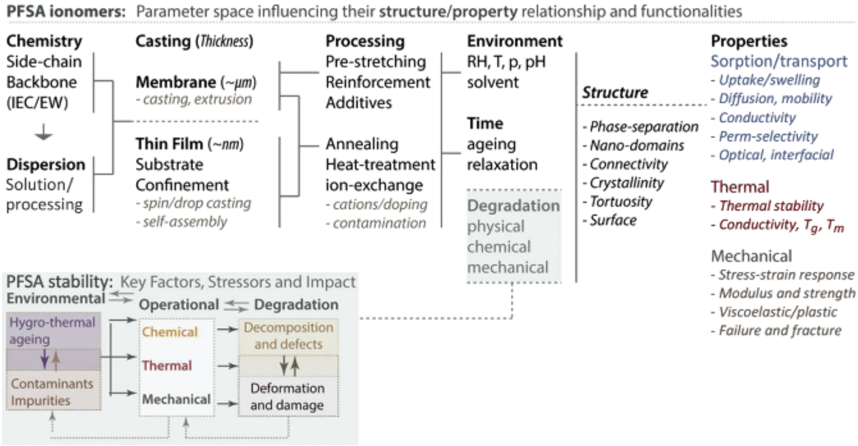
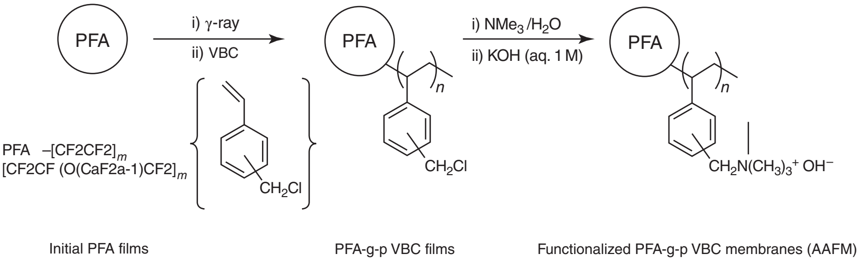


Figure 1.9 Material, processing, and environmental parameter space controlling the structure/property relationship of PFSA ionomers and their stability and degradation. Source: Reproduced from Kusoglu and Weber [116]/with permission of American Chemical Society/CC by 4.0.

fuel cell membranes [118]. After reacting with various monomers, PFA membrane has high radiation resistance, stable free radicals, and a high grafting rate. Therefore, high irradiation doses can be applied to membrane preparation without affecting its inherent mechanical properties [119].

To construct an alkaline anion-exchange membrane (AAEM) (Scheme 1.6), vinylbenzyl chloride (VBC), a versatile monomer, can be copolymerized onto pre-irradiated PFA membrane, followed by quaternary-ammonium-functionalization and hydroxylation [120]. With a maximum power density of 16 mW cm^{-2} and a maximum conductivity of 0.05 S cm^{-1} at 60 °C, this type of AAEM shows great promise for usage in direct alcohol AAEM fuel cells (DA$_3$EMFC).



Scheme 1.6 Preparation process of irradiation grafted membranes. Source: Reproduced from Liu et al. [120]/with permission of Elsevier.

1.4.4 Tetrafluoroethylene Hexafluoropropylene Copolymer-FEP

FEP (chemical structure is shown in Table 1.9) is a random copolymer formed by the polymerization of tetrafluoroethylene and hexafluoropropylene. Its molecular structure is equivalent to the structure formed by the substitution of an

F atom on a PTFE molecular chain with a $–CF_3$ group. Like PTFE, FEP also has a perfluorinated molecular structure with excellent chemical resistance, thermal stability, mechanical properties, electrical insulation properties and strong hydrophobicity. In addition, compared with the defect of poor processing performance of PTFE, the presence of the side group $–CF_3$ makes the FEP molecular chain more flexible, the glass transition temperature and melting point of FEP are reduced, and the melt viscosity is reduced, and the processability is significantly improved [121]. These characteristics make it an excellent membrane-forming polymer material and have attracted widespread attention from researchers worldwide.

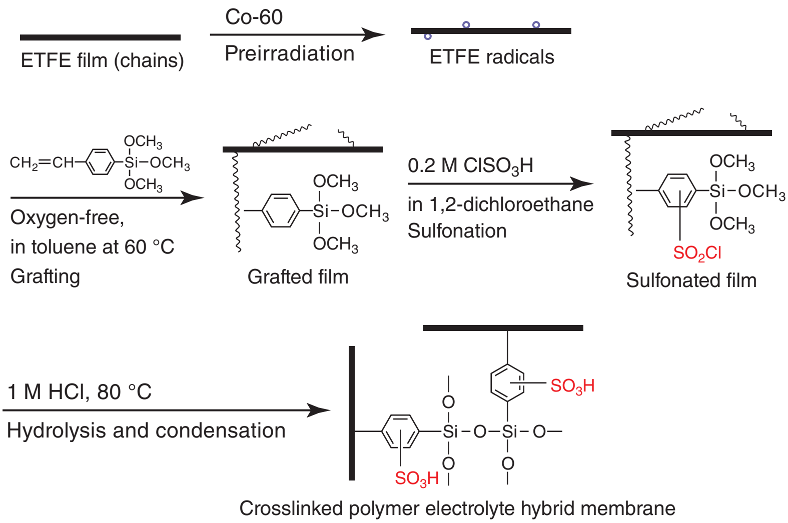
The extremely low surface free energy restricts the development of FEP separation membranes. At present, researchers mostly study the modification of FEP to increase its surface free energy and surface activity to expand the application field of FEP separation membranes. In recent years, researchers have contributed a lot to the preparation of FEP separation membranes. Huang etc. used dioctyl phthalate (DOP) as a plasticizer and composite inorganic particles as a pore-forming agent, and adopted melt spinning FEP hollow fiber microporous membrane was prepared by the stretching method. FEP/activated carbon/inorganic particle hybrid microporous membrane was prepared by hot pressing using composite inorganic particles as a pore-forming agent and activated carbon as an additive, etc. Using FEP dispersion emulsion as the membrane-forming polymer and PVA as the spinning carrier, FEP ultrafine fiber membranes were prepared by electrostatic spinning and suitable sintering process.

1.4.5 Ethylene Tetrafluoroethylene Copolymer-ETFE

A “head-to-tail, tail-to-tail” isomeric form of PVDF can be produced by combining partially fluorinated ethylene tetrafluoroethylene copolymer (ETFE) membrane with hydrocarbon and fluorocarbon structures (chemical structure is shown in Table 1.9). These membranes offer excellent mechanical qualities and strong radiation resistance. High radiation resistance enables it to be pre-irradiated with high gamma rays in subsequent grafts, and good mechanical properties enable it to exist in fuel cell stacks for a long time. Scheme 1.7 illustrates the use of ETFE to prepare a novel cross-linked polymer electrolyte hybrid membrane [119]. Grafted membranes based on ETFE have the benefit of low cost, but they can also produce high thermal stability and proton conductivity through cross-linking [122, 123].

1.5 ECTFE and Other Fluoropolymers

ECTFE is a fluorine-containing polymer formed by alternating polymerization of ethylene monomer and trichloroethylene monomer at 1 : 1. Melting point is 464 °F (242 °C), density is 1.68 $g\,cm^{-3}$. Its molecular structure formula is shown in Table 1.11. In 1946, DuPont first synthesized ECTFE. ECTFE was commercialized for the first time by DuPont in 1974, which was known as Halar®. In 1986, Applied Chemical Organization transferred ECTFE products and technologies to Ausimont USA Inc. In 2001, Ausimont was purchased by the Solvay Group of Belgium.

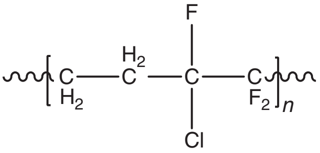
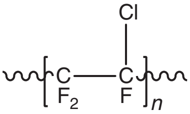
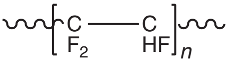
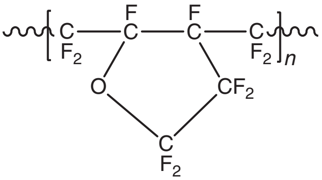
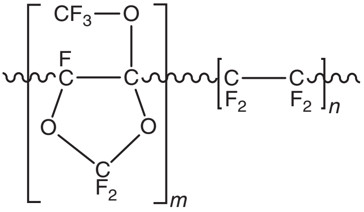


Scheme 1.7 Scheme for the preparation of a new cross-linked polymer electrolyte hybrid membrane using ETFE. Source: Reproduced from Chen et al. [119]/with permission of Elsevier.

As an alternating copolymer of ethylene and chlorotrifluoroethylene, it has a unique chemical structure, where the content of fluorine is 39.5%, and it has three carbon—fluorine bonds and one carbon—chlorine bond [124]. Because of the low polarizability and strong electronegativity of fluorine atom, C—F bond has a large bond energy (485 kJ mol^{-1}). Therefore, ECTFE with a higher fluorine content exhibits high heat resistance, chemical corrosion resistance, durability, and weather resistance, especially for many solvents, hydrocarbons, inactivity of various acids and bases, low capacitance, low flammability, low refractive index, low surface energy (neither oil-wet nor water-wet), and hygroabsorbency [28, 125, 126]. ECTFE is also more resistant to water vapor, hydrogen chloride, and chlorine gas than regular fluoropolymers – of which chlorine permeability is the best – because it contains chlorine atoms. For these reasons, it is frequently employed in severe conditions that are exposed to chlorine. Long-term exposure to UV radiation does not significantly alter the characteristics of ECTFE, making it suitable for usage in the construction sector in products like UV-resistant paint. ECTFE is also very resistant to solvents; at temperatures below 120 °C, no solvent can harm it [127]. ECTFE is therefore better than other fluorinated materials in terms of its ability to withstand high temperatures, strong acids and alkalis, and chemical resistance. As a result, it is the perfect material for creating high-performance microporous membranes.

At present, due to its good toughness and high strength, ECTFE has better weather resistance and chemical corrosion resistance than PTFE and PVDF [128]. It is frequently applied as a coating to prevent corrosion and safeguard pipelines [129, 130]. For instance, it is applied on stainless steel exhaust pipes as a coating to handle different corrosive airflows in a range of industrial settings,

Table 1.11 Chemical structures of ECTFE and other fluoropolymers.

Polymer		Chemical structure
ECTFE		
Other fluoropolymers	PCTFE	
	PVF	
	Cytop	
	Hyflon AD	

including clean rooms. When carrying hydrofluoric acid that contains unique corrosive chemicals, the adhesion and hardness of the ECTFE-coated induced draft fan impeller are twice that of the PTFE coating. Furthermore, ECTFE can be applied on the surface of solar photovoltaic modules as an anti-corrosion film resin. ECTFE resins have proven to offer outstanding chemical, weather, and corrosion resistance in various applications. However, the application of ECTFE as a porous membrane in the field of water treatment is less studied. Table 1.11 lists chemical structures of ECTFE and other fluoropolymers.

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