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# Perfluorinated Ionic Polymers for PEFCs (Including Supported PFSA)

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**Abstract** This article outlines some history of and recent progress in perfluorinated membranes for polymer electrolyte fuel cells (PEFCs). The structure, properties, synthesis, degradation problems, technology for high temperature membranes, reinforcement technology, and characterization methods of perfluorosulfonic acid (PFSA) membranes are reviewed.

**Keywords** Analysis · Cross leak degradation · High temperature membrane · Perfluorosulfonic acid · PFSA · Reinforcement

## Abbreviations

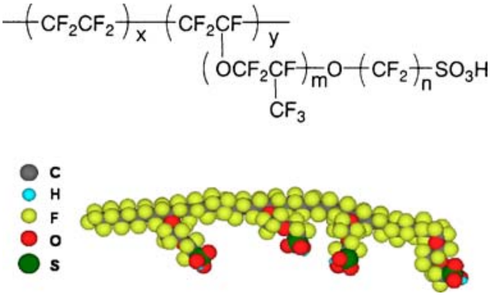
| | |
|---|---|
| DLS | Dynamic light scattering |
| DMFC | Direct methanol fuel cell |
| ETFE | Ethylene–tetrafluoroethylene copolymer |
| EW | Equivalent weight |

| | |
|---|---|
| IEC | Ion-exchange capacity |
| MEA | Membrane electrode assembly |
| MW | Molecular weight |
| PEFC | Polymer electrolyte fuel cell |
| PFSA | Perfluorosulfonic acid |
| PSVE | Perfluorosulfonyl vinyl ether |
| PTFE | Polytetrafluoroethylene |
| SANS | Small-angle neutron scattering |
| SAXS | Small-angle X-ray scattering |
| TFE | Tetrafluoroethylene |
| UAS | Ultrasonic attenuation spectroscopy |

## 1
## Introduction and History of Perfluorinated Membranes

Perfluorosulfonic acid (PFSA) membranes as shown in Fig. 1 were first developed for fuel cells by DuPont as "Nafion"® and installed into the Biosatellite spacecraft in 1967 [1, 2]. Various types of PFSA polymers, such as Flemion®, Aciplex®, and Dow membrane, were developed subsequently. They have excellent chemical stability, high proton conductivity, and high water diffusivity in a wide range of temperatures, brought about by the nature of fluorinated compounds and these non-cross-linked structures [3–5].

Although the PFSA membrane has not been utilized for spaceships after the Biosatellite program up to now, PFSA technology has been utilized in the chlor-alkali electrolysis industry and water electrolysis as one of the key materials [6]. Furthermore, it has also been utilized as a superacid catalyst, separator for the redox flow battery, an ion-permeating membrane for organoelectrosynthesis, and in water-permeating devices such as pervaporation membrane humidifiers and hollow-fiber dryers, etc. Perfluorinated carboxylic acid polymers have shouldered the important roles in chlor-alkali electrolysis and the technology of actuator and artificial muscle, etc.



$$-\!\left(CF_2CF_2\right)_x\!\left(CF_2\underset{\left(OCF_2\underset{CF_3}{CF}\right)_m O\left(CF_2\right)_n SO_3H}{CF}\right)_y\!-$$

**Fig. 1** Chemical structure of perfluorosulfonic acid (PFSA) membranes

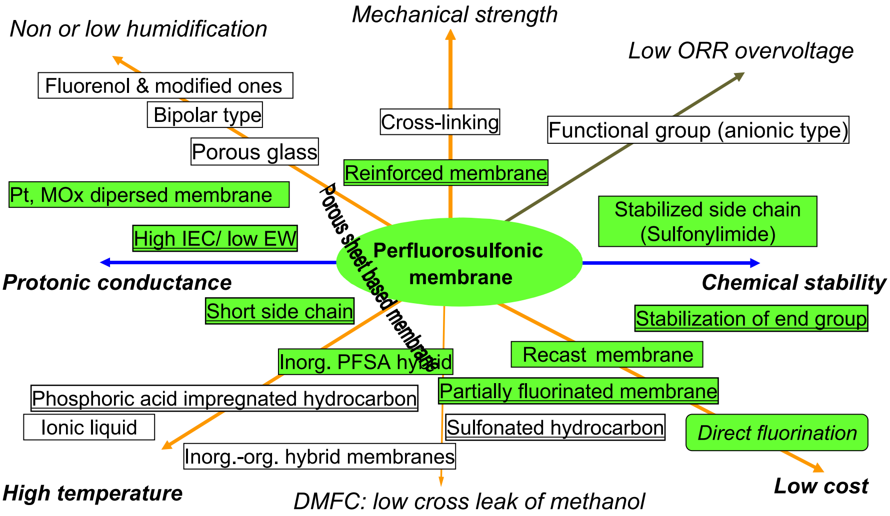


**Fig. 2** Typical proposed candidate electrolytes and technologies for fuel cells. (*Underlined* electrolytes are in/after the stage of stack testing)

The application to fuel cells was reopened by Ballard stacks using a new Dow membrane that is characterized by short side chains. The extremely high power density of the polymer electrolyte fuel cell (PEFC) stacks was achieved not only by the higher proton conductance of the membrane, but also by the usage of PFSA polymer dispersed solution, serpentine flow separators, the structure of the thin catalyst layer, and the gas diffusion layer. Although PFSA membranes remain the most commonly employed electrolyte up to now, their drawbacks, such as decrease in mechanical strength at elevated temperature and necessity for humidification to keep the proton conductance, caused the development of various types of new electrolytes and technologies [7], as shown in Fig. 2.

PFSA membranes with high ion-exchange capacity (IEC) of 1.1 meq/g and long side chains applicable to PFECs [8] were examined. Thin membranes cast from PFSA solution [9, 10] and membranes in which fine particles of catalyst or metal oxides are dispersed [11–13] were proposed for low- or no-humidity operation. Thin membranes can offer not only lower cell resistance but also higher water diffusivity and hence higher power density [8]. To improve the handling characteristics of thin membranes, various reinforcement techniques were proposed [14]. Especially, polytetrafluoroethylene (PTFE) reinforcement technology is typically used for thin membranes. The sulfonimide structure was applied to strengthen the stability of the end sulfonic group [15]. Fluorination of the end groups of the PFSA polymer [16] was reported to contribute to increasing the chemical stability of PFSA under severe conditions, such as low humidity and higher temperature or open circuit voltage (OCV). As for cost reduction, the casting method [17] and various styrene-grafted membranes based on the commercial fluoro compound sheet [18] have been investigated. A newly developed direct fluorination method [19] is expected to be applied to the PEFC membranes. Surface treatment and impregnation of inorganics have been investigated to decrease the swelling in methanol solution for direct methanol fuel cell (DMFC) application. For temperatures over 100 °C, various composite materials with inorganics have been proposed to improve the proton conductivity and stability. Operation under lower humidification, which is convenient to obtain a simpler system and lower system cost, was reported to often cause abnormally rapid degradation of membrane electrode assemblies (MEAs), and the mechanism of the membrane degradation started to be investigated around 2001 by involving many researchers and organizations. As a result, various interesting findings and measures to improve the stability of PFSA have been reported and proposed. Basically, they are based on the analysis results by GE [20]. Hydrogen peroxide formed by the cross leak of hydrogen and oxygen through the membrane is estimated to cause rapid degradation of membranes, especially under low humidity and OCV conditions. Operation over 100 °C is expected to offer such merits as better cell efficiency and smaller radiators in fuel cell electric vehicle applications. Recently, it has been reported that over 5000 h operation is possible at 120 °C and 50%RH using a new perfluoro composite membrane [21].

Decrease in swelling and methanol cross leak of membranes in DMFC applications is one of the most important development items, and various efforts and trials have been performed to improve these characteristics for both perfluorinated and hydrocarbon membranes.

Various reviews on PFSA technology development have been published and detailed explanations of the individual items are available from those materials. In this chapter, the fundamentals of PFSA membranes, the requirements for advanced PEFCs, development trends for high temperature membranes, reinforcement technology, membranes for DMFC, and topics on analysis technology are reviewed.

## 2

## Fundamentals of PFSA Membranes

Fluorine is “a small atom with a big ego”. It took a very long time for it to be handled with ease since its isolation by Moissan. Carbon was found to be able to give extremely comfortable “seats” for it as PTFE by Plankett in 1938, and various fluorinated compounds were prepared and commercialized. The bonding energy of C–F is 485 kJ mol$^{-1}$ and larger compared with those of C–H (350 kJ mol$^{-1}$ for aliphatics and 435 kJ mol$^{-1}$ for aromatics). This basic feature gives remarkable stability to various fluoro compounds.

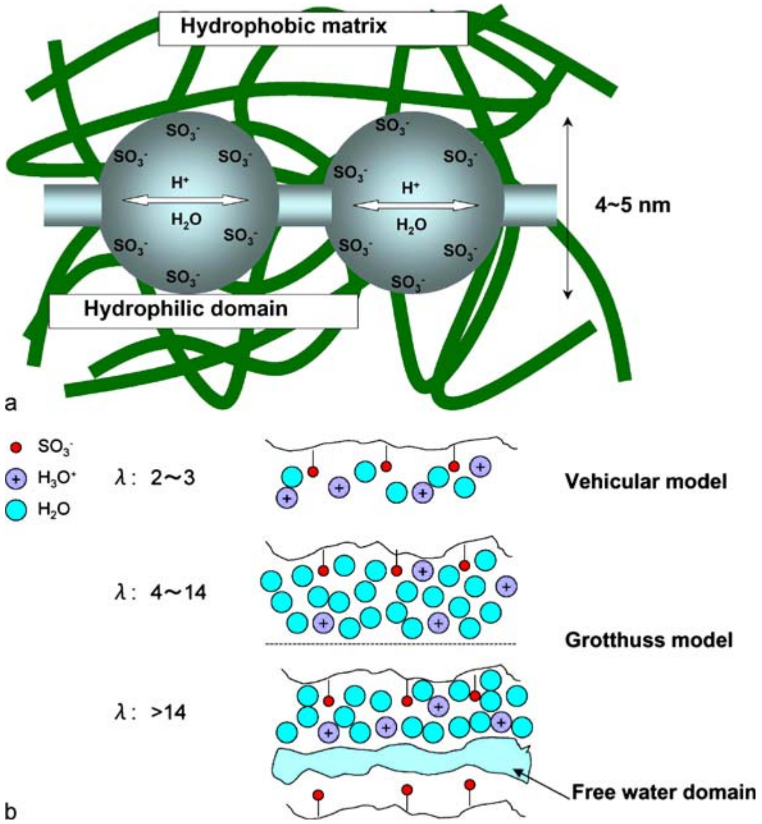


**Fig. 3** Schematic illustration of the PFSA polymer structure. **a** Cluster-network model. **b** Hydration and proton conduction mechanism

PFSA membranes, whose representative polymer structure is shown in Fig. 1, are preferably used for the development of solid PEFCs because they have excellent chemical stability, high thermal stability, and high proton conductivity and, furthermore, are available in larger quantities than other developing membranes. The excellent performance, such as high proton conductivity and water mobility, has been explained by the cluster-network model for the hydrated polymer, as shown in Fig. 3a. This model was originally proposed by Gierke on the basis of analysis by small-angle X-ray scattering (SAXS) [22]. The mechanism of proton conduction is said to be dependent on the molecular ratio of water and the sulfonic acid group at the end of the side chains ($\lambda = H_2O/SO_4^-$), as shown in Fig. 3b.

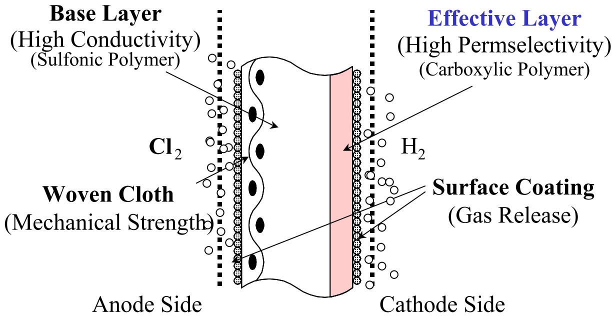
As described before, the commercialization of PEFCs requires lower prices of the membranes and generation systems, compactness of the system, and higher efficiency of power generation. New types of PFSA membranes, new processes of membrane fabrication, and high temperature membranes have been investigated. This article deals with (1) conventional PFSA membranes with long side chains, (2) membranes with short side chains, (3) sulfonimide membranes, and (4) other miscellaneous types of membranes.

## 2.1
## Conventional Perfluorinated Membranes for PEFCs

The molecular structure of a conventional polymer used for a PFSA membrane is shown in Fig. 1. Membranes registered as Nafion® (DuPont), Flemion®, (Asahi Glass), and Aciplex® (Asahi Chemical) have been commercialized for brine electrolysis and they are used in the form of alkali metal salt. Figure 4 shows a schematic illustration of a membrane for chlor-alkali electrolysis. The PFSA layer is laminated with a thin perfluorocarboxylic acid layer, and both sides of the composite membrane are hydrophilized to avoid the sticking of evolved hydrogen and chlorine. The membrane is reinforced with PTFE cloth. The technology was applied to PEFC membranes with thickness of over 50 μm [14].

For the synthesis of this type of polymer, a fluorosulfonyl monomer is frequently copolymerized with tetrafluoroethylene (TFE). The synthetic scheme of this monomer is shown in Fig. 5 [24]. The IEC is about 0.9 to 1.1 meq/g dry polymer. As the IEC increases, water absorption increases, and the crystallinity based on successive sequences of the TFE monomer unit becomes smaller, which lowers the mechanical strength. On the other hand, when the IEC decreases, water absorption becomes smaller, which brings lower proton conductivity.

The term IEC means the number of ion-exchange groups, in the unit of milliequivalents, contained in one gram of dry resin. The term equivalent weight (EW) is also used for expressing the number of ion-exchange groups.



Anodic reaction: $2Cl^- = Cl_2 + 2e^-$

Cathodic reaction: $H_2O + 2e^- = 2OH^- + H_2$

**Fig. 4** Design model of perfluorinated membrane for chlor-alkali electrolysis

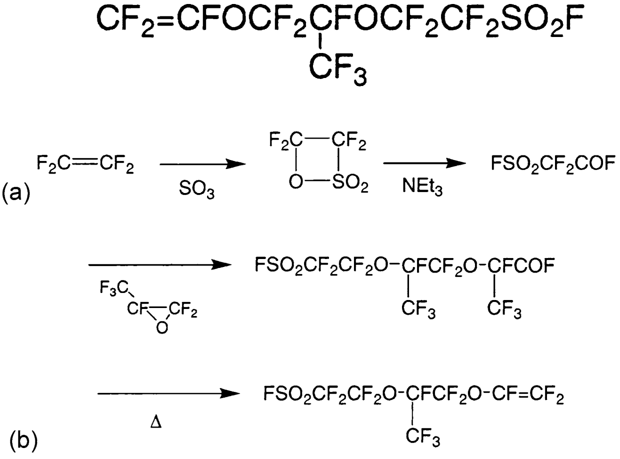


**Fig. 5** Chemical structure and synthetic scheme of fluorosulfonyl vinyl ether (PSVE)

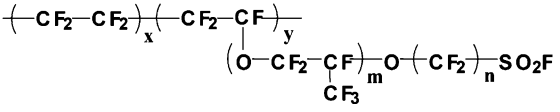


**Fig. 6** Chemical structure of a copolymer of TFE and PSVE

This value corresponds to the average molecular weight per ionic group, according to the following relationship between IEC and EW:

$$\mathrm{IEC} = 1000/\mathrm{EW}\,.$$

A copolymer of TFE and perfluorosulfonyl vinyl ether (PSVE; Fig. 5) given in Fig. 6 is a thermoplastic polymer. It can be extruded to form a thin film. The films with $-SO_2F$ groups can be converted to proton-conductive ion-exchange resins having $-SO_3H$ groups by alkali hydrolysis followed by acidification. This ion-exchange resin can be dissolved or dispersed in polar solvents, such as water, lower alcohols, dimethylformamide, and dimethylacetamide. This liquid composition is used for cast film formation and for an ink to form catalyst layers. An understanding of the characteristics of ionomer dispersed solutions, such as viscosity and structure, is important to improve recast membranes and MEAs. Recent analysis results are explained in Sect. 2.2.

The membrane development for PEFCs comprises many steps, as shown in Fig. 7. The multiple steps in monomer synthesis for PFSA preparation is often said to be one of the major factors in the high cost of the PFSA membranes. In fact, PTFE and ethylene–tetrafluoroethylene copolymer (ETFE), whose synthetic scheme is very simple, are available at comparably low price. As a matter of fact, a considerably large quantity of the ETFE sheet was used

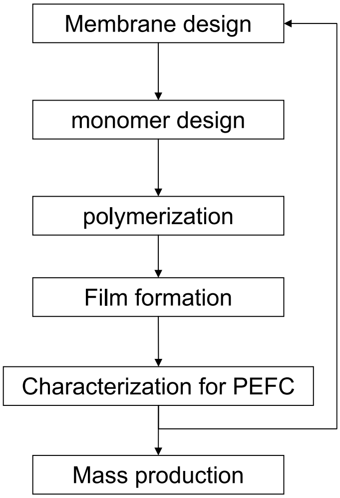


**Fig. 7** General flow chart of membrane development

in the German soccer stadium Allianz-Arena (about 200 000 $m^2$ for the main stadium) [25], and it is to be used for main and swimming stadiums of the Olympic games in Beijing, China (about 300 000 $m^2$ of the film) [26].

Different from PTFE and ETFE, cost reduction of the PSVE polymer is one of the problems for prevailing perfluorinated membranes. Recently, a new direct fluorination process with elementary fluorine was reported to produce perfluorinated fluorosulfonyl polymers, as shown in Fig. 8 [19]. This new process consists of the following features and is free from explosion in the gas phase and the difficulty in finding solvents with stability to fluorine gas and solubility for hydrocarbon compounds, these problems having limited the application of the conventional direct fluorination methods:

1. Alcohol (ROH) as a raw material is reacted with $R_FCOF$ into an ester ($R_FCOOR$) which is not very volatile and soluble in $R_FCOF$.
2. Direct fluorination with elementary fluorine gas.
3. Decomposition of the ester and regeneration of $R_FCOF$.

This process can offer wide selection of the synthetic routes of precursor hydrocarbon, shorter steps, and low-cost production of the perfluorinated polymers [27].

## 2.2
## Membranes with Short Side Chains

So-called Dow membrane with short side chains once attracted much attention, because it showed excellent performance in fuel cell operation compared with Nafion® membranes [28–30]. The polymer structure is shown in Fig. 9.

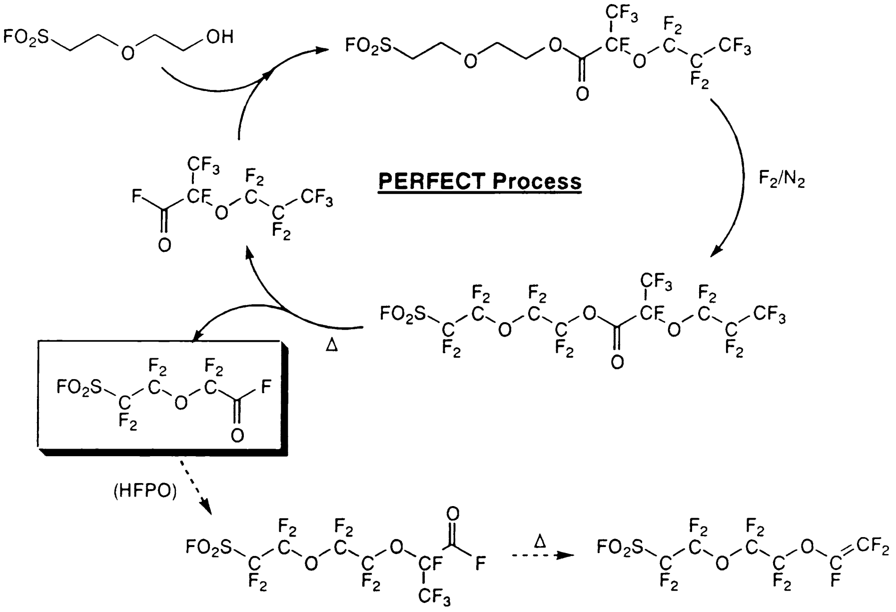
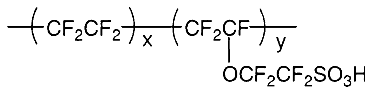


**Fig. 8** Direct fluorination with elementary fluorine to synthesize perfluoro compounds. "PERFECT" means PERFluorination of Esterified Compounds then Thermal elimination



$$-(CF_2CF_2)_x-(CF_2CF(OCF_2CF_2SO_3H))_y-$$

**Fig. 9** Chemical structure of the Dow membrane

$$CF_2{=}CFOCF_2CF_2SO_2F$$

**Fig. 10** Structure of the perfluorosulfonyl monomer of the short side chain membrane

The Dow membranes are prepared by the copolymerization of TFE with PSVE, which is shown in Fig. 10.

An important difference between the Dow and Nafion® membranes was considered to be membrane resistivity, which depends on membrane thickness and IEC [30]. The mechanical strength of the perfluorinated membranes largely depends on the molar content of the TFE unit in the copolymers. Since the molecular weight of the Dow monomer is smaller than that of the Nafion® monomer, a higher IEC can be obtained with the Dow monomer compared with the Nafion® monomer at a similar molar content of TFE unit in the copolymers, while keeping the membrane mechanical strength. Recently, thinner PSVE membranes with long side chains have been available for reduction of membrane resistance [31]; nevertheless, the short side chain membrane is actively being developed. The reason is that the short side chain

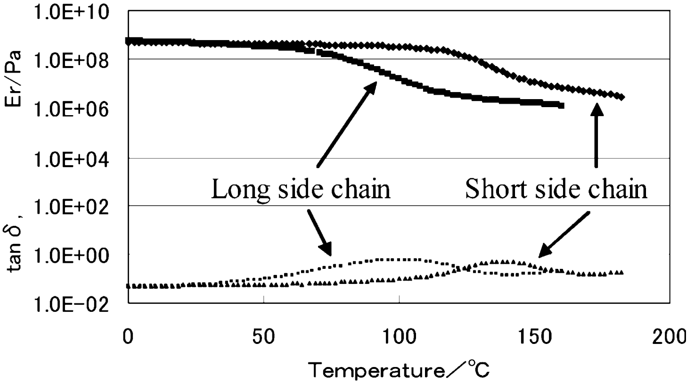


**Fig. 11** Mechanical characteristics of a short side chain membrane

membrane has a higher glass transition temperature than conventional perfluorinated polymers, and the former has an advantage for high temperature operation of a fuel cell. The $T_g$ of a short side chain film in an acid form is much higher than that of the conventional PFSA membrane with long side chains [32]. Although the glass transition temperature of the latter is about 100–130 °C, where the tan $\delta$ peak appears in the dynamic elastic modulus measurement, the modulus of the film suddenly decreases at 70 to 80 °C. As for the short side chain membrane, its softening temperature is over 100 °C, and it is considered to be a preferred material for higher temperature operation. The dynamic mechanical properties of a short side chain polymer are given in Fig. 11 together with those of a conventional perfluorinated polymer. The functional groups of the polymers are sulfonic acid ($-SO_3H$) groups.

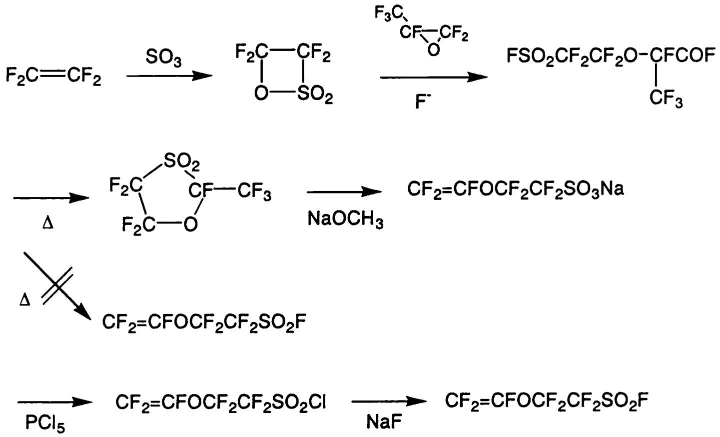


**Fig. 12** Synthetic scheme of the Dow membrane PSVE monomer

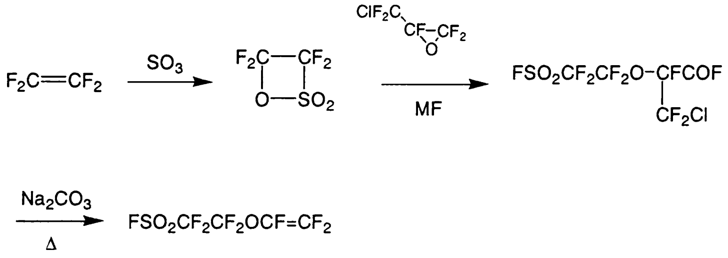


**Fig. 13** New synthetic route to the Dow membrane PSVE monomer

Originally the monomer in Fig. 9 was prepared by DuPont by the synthetic scheme shown in Fig. 12 [33]. Thermolysis of the acyl fluoride in Fig. 12 did not give a desired monomer but gave a cyclo compound. In order to prevent the cyclization, a new synthetic route was developed as shown in Fig. 13, which was applied to the synthesis of Dow membranes [34]. A chlorine atom was introduced to the acyl fluoride to improve the selectivity of vinyl ether formation. The Dow membrane was also developed for brine electrolysis, but was not commercialized probably because of its high cost. Difficulty in the preparation of the acyl fluoride in Fig. 13 is one of the causes. Recently, new synthetic processes for the short side chain monomer were developed, as represented in Fig. 14.

Recently a similar monomer and copolymer to those of the above short side chain type were reported [35–38]. The monomer has four $CF_2$ units (Fig. 15). Its copolymer with TFE exhibited a similar softening point to that

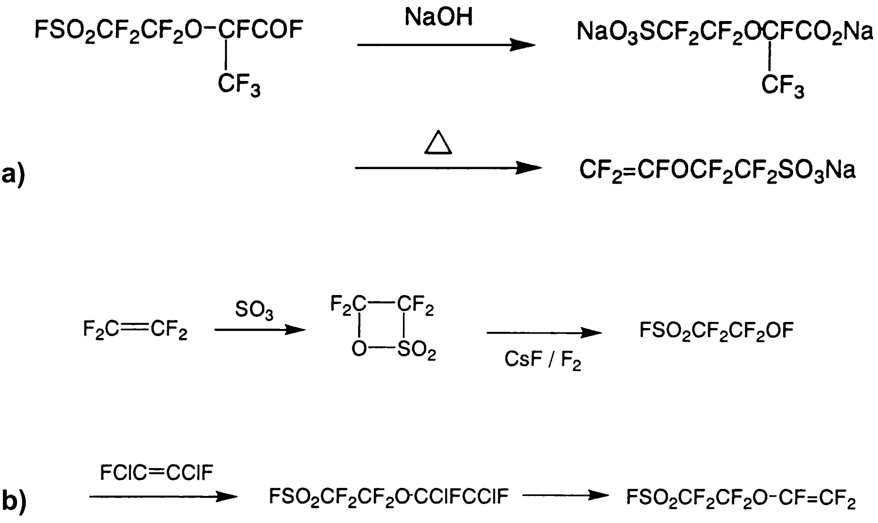


**Fig. 14** New synthetic routes to short side chain PSVE monomer

of the above short side chain monomer which has two $CF_2$ units. The thermal decomposition temperature of the former copolymer was much higher than that of the latter copolymer [38].

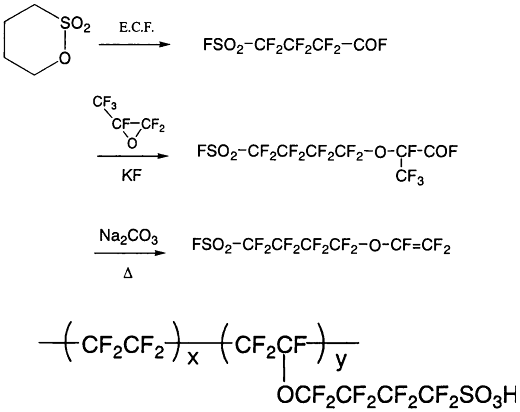


**Fig. 15** New type of PFSA with straight side chains

## 2.3
## Sulfonimide Membranes

Perfluorinated sulfonamide monomers were prepared by DesMarteau. A typical synthetic scheme is given in Fig. 16 [39, 40]. The temperature dependency and humidity dependency of proton conductivity of the sulfonamide copolymer with TFE were examined, and the properties were proved to be similar to those of a sulfonic acid type membrane [41–43]. Fuel cell performance was dependent upon membrane thickness and/or IEC, and there do not seem to be large differences depending on the species of the ion-exchange groups. Synthesis of a short side chain type sulfonimide monomer is also reported (see Fig. 17 [44]).

# 3
# High Temperature Membranes

The development of high temperature membranes applicable to operation at up to 120 °C or higher, no or low humidity, and low pressure conditions has been expected to offer better efficiency and more compact stacks and radiators for automobiles. These expectations for membranes are typically reflected by the DOE's 2010 targets shown in Table 1. Operation at higher temperature (120 °C) and lower humidity (1.5 kPa), lower cross leak, lower

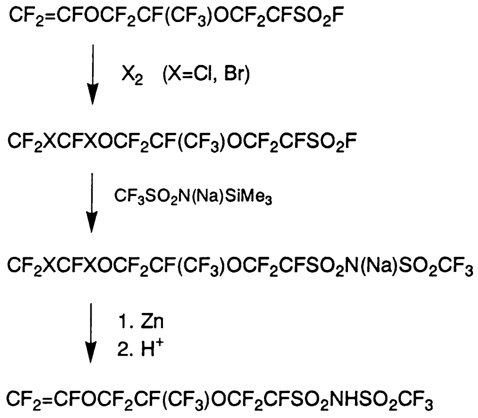


**Fig. 16** Typical synthetic scheme for the perfluorinated sulfonamide monomers

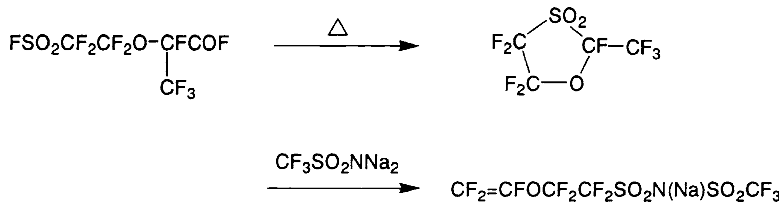


**Fig. 17** Preparation scheme of the short side chain sulfonimide monomer

area specific resistance (0.02 mΩ cm$^2$), lower cost, and higher durability are required by 2010.

To realize the high temperature membrane in general, the drop of mechanical strength and conductivity at elevated working temperature and the chemical degradation problem have to be overcome [46]. Typical measures

**Table 1** The DOE's 2010 targets for membranes [45]

| Item | Target |
|---|---|
| Proton conductivity at < 120 °C, < 1.5 kPa | 0.1 S/cm |
| Proton conductivity at – 20 °C | 0.01 S/cm |
| Oxygen and hydrogen cross leak | 2 mA/cm$^2$ |
| Durability with cycling at > 80 °C | 2000 operating hours |
| < 80 °C | 5000 operating hours |
| Survivability | – 40 °C |
| Cost | \$40/m$^2$ |

to improve the high temperature performance of PFSA membranes aimed at high temperature operation are as follows:

1. Composites with inorganics to improve proton conductance at over 100 °C.
2. New molecular design which can offer lower water uptake at higher temperature and better dimensional stability.

The decrease in mechanical strength of the PFSA membranes under humidified conditions at elevated temperature is the most important issue for high temperature operation. The flexibility of the side chain and conformational changes in the backbone on hydration and proton transfer in the PFSA membranes were investigated using first principles based molecular modeling studies [47, 48]. This electronic structure calculation analysis showed that short side chain PFSA membranes gave lower water uptake and higher proton conductivity with fewer water molecules. The flexibility in both the backbone and side chains of PFSA membranes is important to the effective transport of protons under low humidity. Composite membranes comprising PFSA polymer and inorganic particles, such as silica and zirconia, as a hydrophilic material have been proposed [49]. In the case of the hydrocarbon membrane, the nanosized space in polyimide electrolytes containing trifluoromethyl groups is estimated to offer water adsorbing sites [50]. The stability of the sulfonic group of the side chains in PFSA polymer in air and water was found to offer excellent stability at 120 °C [51]. The side-chain-sulfonated hydrocarbon membranes are thought to be more resistant to hydration than backbone-sulfonated types [52, 53]. The former types, whose structure is similar to that of PFSA in the point of phase segregation in the molecule, can offer higher proton conductivity than the latter ones at higher temperature. Needless to say, a deep understanding of the PFSA structure is required for the development of high temperature PFSA membranes [54, 55]. Here, new monomer structures for PFSA except for short side chain types are reviewed.

## 3.1
## Terpolymers

2,2-Bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (Fig. 18) was copolymerized with TFE and a PSVE monomer shown in Fig. 5. A homopolymer of this third monomer exhibits a glass transition temperature of 330 °C [56]. The terpolymer exhibits a high softening temperature like the above short side chain copolymers [57]. This is one of the another approaches to obtain high temperature membranes. The temperature dependency of the modulus of the terpolymer is compared with that of a conventional copolymer in Fig. 19 [58].

A perfluorophosphonic monomer (Fig. 20) was synthesized and copolymerized [59] with TFE. Terpolymers with TFE and PSVE were also prepared. Base hydrolysis of the copolymers caused C–P bond cleavage (Fig. 21, above).

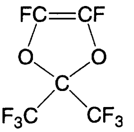


**Fig. 18** 2,2-Bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole

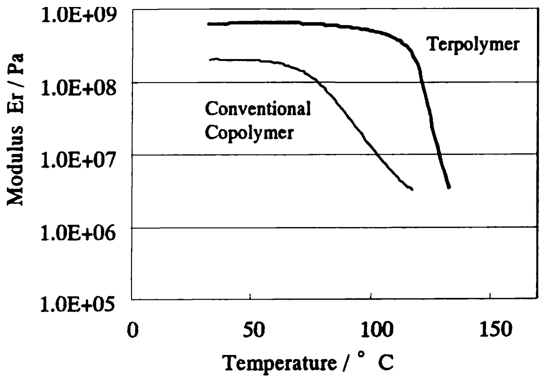
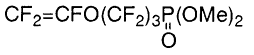


**Fig. 19** Temperature dependency of the modulus of the terpolymer

The quantitative transformation of phosphinic ester polymer was carried out by acid hydrolysis (Fig. 21, below). The IECs of the copolymers were 1.4 to 2.1 meq/g.

The conductivity of the polymers at 25 °C in 1N HCl was a little smaller than that of Nafion®. Similar copolymers with an IEC of 2.5–3.5 meq/g were also prepared [60]. Their films exhibited similar proton conductivity to that of a Nafion® film at 80 °C under saturated water vapor. Preparation of phosphonic monomers requires many steps [59, 61], which makes it difficult to apply phosphonic membranes to fuel cells as well as the estimated high cathodic overpotential.



$$CF_2{=}CFO(CF_2)_3\underset{\underset{O}{\|}}{P}(OMe)_2$$

**Fig. 20** Molecular structure of the perfluorophosphonic monomer

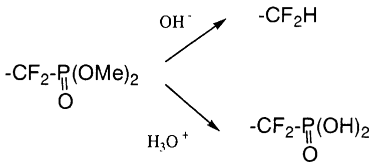


**Fig. 21** Reactions of the perfluorophosphonic monomer with acid and alkali

## 4
## Chemical Degradation Problem

Commercialization of PEFC systems requires high performance and low cost at the same time. Thinner membranes are convenient to get lower cell resistance and higher cell voltage [8] and, furthermore, can render the operation under low- or non-humidified conditions [9]. The membrane or catalyst-coated membrane (CCM) is sandwiched by the gas diffusion layer and separators, as schematically shown in Fig. 22. The usage of thinner membranes often causes not just mechanical damage, and various reinforcement methods have been developed as described in the next section. The nonuniformity of the circumstances surrounding MEAs and membranes in real cells, especially the difference between the edge region and the center, should be considered in the analysis of the degradation phenomena.

In the early stages of PEFC development after Ballard's demonstration, the chemical degradation of PFSA membranes was not considered by most fuel cell researchers except for a few analysts, because the stability of the perfluorinated membranes was believed to be proved by the analysis of membrane degradation in water electrolysis and the long operation in the chlor-alkali electrolysis industry. But the chemical degradation of perfluorinated membranes broke to the surface soon after the research on low-humidity operation began, which aimed to lower the system cost. The degradation of perfluorinated membranes has been recognized as a significant problem for the achievement of long-term durability for practical use. Evidence of membrane thinning and fluoride ion detection in the product water indicates that the polymer is undergoing chemical attack. Various research projects and programs to analyze and

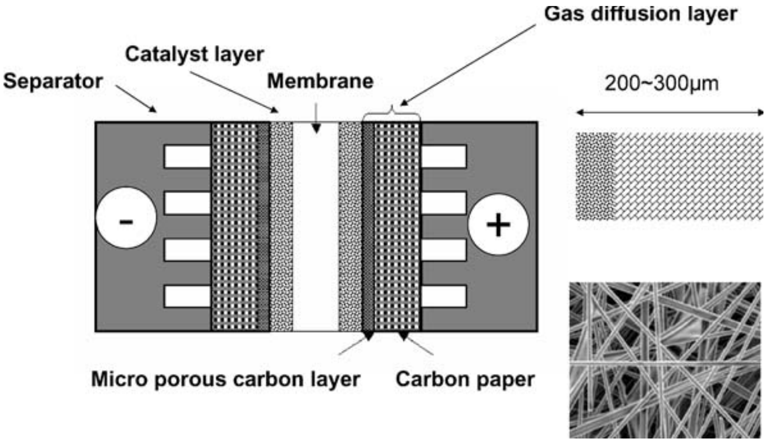


**Fig. 22** Schematic illustration of a MEA and gas diffusion layer and a photo of carbon paper

solve the degradation phenomena were organized after that, and the number of reports on membrane degradation increased dramatically. Basically, the degradation problem has been investigated based on the mechanism in water electrolysis proposed by LaConti, et al. [62–66], where hydrogen peroxide or radicals caused by the cross leak of hydrogen and oxygen through the membrane play an important role. The old report [2] also proposed a typical design for mitigation applicable even to the present situation.

A mechanism of the degradation was postulated and examined. Hydrogen peroxide can be formed during the oxygen reduction reaction:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \,.$$

Hydrogen peroxide can decompose to give OH or OOH radicals. These materials can then attack H-containing or unsaturated groups present in the polymer. Such groups can include $-CF_2COOH$, $-CF_2H$ or $CF{=}CF_2$. Peroxide radical attack on such end groups is believed to be the main degradation mechanism. For a carboxylic end group the following reaction scheme has been proposed, as in Fig. 23 [16].

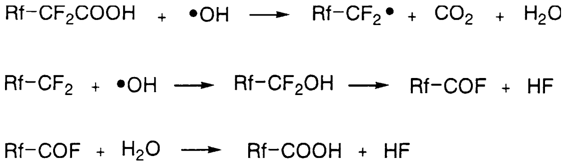
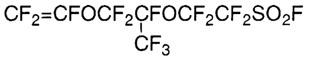


**Fig. 23** Reaction of a carboxylic end group with an OH radical

The chemical degradation was studied both in situ (during fuel cell operation) and ex situ (by Fenton's reagent test) [68]. The structure of the examined polymer is given in Fig. 1. Except for fluoride release, the same product shown below was identified using NMR and mass spectroscopy in both the Fenton's test water and a residue extracted from MEAs that were heavily degraded during fuel cell operation.



$$CF_2{=}CFOCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2SO_2F$$

These features demonstrate similarities between the in situ and ex situ degradation mechanism that involves degradation along a perfluorinated ionomer backbone. Similar results were also obtained after accelerated MEA durability tests under open circuit conditions [69]. For reduction of unstable polymer ends, fluorination of polymer ends by fluorine gas is effective. Membranes were exposed to gaseous hydrogen peroxide in order to examine its influence directly, which resulted in a rapid decrease in molecular weight of the polymer. This means that degradation takes place not only from polymer ends, but also main chain scission happens by chemical attack. The latter explains the decrease in molecular weight [68]. As for the attack to the main chains, several reports on the degradation of fluoropolymers, such as PTFE and PFSA, have been reported previously in alkaline fuel cells (AFCs), DMFCs, water electrolysis, and oxygen reduction gas electrodes for brine electrolysis [70–72].

In the case of the copolymer of $CF_2{=}CFO(CF_2)_4SO_2F$ and TFE, a fragment compound shown below was identified during peroxide testing.

$$HOOC{-}CF_2CF_2CF_2{-}SO_3H$$

Many studies on the effect of the catalyst layer and operation conditions, such as humidification and temperature, on values such as proton conductance, hydrogen leakage through the membrane, fluoride ion ($F^-$) release, molecular weight, and mechanical characteristics, have deepened the understanding of the mechanism of formation of $H_2O_2$, starting sites of decomposition in the membrane molecules, catalyst rearrangement in catalyst layers and membrane, etc. [73–77]. Various types of measures to mitigate chemical degradation have been proposed. In fact, several thousand hours of operation over 90 °C under lower humidity conditions have been reported using perfluorinated sulfonic membranes. Although polymer degradation is a serious problem, it was reported that additives can improve oxidative stability [67]. In addition, recently it was reported that a newly developed MEA with a novel fluorine-based proton-conductive polymer composite reduces the deterioration rate by 100–1000-fold compared with a conventional MEA. It can be operated continuously for more than 2000 h [79], and recently 4000 h, at 120 °C and 50% relative humidity [21]. According to the cross-sectional SEM image of the membrane in the report, the thickness of the cathode decreased by over a half, while those of the membrane and the anode remained at the initial values. The waste of the carbon support was found to be the major factor in the thinning of the cathode. It was clarified that the improvement of the oxidative stability of the carbon support is essential not only in the operation mode of automobiles, but also in the stationary mode at higher temperature. The company reported that a new catalyst with stabilized carbon support gave a more stable cell voltage of $\sim 3\ \mu V/h$ over 4000 h at 120 °C and 50%RH under relatively low pressure conditions (200 kPa).

## 5
## Reinforcement Technology

The PFSA membranes have a tendency to swell considerably when they are soaked in water at higher temperature with a consequent decrease in mechanical strength. The lowering in mechanical strength is detrimental to the use of thinner membranes. On the other hand, thinner membranes have many advantages, such as low internal cell resistance or easy water management. In the early 1980s, reinforcement technologies for perfluorinated membranes were developed aimed at commercialization of chlor-alkali electrolysis, in which the robust membrane was firstly required to have a sufficient mechanical strength to insure durability for long-term operation. In the early stages of development, PTFE woven fabrics and PTFE microfibrils were proposed for reinforcement technology. Finally, PTFE woven fabrics have been recognized as a standard reinforcement method because of their good mechanical strength and chemical stability. The typical membrane for chlor-alkali electrolysis is a bilayer membrane and its major portion is a perfluorosulfonic polymer layer located on the anodic side. PTFE fabrics are embedded in the perfluorosulfonic layer. The cross section of the membrane is shown in Fig. 1. The total thickness of the membrane is approximately 200–300 μm.

On the contrary, in PEFC applications the size of the membrane is small and a higher mechanical strength is not necessarily required. The higher priority is set on the performance of the membrane, and a thin and flat membrane is required to obtain good performance. The performance is also determined by the precise structure of the porous electrodes that are bonded on both sides of the membrane. The flatness of the membrane helps to form proper electrode layers that afford good diffusivity of hydrogen, oxygen, and water vapor to the MEA. Therefore, in PEFC a specified reinforcement technology is required to prepare a thin and flat membrane that provides an appropriate mechanical strength, good chemical stability, higher proton conductivity, and water permeability. PTFE is most often selected as a reinforcing material for its excellent chemical stability and good mechanical strength. A composite comprising an expanded PTFE porous sheet and a perfluorinated ionomer was developed by W.L. Gore & Associates in the 1990s and has been commercialized as “Gore-Select®”. Gore-Select® is characterized by its small thickness (20–40 μm) and excellent mechanical and electrochemical properties and has been widely used for PEFC systems. Gore-Select® shows relatively high specific resistance compared with nonreinforced membranes; however, the membrane resistance is sufficiently low because of its smaller thickness [79]. The PTFE yarn embedded type, which originated from chlor-alkali electrolysis, gives the good mechanical strength. The characteristics of this membrane were studied in NEDO’s PEFC program, Japan. The PTFE fibril type was developed by Asahi Glass Co., Ltd. Even a small quantity of PTFE fibrils (a few wt.%) dispersed in a perfluorosulfonic polymer give the membrane both good mechanical strength and flatness suitable for PEFC application. Continuous film formation technology was also developed [80, 81]. Characterized values of the membrane, such as tensile strength, tear strength, creep property, and compressive property, and the cell performance were reported. Detailed explanation of the reinforcement technology of PTFE porous sheets and PTFE fibrils is available in reference [14].

Nafion® XL, one of the reinforced PFSA type membranes, was announced to give a 1.5 times increase in tensile strength and over 50% reduction in swell over Nafion®NRE211 [82].

## 6
## DMFC Application

Experiments on DMFCs using PFSA membranes at higher temperature in the gas phase, which could give over 0.2 W/cm$^2$, ignited the development of DMFCs for electric vehicle (EV) and portable applications [83]. The PFSA membranes have a tendency to swell extremely when they are soaked in methanol aqueous solution. Reduction of the influence of methanol permeation and deformation or swelling of the membrane have been important issues in DMFC development, as shown in Table 2.

**Table 2** Main research work in DMFC applications

- Operation at high temperature in the gas phase gave 0.2 W/cm$^2$
- Decrease in DMFC permeation using diluted methanol solution
- Modification of PFSA membrane with inorganic/organic fillers
- Development of new polymers: partially fluorinated types, such as styrene-grafted membranes, various hydrocarbon polymers, fullerenol-polymer composite
- Utilization of anionic membranes
- Studies on fuels other than methanol: ethanol, DME, etc.
- Gas phase DMFC using methanol clathrates

### 6.1
### Examples of PFSA Type Membranes for DMFC

The addition of inorganic and organic fillers, introduction of the cross-linking structure, impregnation of ionomer into the porous sheet, surface modification of the PFSA membrane, and various grafted membranes have been proposed as membranes for DMFCs. These efforts decreased the methanol cross leak from several times to a tenth of that for PFSA membranes at best. Typical examples of the investigated methods are explained as follows. The membranes were recast from a PFSA dispersion in which small inorganic particles, such as silica, alumina, and titania, were able to reduce the methanol permeation by several times compared to the conventional PFSA membranes. Generally, the addition rates have optimum values. In recent research, detailed analyses have been available. For example, the interfacial properties such as zeta potential of the particles and positioning the existing sites of the particle in the membrane structure should be of more interest. The analyses with NMR and SAXS are expected to accelerate the deeper understanding of the transport mechanism of protons, water, and methanol in PFSA membranes. Discussions on the effect of size, aspect ratio, and surface properties of the organic fillers on membrane characteristics for DMFCs are expected to be developed.

## 7

## Topics Related to New Analytical Results on the Structure of PFSA Dispersions and Membranes

Some of the properties of electrolyte membranes related to PEFCs, such as ion-exchange capacity (IEC) or equivalent weight (EW), molecular weight (MW) or corresponding parameter, water uptake after immersion in water, gas permeability, and mechanical properties in the dry state, etc., can be evaluated based on conventional procedures [84] and some protocols for measurement were made regionally [85, 86]. Progress in the development of PEFCs requires the introduction of new techniques or the creation of new measurement protocols suitable for a working fuel cell with various expected applications. As a matter of fact, it has been claimed and requested by many concerned to standardize common measuring procedures and some protocols were proposed in NEDO's PEFC programs. IEC or EW, MW, and solvent uptake in water-containing solution are the basic properties to be measured just before advanced evaluation. Properties such as water uptake, proton conductivity, water transport, gas permeation, dimensional stability, mechanical strength, compressive properties, creep properties, and chemical stability are usually evaluated in an atmosphere of controlled temperature and humidity. Pretreatment of membranes before testing is important for reproducible experimental results. More advanced analytical methods have come to be required to understand more detailed behaviors. For example, the conventional method of water uptake measurement is very delicate and requires sufficient skill [84, 87, 88]. A new method, where the amount of tritium is measured using a liquid scintillation counter after exposure to tritiated water vapor and subsequent immersion in distilled water, does not require such skill [89]. This tritium trapping method is also applicable to the measurement of the diffusion coefficients of hydrogen and oxygen in the membrane [90].

The structures of PFSA membranes have been analyzed and discussed by many researchers, and the cluster-network model for hydrated membranes proposed by Gierke [22] has been a basic model symbolic of the PFSA characteristics up to now. As for the structure of the diluted aqueous solution of PFSA, it is important to understand the structure of ionomer dispersion and catalyst ink, comprising catalyst particles, ionomer, and solvent, for the preparation of cast membrane and catalyst layer, respectively. Aldebert et al.

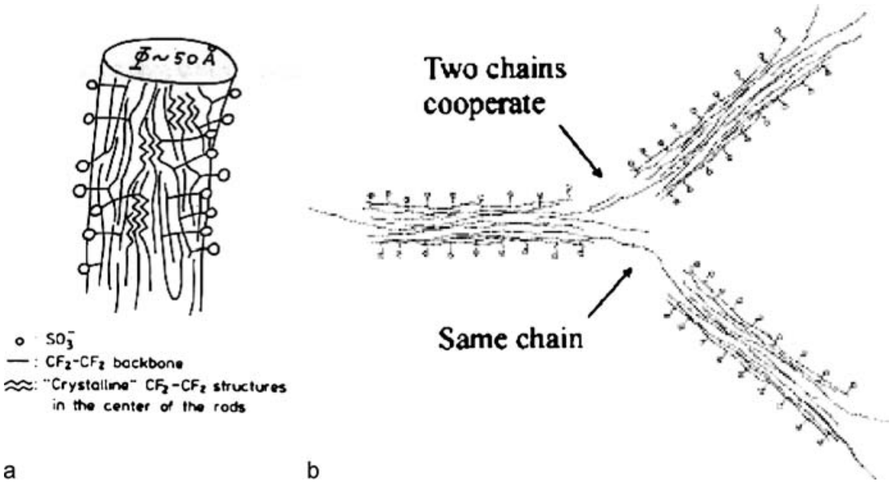


**Fig. 24** Estimated models of PFSA dispersed in diluted aqueous solutions

proposed a rodlike structure by using SAXS and small-angle neutron scattering (SANS) in diluted aqueous solutions, as shown in Fig. 24a [91]. The self-assembling behavior of PFSA in more concentrated aqueous solutions was studied using dynamic light scattering (DLS) and a fringed-rod-based microgel model, as shown in Fig. 24b [93], was proposed based on a fringed-rod model [92].

Gebel proposed a schematic model of the structural evolution from dry membrane to colloidal dispersion of rodlike particles based on the results of the scattering analysis of PFSA over a wide range of water contents, combined with energetic considerations [94].

In the real fabrication process of membrane and MEA, more concentrated solutions which often contain organic solvents are used. Ultrasonic attenuation spectroscopy (UAS), whose principle is illustrated in Fig. 25, can offer detailed information on dispersed particles for a wide particle size range from 10 to 1 mm with subtle radiation energy (~ 10 mW) compared with other methods such as DLS. The application of the UAS technique to solutions of PFSA (over 1 wt. %) was tried and the structure was based on the rodlike micellar model shown in Fig. 26 [95]. The effect of molecular weight, solvent, concentration, and temperature on the size and shape of the dispersed PFSA particles was analyzed as shown in Figs. 27 and 28. Higher concentration and temperature and lower molecular weight gave smaller aspect ratios *R*; alcoholic solutions gave lower aspect ratios than aqueous solutions. The rigidity and hydrophobicity of perfluorinated ionomers are estimated to be related the phenomena.

The requirement to characterize the detailed structure of catalyst layers in MEAs has become more and more clamorous to improve MEA perform-

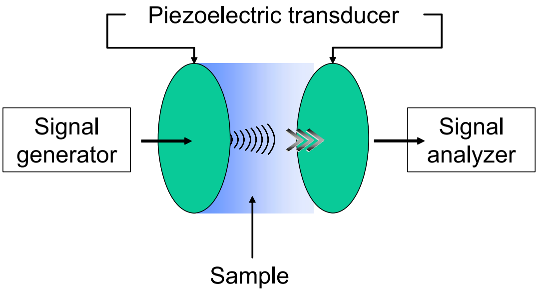


**Fig. 25** Principle of ultrasonic attenuation spectroscopy

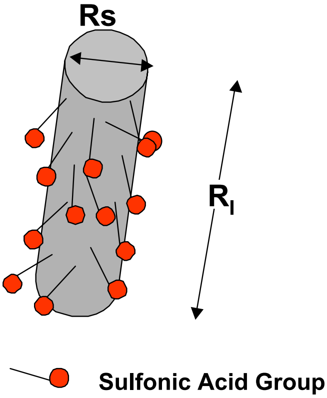


**Fig. 26** Basic model assumed in the analysis of PFSA dispersion by UAS

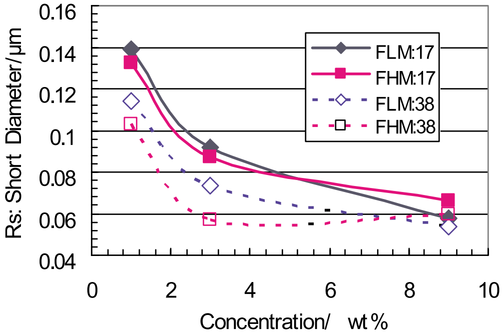


**Fig. 27** Influence of concentration of Flemion® with lower molecular weight (FLM) and higher molecular weight (FHM) on *R* values at 17 and 38 °C in ethanol

ance. For example, many researchers have reported values around 20 to 30% [96, 97] as Pt utilization in MEA from CV measurements in $N_2$ atmosphere [65, 98] as Pt utilization in MEAs is strongly dependent on the preparation procedure using catalyst ink comprising catalyst and ionomer dispersion. Even though relatively higher utilization values have been reported

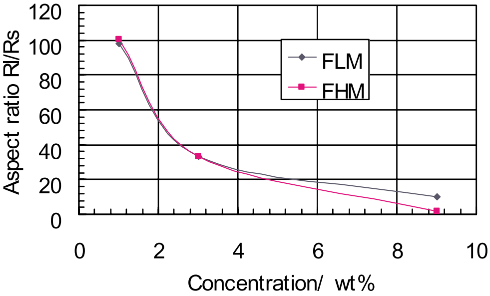


**Fig. 28** Influence of concentration of Flemion® ionomers on the aspect ratio (4Rl/Rs) in aqueous solution at 17 °C

recently, a precise understanding is not sufficient at present. As a matter of fact, it is not easy to estimate the detailed structure of the catalyst layers consisting of catalyst and ionomer with microscopic methods because of the difference in contrast between catalyst metal and ionomer at high magnification. Trial measurements, such as observation of ionomer on catalyst particles in MEAs by field emission scanning electron microscopy (FE-SEM), or HR-SEM, with retarding function or TEM with elemental analysis or TEM with a cryo-system to decrease the damage of organic ionomer on catalysts by the electron beam, are reported. Figure 29 shows the existence of nonuniform coverage of ionomer [95].

Water distribution in membranes or single cells has been analyzed by various optical methods, neutron radiography (NRG) [99–103], and magnetic resonance imaging (MRI) [104–107]. Improvement of space resolution under 10 μm is expected.

As for the chemical stability, the Fenton's reagent prepared from $H_2O_2$ aqueous solution and $FeSO_4$ is often used. But it is well known that chemical degradation caused by $H_2O_2$ is most vigorous at the state of open circuit in dry conditions. Fenton tests are conducted in aqueous solution. A new

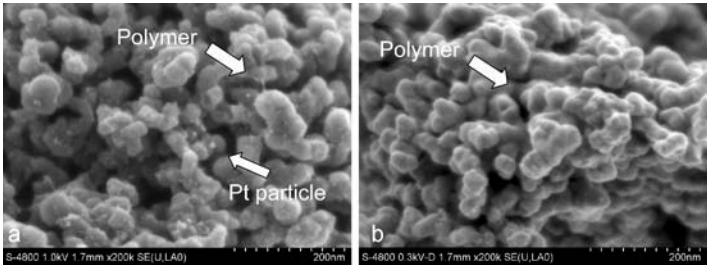


**Fig. 29** **a** FE-SEM image of dried ink of catalyst and ionomer (ACV = 1 kV). **b** FE-SEM image of dried ink of catalyst and ionomer (ACV = 0.3 kV)

method in which humidified $H_2O_2$ gas is introduced into a circumstance-controlled chamber has been proposed to simulate the real operating state of PEFCs. A degradation mechanism consisting of unzipping of polymer ends and scission of main chains is estimated based on the changes of polymer weight, F release, and molecular weight.

Advancement in computer simulation founded on the molecular orbital method is expected to contribute to deeper understanding of the formation of ionic clusters, proton conduction, chemical deterioration of membranes, and water uptake over 100 °C, etc.

## 8

## Summary

Over 160 years and 40 years have passed since the first exhibition of fuel cells by Grove and the first mission of the Gemini spaceship, respectively. In the meantime, "energy conversion took the wrong path in 1894" in spite of Ostwald's farsighted proposal according to the text by Bockris [108]. The PFSA membranes have been the most important components constituting the PEFC systems since the Biosatellite mission, although various new membranes have been studied and developed.

The performance of PEFCs and DMFCs has shown remarkable progress owing to the continuous development and improvement in materials such as membranes, electrocatalysts, and separators, as well as technical methods for MEA fabrication. Especially, PFSA membranes whose technologies have been raised by the chlor-alkali electrolysis industry, and may offer more massive quantity compared with other types of membranes for PEFCs, gave the greatest contribution to the development of PEFC systems. The long-term operation of over 4000 h at 120 °C under lower humidity conditions using a newly developed polymer composite membrane has expanded remarkably the possibility of polymer electrolyte and PEFC systems. The composite technology contributed to the improvement of mechanical and chemical performance.

It goes without saying that the commercialization of PEFC systems requires more progress in membrane performance and production technology. Various technologies in related fields and academic viewpoints and methods are expected to support and accelerate its attainment.

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