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Nafion® perfluorinated membranes in fuel cells

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Abstract

Increasing global energy requirements, localized power issues and the need for less environmental impact are now providing even more incentive to make fuel cells a reality. A number of technologies have been demonstrated to be feasible for generation of power from fuel cells over the last several years. Proton exchange membranes (PEM) have emerged as an essential factor in the technology race. DuPont has supplied Nafion® perfluorinated membranes in fuel cells for space travel for more than 35 years and they have played an integral part in the success of recent work in portable, stationary and transportation applications. The basis for PEM fuel cell emergence and DuPont technology utilization will be discussed.

Keywords: Nafion® membranes; Perfluorinated membrane; Fuel cell; Direct methanol fuel cell; Proton exchange membrane; PEM fuel cell; Membrane electrode assembly; Nafion® dispersions

1. Introduction

Increasing global energy requirements, localized power distribution issues and the need for less environmental impact in the production and use of electrical energy are now providing even stronger incentives to make fuel cells a reality. Over the last year, a number of fuel cell technologies have been demonstrated to be feasible for electric power generation. As work continues to make these technologies commercially viable, proton exchange membranes (PEM) have emerged as a key player in this technology race. For more than 35 years, DuPont has supplied Nafion® perfluorinated membranes for fuel cells in the US space and military programs. Today, Nafion® membranes play an integral role in the success of recent PEM fuel cell demonstration programs in portable, stationary, and transportation applications.

This article will highlight the role Nafion® perfluorinated membranes have played in the advancement of PEM fuel cell technology, and discuss recent product improvements. This article will review DuPont's expectations of technology improvements needed to meet both the cost reduction and performance improvement goals of the emerging PEM fuel cell market over the coming decade.

2. Discussion

The development of Nafion® began in the early 1960s when the DuPont Company's Plastics Exploration Research Group was expanding on fluorine technology that had previously resulted in development of Teflon® fluorocarbon resins and Viton® fluoroelastomers [1,2]. The group was studying new monomers for copolymerization with tetrafluoroethylene (TFE). They also developed a general method to synthesize perfluorinated vinyl ethers from perfluorinated acid fluorides, which resulted in vinyl ether monomers, the starting point for Nafion® as well as other novel commercial polymers.

One of the acid fluorides studied, based on the reaction product of TFE and sulfur trioxide, led to an unusual TFE copolymer containing branches with pendant sulfonic acid groups (Fig. 1). Why make such materials? Considering the properties, which make Teflon® so valuable for many applications—in particular its unequalled dielectric properties, the exceptionally low coefficient of friction, antistick properties and chemical barrier properties—one would

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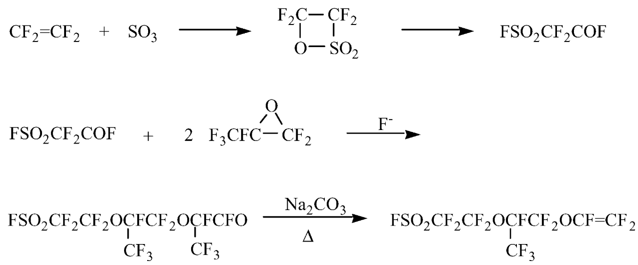

Fig. 1. Synthesis process for Nafion® membrane comonomer PSEPVE.

expect that all of these properties would be adversely affected by the introduction of sulfonic acid groups. On the other hand, this proposed copolymer was believed to be fundamentally different from all other TFE copolymers made before, having the potential to interact with the environment instead of merely resisting severe chemical or thermal environments.

Many of the various perfluorinated copolymers under consideration in the early 1960s appeared to be good candidates that would meet identified market needs. Several promised a combination of melt fabricability with improved high temperature mechanical properties without sacrificing any of the other desirable properties of Teflon®.

Although the copolymer that became known as Nafion® did not have the properties believed at that time to be desirable in a fluorocarbon polymer, DuPont proceeded with its development because it was truly different from any previous made fluorocarbon polymer. The Nafion® polymer functionally interacted with its environment, whereas perfluorinated polymers were valued for their inertness. A number of excellent review articles exist covering the subject of perfluorinated ionomer membranes with emphasis on transport processes [3,4], applications [5], and structural studies and physical properties [6–8].

The applications for this unique polymer would have to be found outside the field of traditional fluorocarbon polymers; and identifying these applications became one of DuPont's most important objectives. By 1964, DuPont recognized that Nafion® had properties that were very desirable as a membrane separator in chloralkali cells used for production of chlorine and caustic soda [9,10]. However, in the 1960s the chloralkali industry was not ready for this development—the cost of energy was low and there were no environmental concerns such as later developed on mercury emissions in Japan.

Meanwhile, in the United States, GE was developing PEM fuel cells for the US space program [11,12]. The fuel cell was supposed to provide electricity and water for an animal orbiting in space in a satellite—the BIOS satellite program. Initially, GE was using membranes made from polystyrene sulfonic acid polymer as the electrolyte in these fuel cells. However, these fuel cells were failing prematurely because the membranes were chemically unstable to the oxidative environment of the fuel cell. Fortuitously, GE was contacted during DuPont's search for applications of our new polymer. GE determined that membranes from the Nafion® polymer had the required oxidative stability and proton conducting property that would enable GE to meet their commitment to the NASA space program. This was the beginning of Nafion® membranes in PEM fuel cells [6,9]. Looking back, it is fair to say that in 1966, Nafion® enabled the PEM fuel cells to become a viable technology.

Although Nafion® demonstrated the viability of PEM fuel cell technology during this period, large commercialization of the PEM fuel cell technology remained elusive. The primary applications were in space and military markets. In the meantime, the acceptance of polymeric membranes as separators in chloralkali cells grew because of environmental issues (mercury poisoning in Japan), rising cost of energy and several key advances in Nafion® membrane-based technology for chloralkali applications [10].

During the period 1977–1984, DuPont invested in building a monomer, polymer, and membrane fabrication plant in Fayetteville NC to meet the needs of the Chloralkali market (Figs. 2 and 3). Today, the Chloralkali industry is the largest market for our Nafion® products.

During the early 1990s, the interest in PEM fuel cell technology as an alternative power source to internal combustion engine began to gain support. The US Department of Energy sponsored Partnership for New Generation Vehicles (PNGV) program was the prime mover (this DoE program is now known as the FreedomCar). We believe future global competitiveness of US industries was the essential driver behind this sponsorship. Sensing the potential of this market, DuPont began to refocus some of our efforts in developing Nafion® membrane technology for the emerging PEM fuel cell industry.

Before describing recent advances and our view of the future membrane needs of this market, we would like to acknowledge the critical contribution that the chloralkali market has made to the emerging PEM fuel cell industry. In our mind, it is clear that unless the perfluorinated membrane-based chloralkali technology materialized and there was a business for supplying Nafion® to this industry—there would be no commercial supply of Nafion® membrane to the PEM fuel cell industry. In today's business climate the investment hurdle would likely be too high to build a commercial-scale plant solely to support PEM fuel cell technology advancement and its limited early market opportunity.

The development of Nafion® membranes and polymer dispersions parallels the advances in fuel cell design—including a 10-fold reduction in catalyst loading and improvements in the gas diffusion layer performance, and bipolar plates.

The initial Nafion® extrusion-cast membranes were N-115 and N-117 (5 and 7 mil thick films), which satisfied the high catalyst loadings and low current density operating modes of the pioneering fuel cell efforts. As developers began to reduce catalyst loadings and increase the current

Fig. 2. DuPont Fayetteville Works, North Carolina.

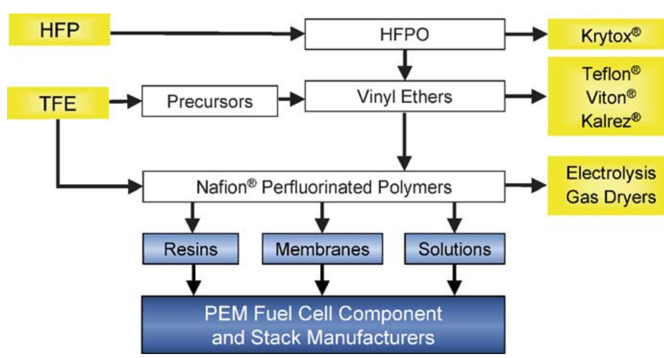

Fig. 3. Nafion® manufacturing steps.

density, the thick membranes experienced water management and performance drop-off problems.

The high current density operation tended to dehydrate the membrane, which resulted in reduced conductivity. Initial remediation required humidification of the fuel and use of lower equivalent weight material, which inherently had higher conductivity and was less affected by the dehydration effect. DuPont responded with membranes that were thinner and/or made from lower equivalent weight. Thus, the introduction of N-105 (a low EW 5 mil), N-1135 and N-1035 (standard and low EW versions, 3.5 mil thick. These were soon followed by N-112, 2 mil thick membrane made from standard EW polymer Fig. 4 shows the performance improvement achieved with thinner membranes.

Up to this point, membranes were supplied to the industry as ‘‘cut pieces’’. Membrane electrode assemblies, which

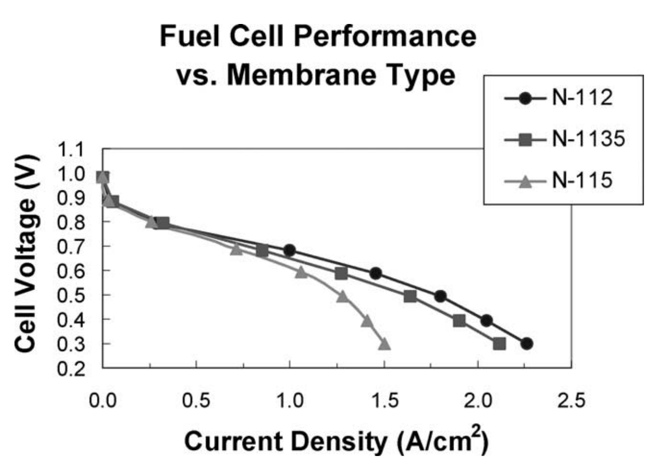

Fig. 4. Thin membrane performance benefit.

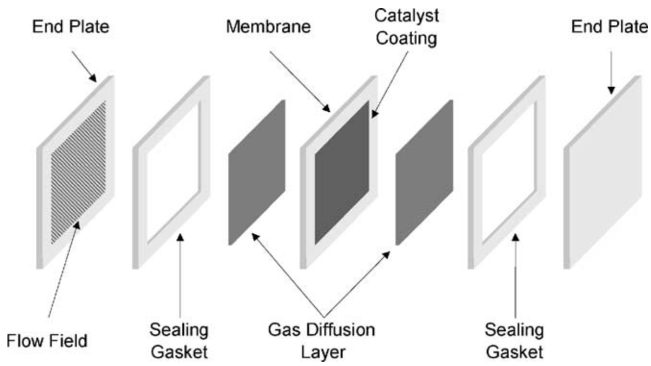

Fig. 5. Membrane fuel cell components.

consisted of core Nafion® membrane, catalyst coating on both sides and finally a gas diffusion media completing the "5-layer" structure (Fig. 5), were the result of several manually-intensive operations.

During this time period, DuPont initiated a technical program to produce membrane in a form that would be suitable for automated manufacturing facilities, characterized by high volume and high speed processes that also require high quality and low cost starting materials. Fig. 6 shows a schematic of such a process.

One initial output was the development of the roll format for extrusion-cast membrane products. Typically, membrane rolls can be in the range of 12–60 in. in width, and 150–500 feet in length. Extrusion-cast membranes range in thickness from 2 to 10 mil, and satisfy a variety of fuel cell, humidification, instrumentation and electrochemical applications, including water electrolysis for oxygen and hydrogen generation.

Table 1
Current Nafion® membranes offering

NR 111 and NR 112 (1100EW)
1 and 2 mil thickness
Roll format, solution cast film
N 112, N 1135, N 115, and N 117 (1100EW)
2–7 mil thickness
Pieces or rolls, extrusion cast film
N 1035, N 105 (1000EW)
3.5 and 5.0 mil thickness
Pieces or rolls, extrusion cast film

Further demands for better performance, longer rolls, higher volumes, and lower pricing led to the development of solution-cast membranes. These membranes are available in thickness ranging from 0.5 to 2 mil, and are characterized as having very uniform thickness and improved overall quality compared to the extrusion-cast membranes. This product is available in widths up to 5 feet, and lengths exceeding 1000 feet. This product is best suited for automated membrane electrode assembly production; for example, where Nafion® membrane is laminated to catalyst-coated gas diffusion media. Table 1 summarizes the current membrane offerings for the fuel cell industry.

The Nafion® polymer dispersions have also undergone several developmental changes since their first commercialization, including the introduction of two polymer equivalent weights available in three polymer concentrations and solvent compositions. These product offerings include a 5%, 10% and 20% Nafion® polymer content (Table 2). Nafion® polymer dispersions are used to formulate catalyst coatings, to pre-treat gas diffusion media, and make thin films and

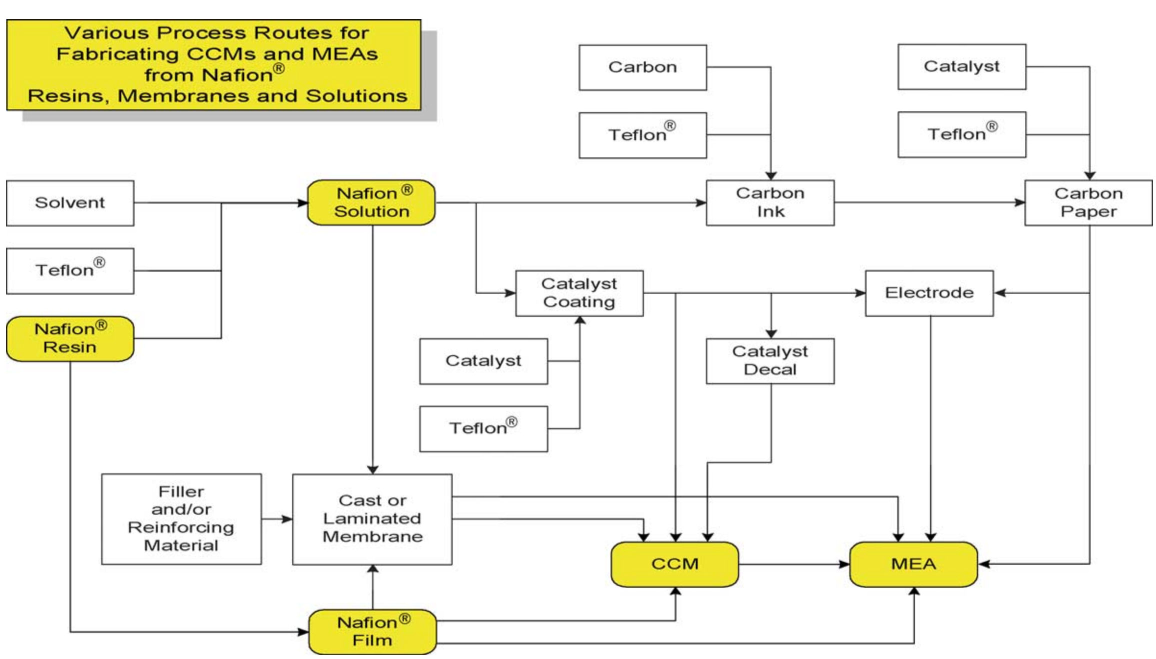

Fig. 6. Various process routes for high speed manufacturing of fuel cell components.

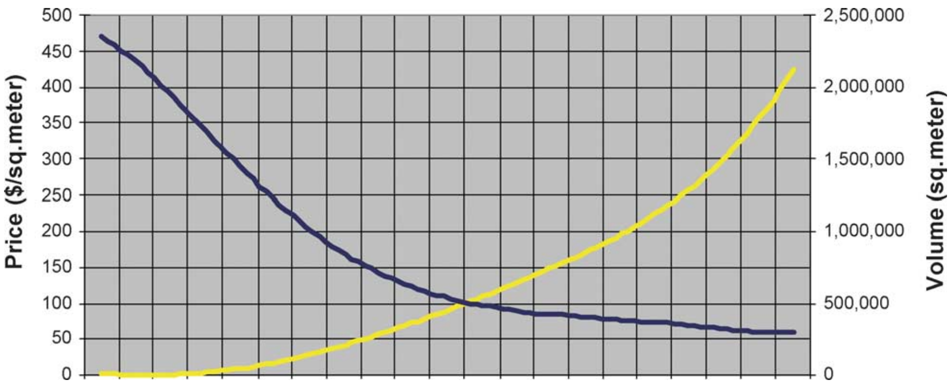

Fig. 7. Price projection for Nafion® N112 membrane.

Table 2
Current Nafion® dispersions offering

SE 5112 and SE 5012
5% polymer (1000EW or 1100EW)
Organic solvents
SE 10172 and SE 10072
10% polymer (1000EW or 1100EW)
Water-based
SE 20192 and SE 20092
20% polymer (1000EW or 1100EW)
Organic solvents

membranes for instruments as well as fuel cell applications, including PTFE reinforced membranes.

Efficiencies have allowed the prices of Nafion® membrane and polymer dispersions to be reduced by 50% over the past 3 years. Selling prices for solution-cast membranes are expected to approach \$25 m^{-2} as large-scale applications are commercialized (Fig. 7).

In our view, the commercialization and competitiveness of PEM fuel cells will depend on continuous innovation and improvement of the membrane. It is clear to us that direct methanol fuel cell technology and PEM fuel cell technology operating at higher temperatures (120–150 °C) will have important market niches as the broader PEM fuel cell market emerges. Anticipating these needs, we have invested in membrane development that will meet the requirements of direct methanol and higher temperature PEM fuel cell technology. We plan to offer these membranes in the future.

The DMFC membrane development has enabled both reduced methanol crossover and improved performance (Fig. 8). This was accomplished with a reduction in membrane thickness, providing the crossover performance of 7 mil membrane in a 2 mil structure, leading the way to reduced material cost as well.

The product development cycle for all products focuses first on performance, then reliability, and finally cost. The cycle is repeated as part of a continuous improvement process for both existing products and the introduction of new fuel cell components. Improvements to mem-

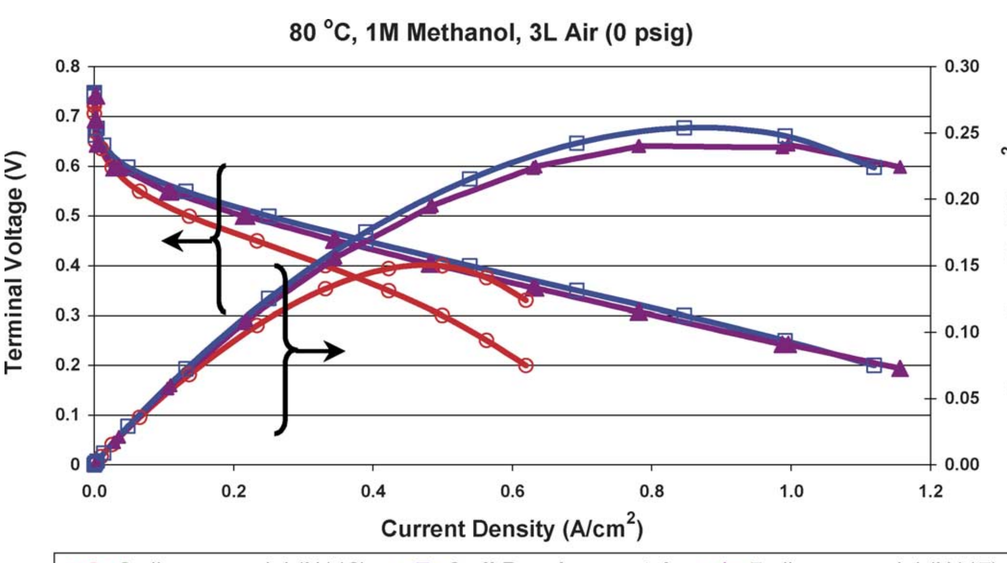

Fig. 8. DMFC performance improvement with Nafion® developmental membrane.

brane chemical stability, mechanical durability, and per-for-mance at higher operating temperatures are essential requirements of DuPont's innovative product pipeline.

3. Conclusion

In conclusion, the advantages that Nafion® brings and will continue to deliver to the emerging fuel cell industry are:

1. Established manufacturing facilities.
2. Production capacity to satisfy current and future demand.
3. Improved performance and quality leading advanced fuel cell design.
4. Reduced raw materials cost expanding the viable application horizon.
5. Simplified product fabrication reducing unit cost and enabling high volume component production.

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