

# A short history of Nafion<sup>®</sup>

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## Résumé

### Une courte histoire du Nafion<sup>®</sup>

Le Nafion<sup>®</sup> est une résine échangeuse d'ions entièrement fluorée, formée d'une colonne vertébrale ne contenant que des groupes CF<sub>n</sub> sur laquelle sont branchés des groupements d'acide sulfonique. La combinaison unique des diverses propriétés de ce matériau, telles que la forte acidité, la stabilité chimique et thermique conduit à un produit exceptionnel à beaucoup d'égards. Il est en effet utilisé comme catalyseur acide, membrane en électrosynthèse, séparateur dans les piles à combustible et dans les systèmes de séchage de gaz. Initialement, la synthèse du Nafion<sup>®</sup> était considérée par DuPont comme un exemple de recherche fondamentale plutôt qu'appliquée.

## Mots-clés

**Nafion<sup>®</sup>, histoire, résine échangeuse d'ions, électrosynthèse, piles à combustible.**

## Abstract

Nafion<sup>®</sup> is a fully fluorinated ion exchange resin consisting of a fluorinated backbone and pendant sulfonic acid groups. The combination of strong acidity, chemical and thermal stability results in a unique material with many uses: acid catalyst, membrane in electrosyntheses, separator in fuel cells and in gas dryers. The synthesis of Nafion<sup>®</sup> by DuPont was an example of fundamental rather than applied chemical research.

## Keywords

**Nafion<sup>®</sup>, history, perfluorinated, ion exchange resin, electrosynthesis, fuel cells.**

Nafion<sup>®</sup>, introduced by DuPont in the 1960's was the first commercially produced perfluorinated ion exchange resin. It is a completely fluorinated polymer containing pendant sulfonic acid groups and combines the chemical, thermal and oxidative stability of perfluorinated polymers such as polytetrafluoroethylene with the strong acid properties of a fluorinated sulfonic acid. Nafion<sup>®</sup> is a copolymer of tetrafluoroethylene and the perfluorovinyl ether, perfluoro(4-methyl-3,6,-dioxaoct-7-ene) sulfonic acid, CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>H (figure 1).

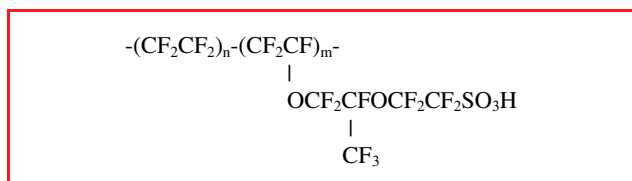


Figure 1 - The structure of Nafion<sup>®</sup>.

## A brief history

A product announcement by DuPont in September 1969 described Nafion<sup>®</sup> known originally as XR in the following way:

*"A new thermoplastic polymer family – offering features of both fluorocarbon polymers and ion exchange resins – has been developed by DuPont's Plastics Department.*

*The new composition is currently called XR. It is expected to provide unique property advantages for electrochemical, aerospace, and chemical industries.*

*Based on advanced fluorocarbon chemistry, the polymer exhibits such features of fluorocarbons and ionomers as ionic conductivity, permeability, transparency, toughness,*

*chemical inertness, flexibility and adhesion to most substrates.*

*DuPont identifies XR polymer as a perfluorosulfonic acid copolymer that contains no covalently bonded hydrogen or chlorine. Therefore, it can operate in strong oxidizing media at high temperatures with long term chemical stability.*

*The fluorinated polymer contains pendant sulfonic acid groups, which produce an exceptionally strong acid resin. The number of sulfonic acid groups can be varied to provide different ion exchange capacity, electrical and mechanical properties.*

*The polymer is unique in its chemical, thermal and oxidative stability. The limits of stability have not been determined, but tests indicate it is stable at elevated temperatures for prolonged periods in such severe environments as potassium hydroxide, hydrogen peroxide, and nitric, phosphoric, and sulfuric acids.*

*One of the first uses of the material has been in film form by General Electric as a solid electrolyte in a 350-watt fuel cell developed for NASA. The solid electrolyte of the fuel cell is a thin but tough sheet of perfluorosulfonic acid copolymer, to which metallic electrodes are bonded. Hydrogen fuel and oxygen are continually supplied to opposite sides of the cell. General Electric evaluated a number of materials for the electrolyte and chose DuPont's new product because of its chemical inertness."*

The development of Nafion<sup>®</sup> at DuPont had its genesis in the late 1950's with three fundamental chemical discoveries. First was the preparation and commercialization of Surlyn<sup>®</sup>, a family of hydrocarbon ionomers based on copolymers of ethylene and methacrylic acid by Richard Rees in the Polychemicals Department of DuPont [1]. Second was the preparation and rearrangement of 2-hydroxytetrafluoroethanesulfonic acid β-sultone to fluorosulfonyldifluoroacetyl

fluoride by David England in the DuPont Central Research Department [2-3]. Third was the preparation of the first perfluorinated epoxide, hexafluoropropylene oxide (HFPO) by Herbert Eleuterio in the Polychemicals Department of DuPont [4]. His discovery was key to the development of Nafion<sup>®</sup>. The chemistry of HFPO was elucidated by the Exploratory Research Group in the Polychemicals Department under the direction of W. Frank Gresham (figure 2).

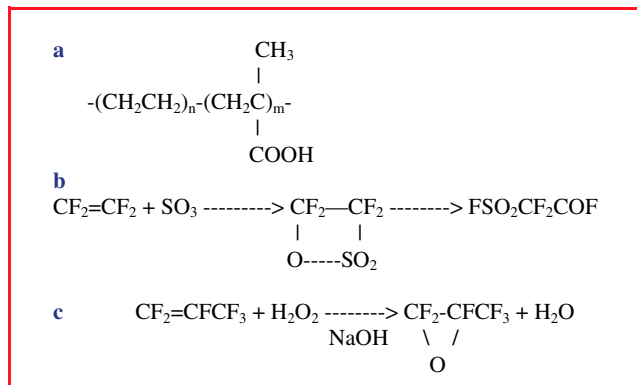


Figure 2 - The genesis of the development of Nafion<sup>®</sup>: a): Surlyn<sup>®</sup>; b): D.C. England; c): HFPO.

This research group also discovered a general route for the preparation of perfluorovinyl ethers based on HFPO [5]. Reaction of a perfluorinated acyl fluoride with HFPO catalyzed by fluoride ion yielded a perfluorinated 2-alkoxypropionyl fluoride that could be decarboxylated to give a perfluorovinyl ether. These vinyl ethers were shown to copolymerize with tetrafluoroethylene and led to the commercialization of Teflon<sup>®</sup> PFA, Kalrez<sup>®</sup> as well as other products. An example of a vinyl ether synthesis is shown (figure 3).

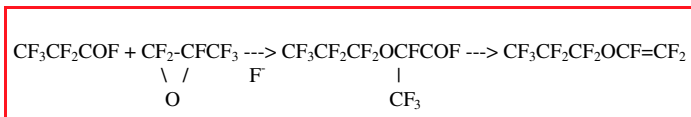


Figure 3 - Example of a vinyl ether synthesis.

As noted, this same exploratory research in the Polychemical Department of DuPont also developed the hydrocarbon ionomer Surlyn<sup>®</sup>. This led to the exploitation of England's synthesis of FSO<sub>2</sub>CF<sub>2</sub>COF as the starting material to prepare a perfluorinated vinyl ether containing a sulfonyl fluoride group. The sulfonyl fluoride could then be converted to a sulfonic acid after copolymerization with tetrafluoroethylene to give a perfluorinated ionomer. When this work was started, no specific application or product was the goal of the project. It was believed that a perfluorinated ionomer would have an unusual combination of properties that would make it useful for some unspecified commercial or industrial application. This was a clear example of a technology push project that was common for DuPont at that time but rare at present. Please also note that the syntheses of HFPO, 2-hydroxytetrafluoroethanesulfonic acid β-sultone and FSO<sub>2</sub>CF<sub>2</sub>COF in themselves were also the result of technology push research projects with no specific final product as the goal.

The reaction of FSO<sub>2</sub>CF<sub>2</sub>COF and HFPO gave a one to one condensation product in very high yield. Unfortunately, all attempts at decarboxylation of this product lead not to the

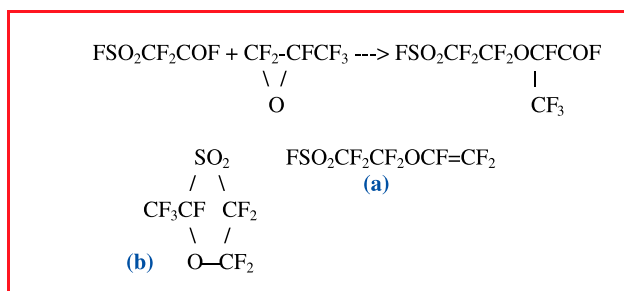


Figure 4.

desired vinyl ether (figure 4a), but quantitatively to a cyclic sulfone (figure 4b). The vinyl ether was ultimately synthesized by a number of routes and is under active investigation as a commercial monomer [6]. The successful preparation of a perfluorinated vinyl ether containing a sulfonyl fluoride was done by Don Connolly by the addition of two moles of HFPO to FSO<sub>2</sub>CF<sub>2</sub>COF. The subsequent decarboxylation gave a vinyl ether rather than cyclization to an unfavored eight membered ring cyclic sulfone [7]. This was the synthetic route to PSEPVE, the comonomer in Nafion<sup>®</sup> (figure 5).

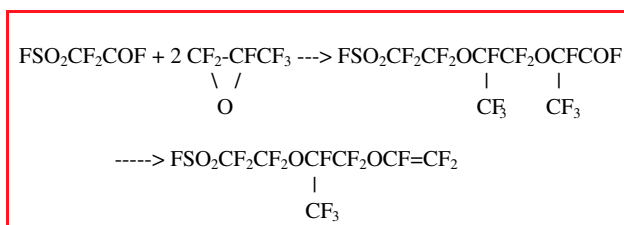


Figure 5 - PSEPVE: the comonomer in Nafion<sup>®</sup>.

PSEPVE was copolymerized by Connolly with tetrafluoroethylene as well as with other monomers to give a variety of polymers containing sulfonyl fluoride groups [7]. The copolymer with tetrafluoroethylene is thermoplastic and can be molded or extruded into a variety of shapes and forms. Once the sulfonyl fluoride form is hydrolyzed into either a sulfonate salt or the sulfonic acid, molding or extrusion is either impossible or extremely difficult. In practice the copolymer in the sulfonyl fluoride form is fabricated into the desired shape and subsequently hydrolyzed to the desired ionic form.

## Properties and applications

The structure and physical properties of Nafion<sup>®</sup> have been the subject of many research studies since its commercialization. An excellent recent review of the structure of Nafion<sup>®</sup> by Mauritz and Moore has been published recently [8].

The sulfonic acid form of Nafion<sup>®</sup> containing pendent -OCF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>H groups is a strong acid equivalent in strength to trifluoromethylsulfonic acid. Unlike hydrocarbon based sulfonic acid resins such as Dowex-50, the sulfonic acid form of Nafion<sup>®</sup> is stable in corrosive environments and at elevated temperatures. These properties make Nafion<sup>®</sup> an excellent catalyst for a wide variety of organic reactions. Its use as an acid catalyst has been described in a series of publications by George Olah. The early work has been summarized in reviews [9]. The low surface area of Nafion<sup>®</sup> beads and film was a drawback to its use as an acid catalyst.

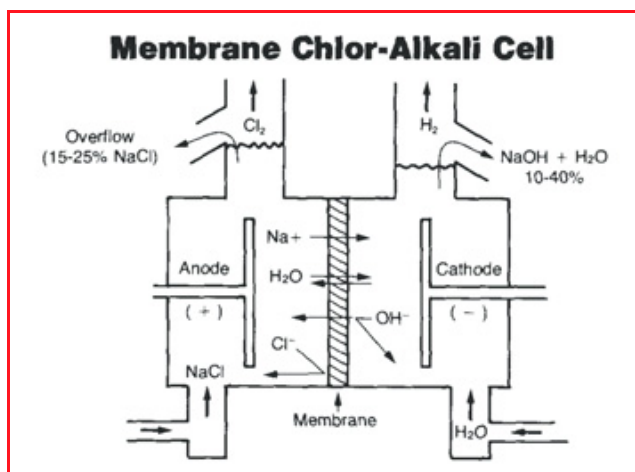


Figure 6 - Membrane chloralkali cell.

However, the preparation of a nanocomposite of Nafion<sup>®</sup> and silica, Nafion<sup>®</sup> SAC, with a surface area of greater than 200 m<sup>2</sup>/g results in increased reaction rates with decreased amount of catalyst [10]. It is interesting to note that the increase in reaction rate between Nafion<sup>®</sup> SAC and Nafion<sup>®</sup> beads is much less in systems where the reaction mixture can swell the Nafion<sup>®</sup> beads.

The first planned commercial application of Nafion<sup>®</sup> was its use as an acid catalyst for the preparation of glycolic acid. Process development proved that Nafion<sup>®</sup> was an excellent catalyst in the planned reaction but the application was not commercialized when an entirely different synthetic route was chosen. At present Nafion<sup>®</sup> is used as an acid catalyst in a number of proprietary commercial processes.

It was recognized from the start that Nafion<sup>®</sup> possessed a combination of properties such as ionic conductivity along with thermal and chemical stability that would be useful in electrochemical applications in harsh environments. One of the first uses of Nafion<sup>®</sup> to exploit these properties was as a membrane in the chrome plating industry. Nafion<sup>®</sup> was a component of electrolytic cells used to restore the plating liquor continuously by selectively removing the iron, copper, nickel and aluminum impurities and at the same time oxidizing any reduced chromium. The result was a greatly reduced waste stream of highly acidic metal contaminated waste chrome plating solution.

Nafion<sup>®</sup> was also the membrane material used in an electrochemical unit for the generation sodium hypochlorite from aqueous sodium chloride. The hypochlorite product was used for the disinfection of sewage and for purification of swimming pool water and had the advantage of eliminating the use and hazards associated with the handling of chlorine.

These relatively small uses of Nafion<sup>®</sup> led to the development of the membrane process for the coproduction of sodium hydroxide and chlorine. The use of perfluorinated membranes such as Nafion<sup>®</sup> as the key component in the commercial production of sodium hydroxide and chlorine was revolutionary. For almost one hundred years, these materials had been produced by the electrolysis of sodium chloride using either an asbestos diaphragm or a mercury electrode [11]. Nafion<sup>®</sup> changed everything and for the last twenty years all new plants built worldwide have used the membrane process. The development and commercial acceptance of this process took time. Even today a large number of older mercury and diaphragm plants are still operating. However, the lower operating costs, ease of

operation and the purity of the products are superior in the membrane process and the old mercury and diaphragm plants are being phased out, giving way to membrane based facilities [12].

The sulfonic acid form of Nafion<sup>®</sup> membrane had a major problem. There was appreciable back migration of hydroxide ion through the membrane from the cathode compartment to the anode compartment resulting in low current efficiency and impurities in the products. This migration needed to be minimized or eliminated completely in order to produce a commercially viable membrane based chloralkali cell (figure 6). The final membrane structure was required to be stable for thousands of hours under the conditions of the chloralkali process, i.e. 90° with up to 50% aqueous sodium hydroxide and chlorine in the anode compartment. The Nafion<sup>®</sup> backbone and sulfonic acid was stable under these conditions, so a series of variations were tested to meet the desired goals.

The first attempt was the preparation of a Nafion<sup>®</sup> bimembrane constructed of a lower equivalent weight Nafion<sup>®</sup> sulfonic acid facing the anode and a thin layer of higher equivalent weight Nafion<sup>®</sup> sulfonic acid facing the cathode. This construction was stable in the chloralkali environment and significantly reduced back migration of hydroxyl ion. This reduction in back migration was not high enough to produce the desired current efficiency and it had the additional drawback of increasing the voltage of the cell. The next three variations all involved the conversion of a thin layer of the sulfonic acid to sulfonamides, -OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>NHR, by treatment of the sulfonyl fluoride polymer with either ammonia, methylamine or ethylene diamine (figure 7). The three sulfonamides were stable enough to be used as membranes in chloralkali cells. However, there was still too much back migration of hydroxide ion which resulted in insufficient current efficiency. This coupled with high cell voltage resulted in power consumption that was too high for large scale commercial installations.

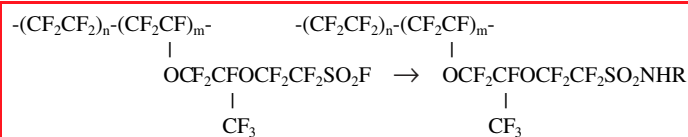


Figure 7.

The problem was resolved by the construction of a Nafion<sup>®</sup> bimembrane consisting of a thin layer of a perfluorinated carboxylic acid polymer bonded to a thicker layer of the perfluorinated sulfonic acid Nafion<sup>®</sup>. The carboxylate layer was positioned to face the cathode compartment and almost completely eliminated back migration of hydroxyl ion resulting in high cell current efficiency. The perfluoro carboxylate polymer chosen was analogous to the sulfonate polymer (figure 8). The monomer

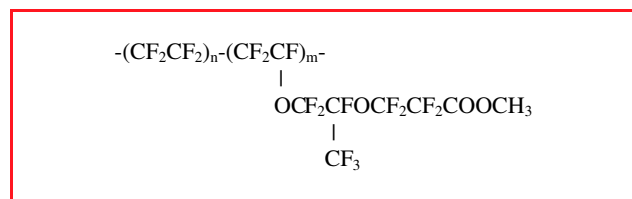


Figure 8 - Carboxylate polymer.

