Fluoropolymer membranes

by Vincenzo Arcella, Giulio Tommasi

Membranes made with fluorinated polymers are of particular interest for their unique surface properties and their chemical resistance. A process developed by Ausimont is particularly suited to produce special sophisticated fluoromonomers. By selecting the appropriate combination of tetrafluoroethylene (TFE) and such comonomers, any combination from glassy amorphous hydrophobic polymers to rubbery amorphous hydrophilic polymers can be obtained.

Transport phenomena involving semi-permeable membranes are most diffused in nature. They are present in many life basic mechanisms of the animal and vegetable world assisting cellular exchange processes. Membranes are capturing increasing interest in the industry for their capability to replace traditional unit operations of the chemical industry, such as distillation, with more effective and economic processes, such as reverse osmosis and ultrafiltration. One example is their use in sea and brackish water desalination, where membrane processes offer a reliable and economic way to produce potable water for arid areas [1].

In the scientific community membrane processes are receiving even greater attention since they offer in many cases the key to processes not easily achievable by conventional routes. Membrane reactors [2] and membrane contactors [3] are among the most recent examples of these new developments.

In this context membranes made with fluorinated polymers are of particular interest. The presence of the strong fluorocarbon bone gives the macromolecular structure a capability to withstand very aggressive conditions that increases with the increase of the fluorine content in the polymer. Both highly hydrophobic and highly hydrophilic membranes have been developed from appropriate fluoropolymers which in turn were obtained synthesizing well defined monomer mixtures, polymerized under particular conditions. Tetrafluoroethylene (TFE) is generally the basic monomer combined with other fluromonomers. Among these accompanying fluoromonomers, one plays a fundamental role, i.e. gives the desired applicative property.

To understand the role played by the "fundamental" comonomer, it can be worth to consider that while the homopolymer of TFE, polytetrafluoroethylene (PTFE), is one of the most highly crystalline, hydrophobic, and insoluble in most solvents among known polymers, the TFE copolymer with the "fundamental" monomer shows properties that can be dramatically different. Glassy amorphous soluble hydrophobic polymers, or rubbery amorphous soluble hydrophilic polymers can be obtained, and many possible variations from glassy to rubbery, or from amorphous to crystalline, or from hydrophobic to hydrophilic can be achieved by selecting the appropriate comonomer.

It is evident that the availability of these special fluoromonomer is of crucial importance.

Hydrophilic ion exchange membranes have been developed since many years and have found applications in the chloroalkali process and in fuel cells. Hydrophobic amorphous membranes have also appeared in the technical literature for gas separation and contactors.

Recently Ausimont has decided to exploit its skill in fluorine chemistry and its capability of developing and producing suitable monomers and polymers for applications in the membrane field. Two major areas of development are new monomers and polymers for the production of both hydrophilic and hydrophobic films and membranes to be used in many different applications, such as fuel cells, microfiltration, ultrafiltration, semiconductor protective films, gas separation and contactors.

Hydrophilic membranes

Perfluorinated ionomers are commonly used in the chloroalkali industry [4]. More recently a great interest has been devoted to their use in the PEM (polymer electrolyte membrane) fuel cell technology [5]. Fuel cells are devices that convert directly the chemical energy of reaction of a fuel and an oxidant into electrical energy. PEM fuel cells utilize a polymeric proton exchange membrane to separate the fuel and the oxidant while

---

Vincenzo Arcella, Giulio Tommasi, Ausimont SpA, CRS - Viale Lombardia, 20 - 20021 Bollate (Mi).

allowing the transport of protons from anode to cathode. When the fuel is hydrogen and the oxidant is oxygen, the only products are electric power, water and some excess heat.
A fuel cell is schematized in Figure 1.

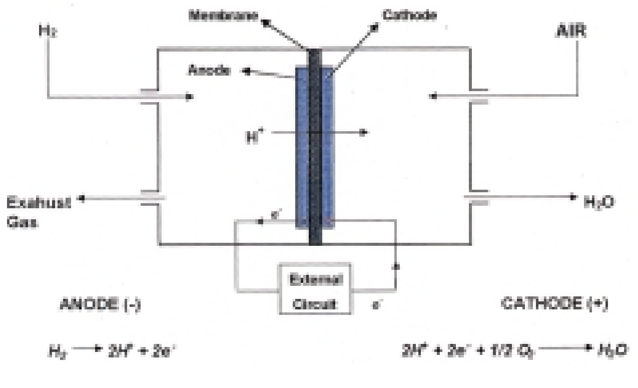


Figure 1

In order to have a reliable and long life fuel cell device, the ideal membrane should inhibit the contact between fuel and oxidant gases conveyed at the two electrodes at membrane sides, and promote fast proton transport through the membrane over a wide range of temperatures and gas humidification conditions.
Perfluorinated ionomers are obtained by copolymerizing TFE with functionalised perfluorovinyl ethers obtaining the structure shown in Figure 2.

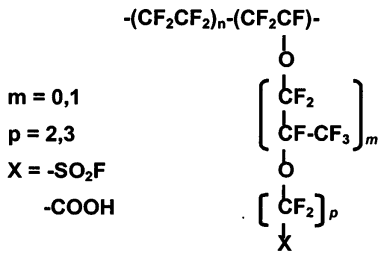
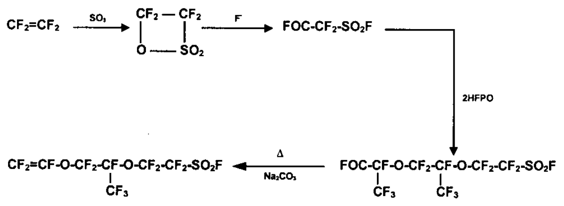


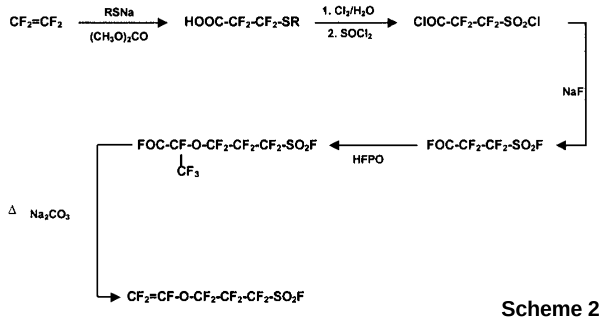
Figure 2

Sulphonic acid membranes are commonly used in PEM fuel cell technology, obtained from copolymers of TFE with sulphonyl fluoride monomers (X=SO_2F).
Many reaction routes to sulphonyl fluoride monomers have been patented. In a process patented by DuPont [6], TFE is reacted with SO_3 to produce a β-sultone, a ring which is opened by fluoride ion to give a fluorosulphonyl acetyl fluoride. An adduct is then obtained by reaction with hexafluoropropene oxide (HFPO), which gives on pyrolysis the sulphonyl fluoride monomer. (Scheme 1).



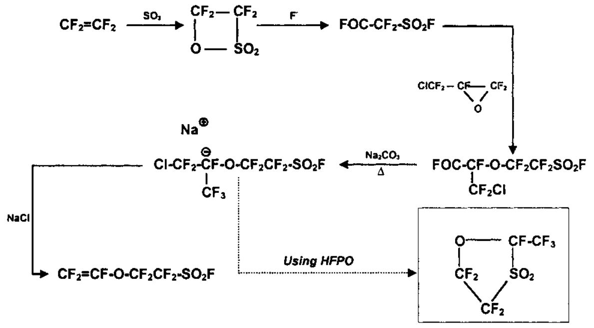
Scheme 1

In a different process patented by Asahi Chemical [7] a sulphonyl fluoride monomer is obtained according to Scheme 2.



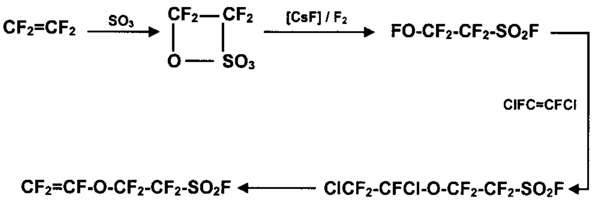
Scheme 2

A process to produce a sulphonyl fluoride monomer characterized by having a short side chain carrying the functional group has been patented by Dow [8], according to Scheme 3.



Scheme 3

The use of 3-chloro pentafluoropropene oxide (CPFPO) is crucial because it allows the pyrolysis of the 1:1 adduct to give the sulphonyl fluoride monomer instead of a cyclization product as obtained from the 1:1 HFPO adduct.
The short side chain monomer is particularly interesting since its lower molecular weight results in higher reactivity during the polymerization with TFE, yielding higher molecular weight, i.e. mechanically stronger, polymers. In addition, as it will be seen in the following, higher concentration of ion exchange groups can be incorporated.
More recently Ausimont has successfully applied its proprietary fluorovinylether monomer process to produce the sulphonyl fluoride short side chain monomer. This process is particularly simple and effective as described by Scheme 4.



Scheme 4

Ausimont can produce this monomer in large scale in its fluorovinylether monomer industrial plant.

In order to take the opportunity to fully exploit its fluorine technology and industrial assets, Ausimont has made the strategic decision to participate to the fuel cell business. A fuel cell membrane project has been established and started. The objective of the project is to develop a family of new perfluorinated sulphonic acid membranes for fuel cell applications.

Thanks to the high reactivity of the short side chain monomer and using the Ausimont proprietary microemulsion polymerization process that enhances the monomer propagation reaction, high molecular weight copolymers with TFE have been prepared, ranging from highly crystalline to amorphous systems.

Molding or continuous film extrusion can be used with semicrystalline melt processable copolymers to prepare, after hydrolysis, sulphonic acid self supported membranes. In this case, in order to produce very thin membranes, the membrane must show a low level of hydration. The combination of the short side chain monomer and the microemulsion polymerization process allows to fully answer this need.

When the amount of the sulphonyl fluoride monomer in the copolymer exceeds around 20% on a molar base, i.e. the equivalent weight is lower than about 750, the polymer is amorphous with a glass transition temperature close to room temperature and shows rubber like behaviors. The polymer can be easily shaped to obtain a flat sheet film with very low mechanical properties. Hydrolysis of this films does not result in a sulphonic acid membrane since the complete absence of crystallinity causes the polymer to be dissolved in the aqueous solution. Appropriate cross-linking can avoid this problem.

Sulphonic acid membranes with thickness in the range of 100-200 µ and equivalent weight as low as 500 have been prepared from cross-linked sulphonyl fluoride films. Although these membranes maintain their mechanical integrity after ageing in boiling water for many hours, mechanical strength is not yet completely satisfactory for application in fuel cell devices. Mechanical strength can be improved by introducing suitable reinforcing materials, such as PTFE fabrics. Composite low equivalent weight sulphonic acid membranes with thickness lower than 50 µ have been prepared and are under evaluation. The cell voltage *vs*. current for a prototype, low equivalent weight, 40 µ thickness, composite membrane is reported in Figure 3.

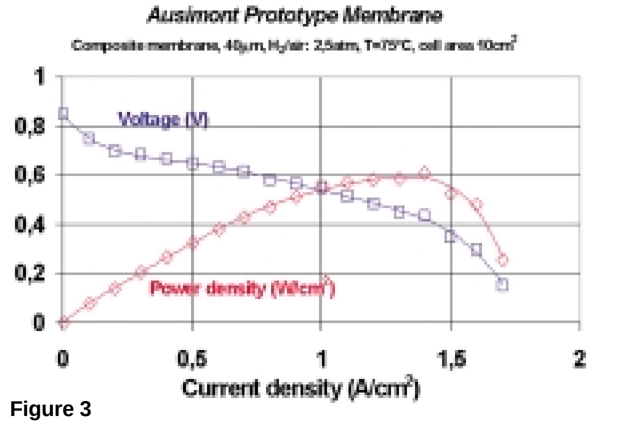
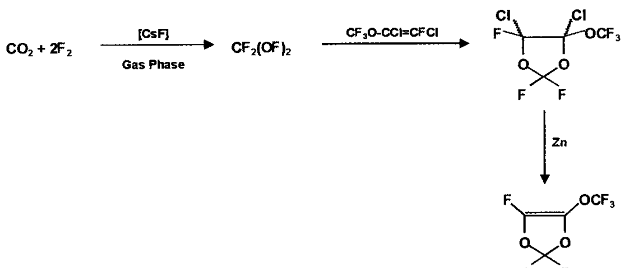


Figure 3

Hydrophobic membranes

Ausimont has successfully applied its proprietary fluorovinylether monomer process to produce a special cyclic monomer, the 2,2,4 trifluoro, 5 trifluorometoxy - 1,3 dioxole (TTD) [9]. This process is described by Scheme 5.



Scheme 5

Copolymers of tetrafluoroethylene (TFE) and TTD are amorphous perfluoropolymers with glass transition temperature (Tg) higher than room temperature, showing a thermal decomposition temperature exceeding 400 °C, and are highly transparent to light from deep UV to near infrared. This new family of perfluoropolymers, known commercially as Hyflon AD, excels in a wide range of innovative areas [10], and developmental applications are currently under evaluation.

An important peculiarity of these polymers is also their high solubility in fluorinated solvents, with low solution viscosities. This aspect allows an easier purification of polymer solutions and, in addition, allows and simplifies the preparation of membranes with desired thickness by solution casting methods [11]. Different membranes have been prepared in flat sheet, tubular and hollow fiber forms and their performances in different applications are currently studied in cooperation with the Department of Chemical and Materials Engineering at the University of Calabria.

Flat sheet asymmetric membranes were prepared following the dry-wet phase inversion method [12] with 10% wt/wt polymeric solutions; the solvent was Galden HT, the non solvent was *n*-pentane.

Flat sheet composite membranes of 1 µ thickness film on a PVDF support, were prepared using both Hyflon AD 60 and Hyflon AD 80. The membranes were prepared by the spin coating process.

Permselective properties of asymmetric and composite membranes to various single gases were determined by a system of volumetric cells [13]. Characterization of both composite and asymmetric membranes, in steady state conditions, gave selectivity values for O_2/N_2 and CO_2/N_2 respectively around 3 and 8 in the pressure range of 5 to 7,5 bar.

Permeability to N_2, O_2, CH_4, H_2 and CO_2 of Hyflon AD-PVDF composite membranes are reported in Table 1.

Table 1

Polymer type	*P (Barrer)**				
	O_2	N_2	CH_4	H_2	CO_2
Hyflon AD 60	51.4	16.5	8.01	202	124
Hyflon AD 80	190	76.8	48.9	563	473

* 1 Barrer = 10^{-10}[cm^3(StTP)·cm]/[cm^2·cm Hg·s]

Measures of contact angle to distilled water in comparison to other commercial membranes are reported in Figure 4. Contact angles of about 120° demonstrate a high hydrophobic character.

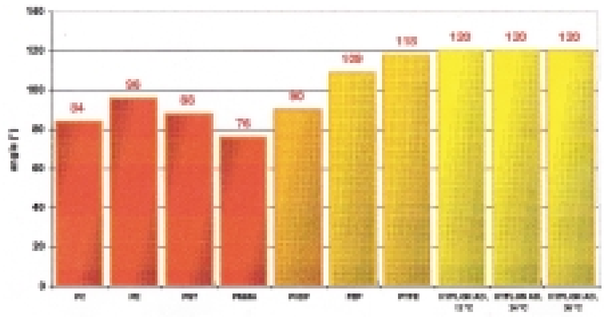


Figure 4

Measures of contact angles to hexadecane, in comparison with other materials, demonstrate that Hyflon AD membranes have also a good organophobic character that should lead to excellent fouling resistance and inertness. Results are reported in Figure 5.

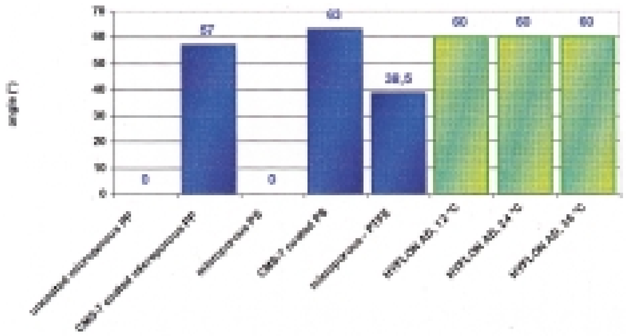


Figure 5

In consideration of the very high contact angle obtained with these membranes, possible useful applications in the field of gas-liquid separations have been envisaged. In some relatively new processes, like membrane distillation and membrane contactors, the requirements are very clear: in order to avoid wetting, the surface energy of the membrane must be as low as possible. This means that very hydrophobic materials must be used in combination with liquids with high surface tension such as water. Since selectivity is determined by vapor-liquid equilibrium, only the permeate flux can be optimized and it depends on the membrane thickness and the presence of pores. High porosity can result in high permeate flux. Furthermore, in order to reduce the transport resistance, the membrane should be as thin as possible. Last but not least, wettability must remain low, which is controlled by pore size distribution and surface energy.

Hydrophobic microporous composite membranes of Hyflon AD on PVDF have been prepared and characterised. The membrane surface has been analyzed by AFM which allows a quantitative determination of the pore diameter distribution. A picture of the membrane surface obtained by AFM is reported in Figure 6.

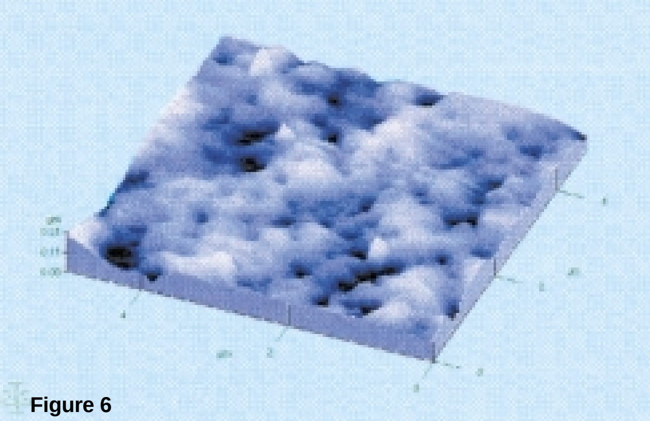


Figure 6

The pore size distribution has resulted very narrow as demonstrated by Figure 7.

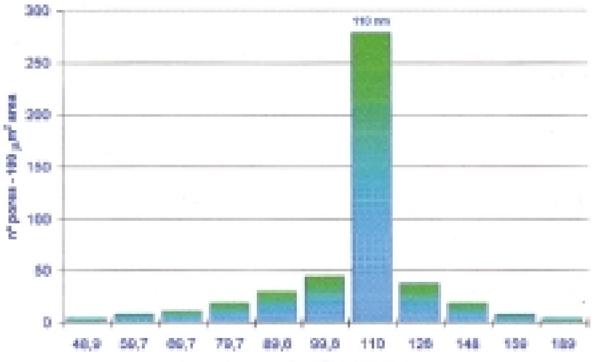


Figure 7

All membranes showed no permeation to water at pressures as high as 10 bar.

Gas permeation tests with nitrogen, oxygen and carbon dioxide carried out at 27 °C are reported in the Figure 8.

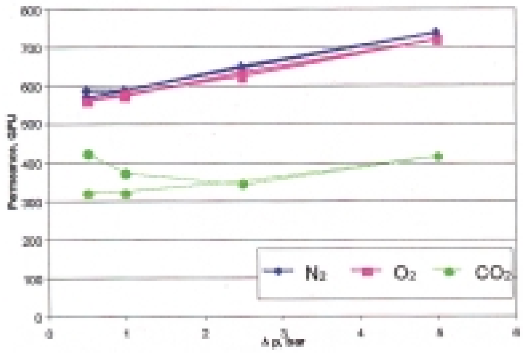


Figure 8

Knudsen diffusion appears to be the main transport mechanism as shown by the increase in permeance with increasing applied pressure difference. This observation has been confirmed also by selectivity values nearest to Knudsen selectivity values.

Oxygen permeation data of the Hyflon AD membrane in comparison with other different types of membranes are reported in the Table 2.

Table 2

Membrane Material	*Permeance O_2 (GPU)*
Permea polysulfone[8]	15
Ethyl Cellulose[8]	100
Silicone Rubber[8]	500
Generon Polycarbonate[8]	7
Dow 4-Methylpentene-1[8]	90
Hyflon® AD 60 on PVDF	*700 (5 bar, 27 °C)*
Goretex	350 (5 bar, 16 °C)

Conclusions

Fluoropolymer membranes offer in many cases the key to processes not easily achievable by conventional routes. The chloro-alkali process, fuel cells and more recently membrane reactors and membrane contactors are among the most important examples.

A proprietary process developed by Ausimont is particularly suitable to produce special fluoromonomers of crucial importance for the development of advanced fluoropolymer membranes.

Based on a sulphonyl fluoride short side chain monomer and a proprietary microemulsion polymerization process available from the Ausimont technology, self supported and composite sulphonic acid membranes for fuel cell applications are currently under development.

Based on a proprietary cyclic monomer, amorphous perfluoropolymers known commercially as Hyflon AD, having glass transition temperature (Tg) higher than room temperature, thermal decomposition temperature exceeding 400 °C, and highly transparent to light from deep UV to near infrared, have been used to prepare composite and self supported hydrophobic membranes.

Membranes, prepared in flat sheet, tubular and hollow fiber forms and their performances in different applications are currently studied in cooperation with the Department of Chemical and Materials Engineering at the University of Calabria under the direction of Enrico Drioli.

Hyflon AD membranes provide a unique combination of excellent organophobicity, hydrophobicity and chemical/wear resistance. In particular porous composite membranes show gas fluxes many times those of commercial gas separation membranes.

References

[1] T.deV.Naylor, Polymer Membranes, *Rapra Review Reports* 1996, **8**.

[2] J.A. Dalmon, Catalytic Membrane Reactors, in Handbook of Heterogeneous Catalysis, G.Ertl *et al.,* (Eds.), VCH Pub.,1997, chapter 9.3.

[3] A. Criscuoli, E.Drioli, Proc. of the Workshop on “Membrane Distillation, Osmotic Distillation and Membrane Contactors”, Cetraro, 1999.

[4] D.E. Maloney; Modern Chloro-Alkali Technology, **1,** 173.

[5] P. Savage, Chem.Week, March 18,1987, 13.

[6] *US Pat.* 3.282.875 (to Du Pont).

[7] *US Pat.* 4.597.913 (to Asahi Chemical).

[8] *US Pat.* 4,358,412 (to Dow Chemical Co).

[9] *E Pat.* 0633257A1 (to Ausimont).

[10] *E Pat.* 97106156 (to Ausimont).

[11] V.Arcella, P.Colaianna, *et al.,J. Memb. Science*, 1999, **163,** 203.

[12] K. Kimmerle and H. Strathmann, *Desalination*, 1990, **79,** 283.

[13] E. Drioli *et al., Gas Sep. Purif*., 1991, **5,** 252.