Chapter 32

Composite perfluorinate membranes

M. Nakao and M. Yoshitake

Asahi Glass Co. Ltd., Yokohama, Japan

1 INTRODUCTION

Reinforcement of perfluoro-sulfonic acid membranes has become more important in view of commercialization of the fuel cell and it has been accomplished on a commercial scale. Perfluoro-sulfonic acid membranes have a tendency to swell when they are soaked in water at high temperature and they consequently decrease in mechanical strength. The lowering in mechanical strength is detrimental for the use of thinner membranes. On the other hand, thinner membranes have many advantages such as low internal cell resistance or easy water management.[1–3]

In the early 1980s reinforcement technologies for perfluorinated membranes were developed aiming at commercialization of chlor-alkali electrolysis, in which the robust membrane was first required to have sufficient mechanical strength to ensure durability for long term operation. In the early stage of the development, PTFE woven fabrics and PTFE micro-fibrils were proposed for reinforcement technology.[4–7] Finally PTFE woven fabrics have been recognized as a standard reinforcement method because of their good mechanical strength and chemical stability.[8] The typical membrane for chlor-alkali electrolysis is a bilayer membrane and its major portion is a perfluoro-sufonic polymer layer. PTFE fabrics are embedded in the perfluoro-sulfonic layer. A cross-section of the membrane is shown in Figure 1. The total thickness of the membrane is approximately 200–300 μm.

On the contrary, in proton exchange membrane fuel cell (PEMFC) applications, the size of the membrane is small and the larger mechanical strength is not necessarily required. A 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 the proper electrode layers that afford good diffusivity of hydrogen, oxygen and water vapor. Therefore, in PEMFC a specified reinforcement technology is required to prepare a thin and flat membrane that provides the appropriate mechanical strength, good chemical stability, higher proton conductivity and water permeability. Table 1 shows a comparison of the available reinforcement technologies for PEMFC. PTFE is selected as a reinforcing material for its excellent chemical stability and good mechanical strength.

A composite comprised of 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®.[9–11] Gore-select® is characterized by its small thickness (20–40 μm) and excellent mechanical and electrochemical properties and has been widely used for PEMFC systems. Gore-select® shows relatively high specific resistance compared with nonreinforced membranes, however, the membrane resistance is sufficiently low because of its smaller thickness.

A PTFE-yarn embedded type, which originated from chlor-alkali electrolysis, gives good mechanical strength. The characteristics of this membrane have been studied.[12, 13] Many attempts have been made to make a

Handbook of Fuel Cells – Fundamentals, Technology and Applications, Edited by Wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm. Volume 3: *Fuel Cell Technology and Applications*. ISBN: 0-471-49926-9.

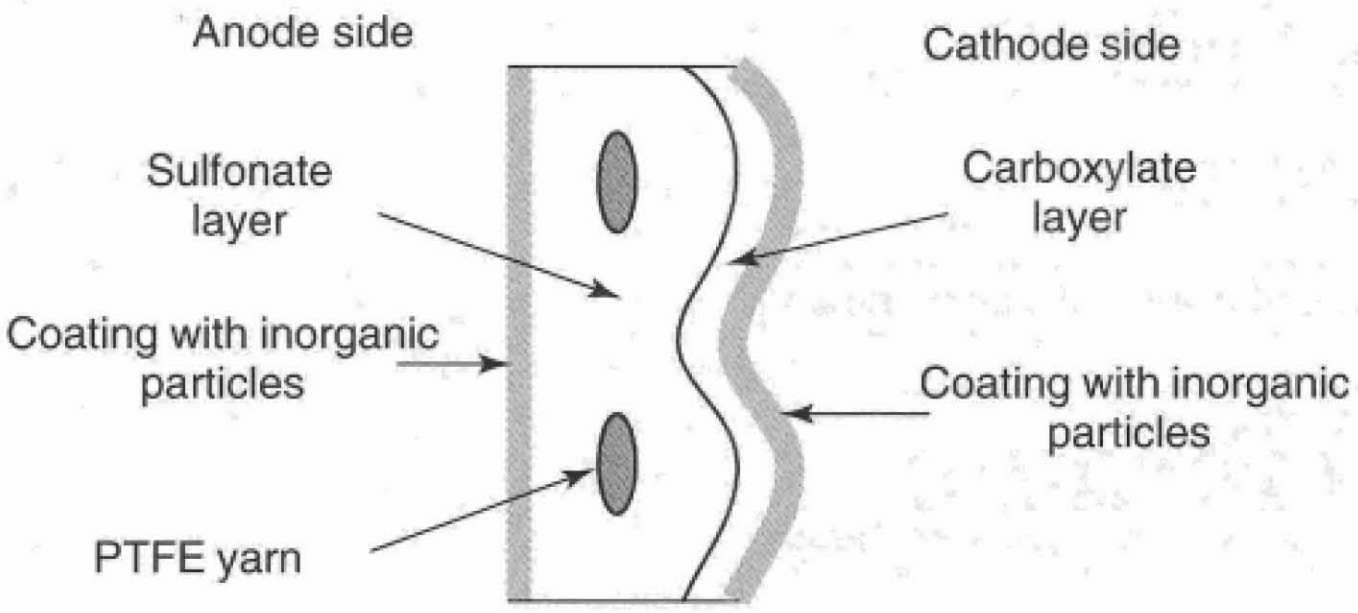

Figure 1. Schematic figure of the membrane for chlor-alkali electrolysis.

thinner cloth-reinforced membrane, however, membranes less than 80 μm have not been reported.[13] A thinner membrane with PTFE yarn reinforcement will be realized only when a special thin PTFE yarn is commercially available.

A PTFE-fibril type has been recently developed by Asahi Glass Co., Ltd.[14–16] A small amount of PTFE fibrils dispersed in a perfluoro-sulfonic polymer give the membrane both good mechanical strength and flatness suitable for PEMFC application. Continuous film formation has been achieved with a newly developed process.[17]

2 PTFE POROUS SHEET REINFORCEMENT

2.1 Introduction

A reinforced membrane composed of a PTFE porous sheet and a perfluorinated ionomer is a new product, specially designed to fulfill the requirements of PEMFC operation. The major difficulty in fabricating the above composite membrane is to impregnate a perfluorinated ionomer uniformly into porous hydrophobic PTFE without forming cavities. Several methods have been proposed to make the composite membranes, and one example was described in US patent 4,469,744 in which vacuum impregnation is applied using a porous PTFE sheet of 127 μm.[18] The W.L. Gore group has accomplished this technology on a commercial scale by using its proprietary PTFE porous sheet, Gore-tex® with a thickness less than 25 μm, and named it Gore-select®. It has a variety of thicknesses from 20 to 40 μm and is now widely adopted for PEMFC systems. Gore-select® is also used as a substrate for Primea® which is a registered name of Gore's proprietary membrane electrode assembly (MEA). Although some performance data of Primea® has been provided by the Gore group, the details of the membrane characteristics have not been disclosed in the form of technical papers. Therefore, in this section the relevant data were collected from the patents or the other available published materials.

2.2 Preparation

According to US patent 5,547,551 Gore-select® is prepared by the scheme illustrated in Figure 2.[10] A perfluorinated ionomer solution with a specified surfactant is impregnated from both sides of a thin PTFE porous sheet (Gore-Tex®) having a thickness less than 25 μm followed by repetition of the drying and rinsing processes three times. Judging from the patent description it is speculated that a thicker membrane larger than 30 μm may have a multilayer structure because the patent claims the use of a thin porous sheet less than 25 μm for the perfect impregnation of the ionomer into a PTFE porous sheet.

2.3 Properties

Properties of Gore-select® are summarized in Table 2 and compared with those of Nafion® 117. These data give only the relative values and are not the standardized ones. Judging from the porosity of the Gore-tex®, it

Table 1. Comparison of reinforcement technologies.

Type of reinforcement	Mechanical strength	Thin thickness <50 μm	Smooth surface	Content of reinforcing material
PTFE porous sheet	High	Possible	Easily available	20~30 wt%
PTFE-yarn embedded	Very high	Difficult	Available	10 wt%
PTFE-fibril dispersed	High	Possible	Easily available	2~5 wt%

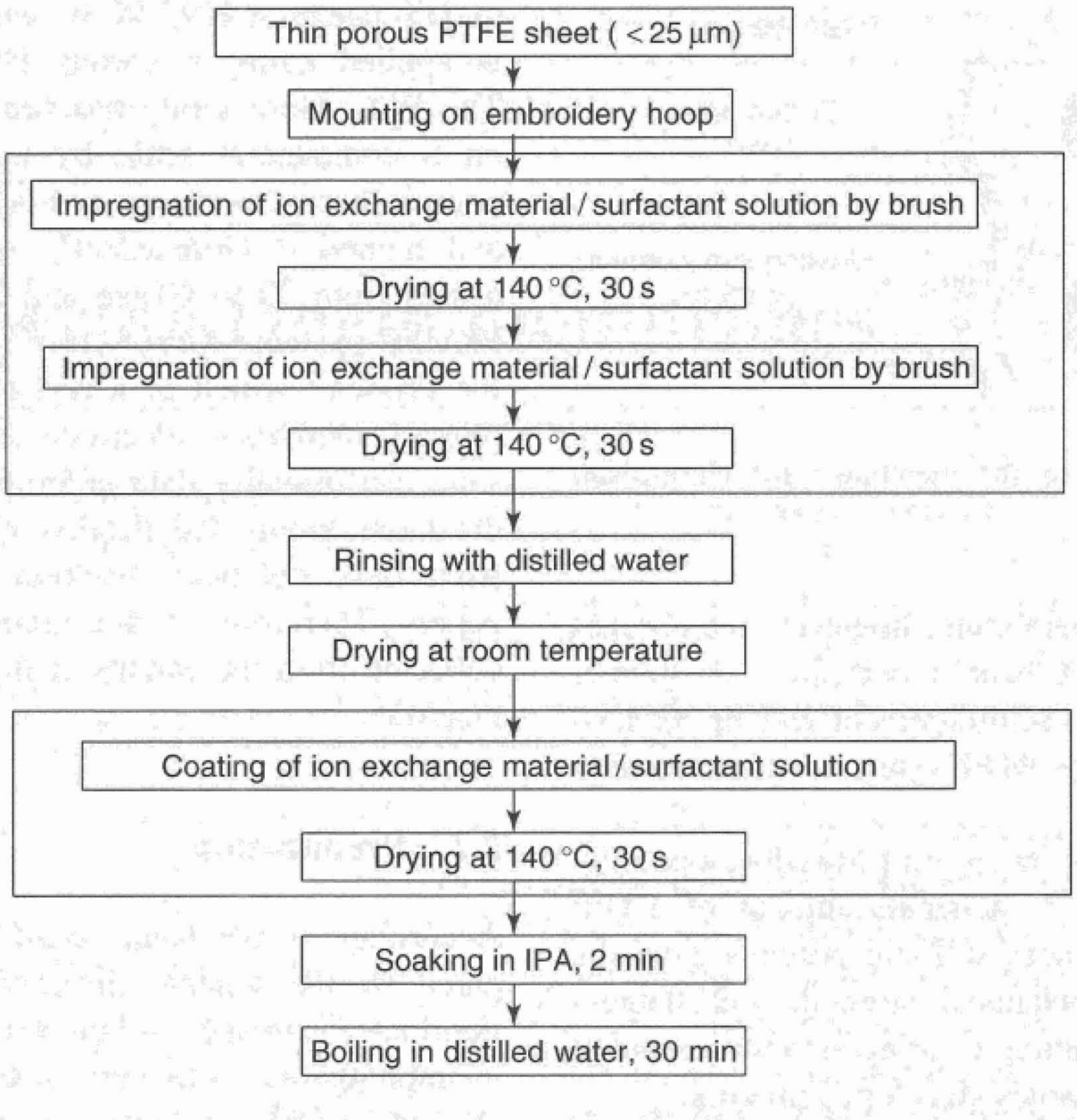

Figure 2. Fabrication scheme of Gore-select® described in the patent.

Table 2. Characteristics of Gore-select®.[9, 10, 19]

	Gore-select®	Nafion® 117 Ref.
Thickness (μm)	20	200
Equivalent weights (EW)	1100	1100
Water uptake (%)	32	34, 32
Ionic resistivity ($\Omega\,cm^2$)[a]	22.7	7
Tensile strength (kPa)[b]		
Machine direction (MD)	32 448	15 914
Transverse direction (TD)	17 727	10 839
Water vapor transmission rates ($g\,m^{-2}$) in 24 h	25 040	23 608
Shrinkage at dehydration[c]		
MD (%)	2.90	10.55
TD (%)	2.95	11.80

[a] Membranes were boiled in deionized water prior to use, and measured using a standard 'Kelvin' four-point probe in which the membranes were immersed in 1 M H_2SO_4 at 25 °C.

[b] The membrane samples were oven dried, then fully hydrated by boiling in deionized water, and measured using an Instron Model 1122 instrument.

[c] Membrane samples were first fully hydrated by boiling in deionized water, and a predetermined force was applied to the samples. The changes in sample dimensions during drying were detected by a quartz probe using Thermomechanical Analyzer 2940.

contains a certain amount of PTFE (probably 20–30 wt%), and this causes a slight decrease in the specific conductivity. However, Gore-select® shows excellent proton conductivity because of its small thickness (20–40 μm) as shown in Table 2. In this table, Gore-select® also shows higher tensile strength and smaller dimensional change in comparison with Nafion® 117. The dimensional change of Gore-select® was studied by Mitsubishi Electric in the mixed solvent system of iso-propyl alcohol (IPA) and water, and better dimensional stability

Table 3. Physical properties of current and new Gore-select®.

	Current Gore-select®		New Gore-select®	
	MD	TD	MD	TD
Thickness (μm)	30	30	30	30
Yield elongation (%)	82	132	10	90
Yield strength ($\mathrm{kg\,mm^{-2}}$)	3.6	3.5	4.9	4.1
Coefficient of elasticity ($\mathrm{kg\,mm^{-2}}$)	39.4	37.5	106.7	47.2

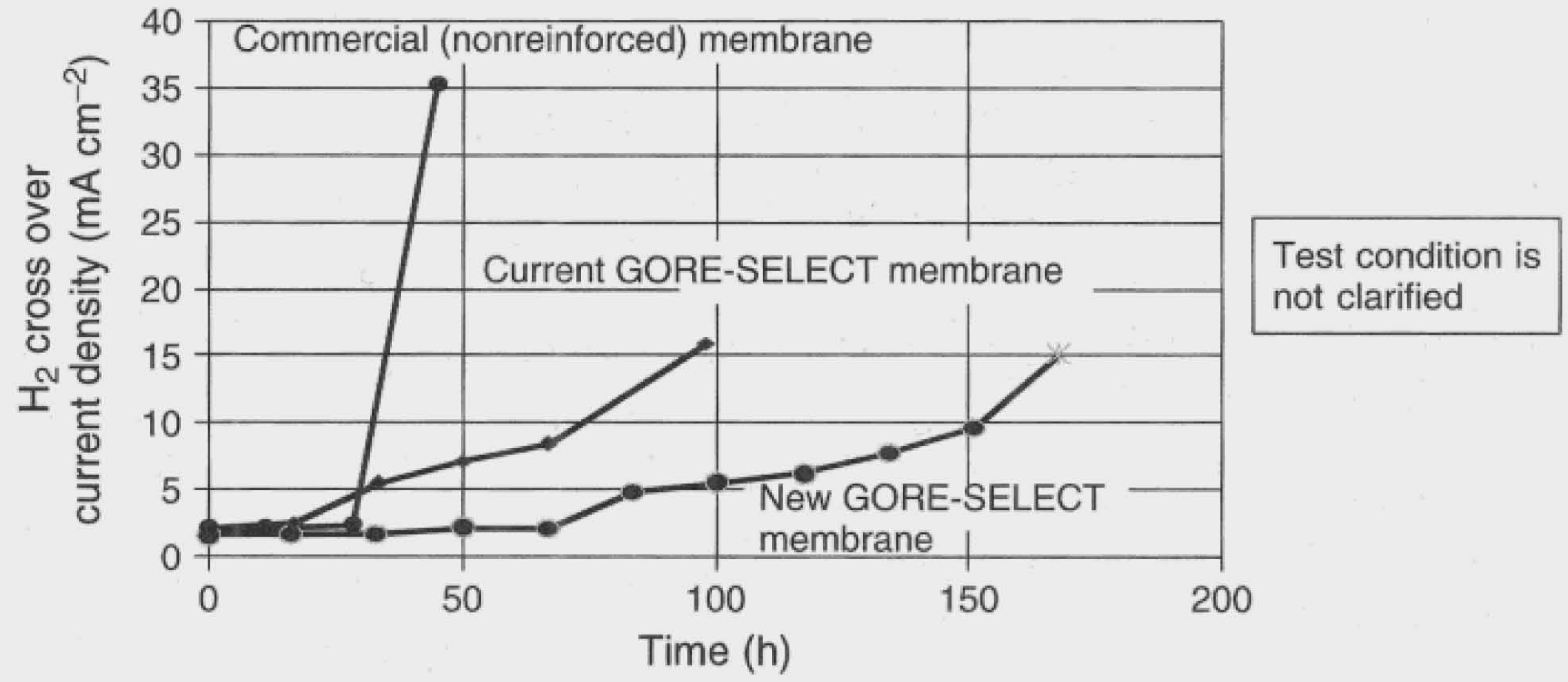

Figure 3. Durability of new Gore-select® at accelerated life test.

was obtained in comparison with typical nonreinforced membranes.[20]

Recently, W.L. Gore has been developing new membranes that are specially designed to prolong the life of Primea®, Gore's MEA. Physical properties of the new membrane are described in Table 3 and the results of the accelerated test are shown in Figure 3.[21] In the accelerated test hydrogen cross leak through the membrane was measured as an indication of membrane deterioration. The new membrane shows great improvement in durability when compared with current membranes.

3 PTFE FIBRIL REINFORCEMENT

3.1 Introduction

The concept of PTFE fibril reinforcement was originally developed for chlor-alkali electrolysis by Asahi Glass, and this idea has been refined for use in PEMFC applications. In PEMFC applications, the preparation process of the MEA or the actual use in fuel cell operation requires a certain degree of mechanical properties such as tear strength, creepage, and dimensional stability. The new reinforcement technology was developed for this specific purpose. The key concept is to disperse a small amount of PTFE fibers in the polymer matrix consisting of a perfluoro-sulfonic resin with higher ion exchange capacity (EW : 909). In addition, an innovative process has been introduced to make a thin film by adopting a new stretching method in which the thicker base film is enlarged evenly into a thin film less than 50 μm.

3.2 Structure

Figure 4(a) shows the schematic illustration of the fibril reinforced membranes. Two to five percent of PTFE microfibers weight is dispersed in the perfluoro-sufonic resin. Figure 4(b) shows a scanning electron microscope (SEM) image of the cross-section of the membrane that was torn up. This photo indicates that PTFE fibrils are stretched to over 50 μm and the stretched fibrils restrain swelling or shrinkage of the polymer and stabilize the dimension.

As one of the mechanical properties of this composite material, tensile strength of the composite is expressed by the following equation using parameters of length, radii of fibers and adhesivity between the fiber and the matrix polymer:[22]

$$T_{\mathrm{c}} = K V_{\mathrm{f}} T_{\mathrm{f}} \frac{1 - l_{\mathrm{c}}}{2l} + (1 - V_{\mathrm{f}}) T_{\mathrm{m}}$$

where K is the orientation of fiber, V_{f} is the volume fraction of filler, T_{f} is the tensile strength of filler, $l_{\mathrm{c}} =$

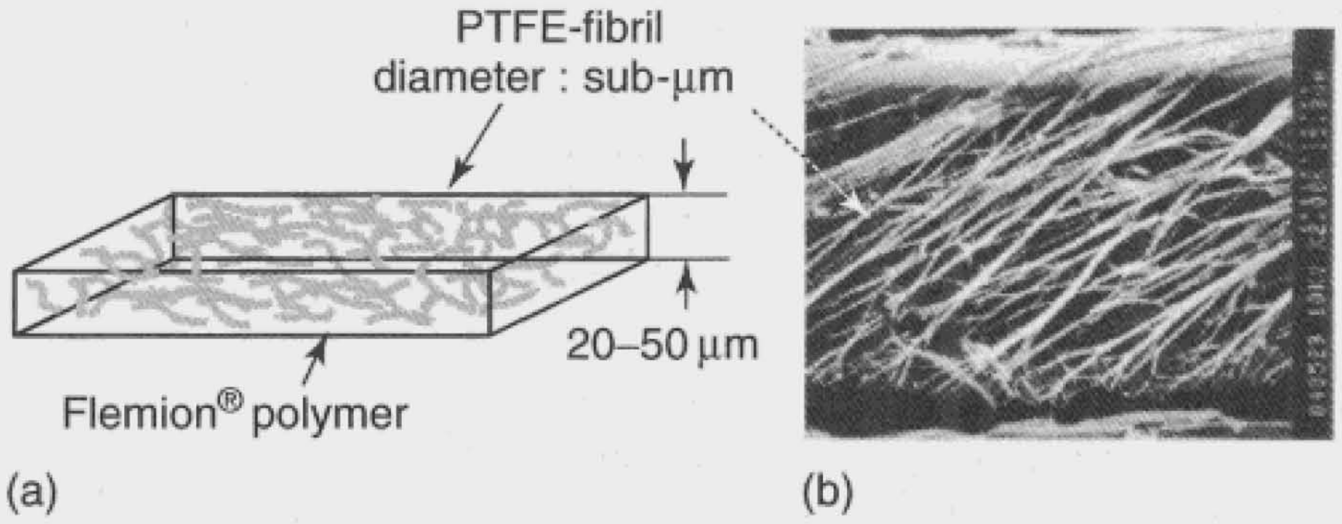

Figure 4. Schematic figure of fibril-reinforced membrane and its cross-sectional image after tearing.

$dT_f/(2\tau)$, d is the radii of filler, τ is the shear strength at the interface of the matrix and the filler, l is the length of the filler and T_m is the tensile strength of the matrix.

Although PTFE itself is not always the best filler material from the point of elasticity and shear strength at the interface of the matrix and the filler, it is however, PTFE is the best material from the point of view of chemical stability. Various mechanical properties are controlled by optimizing the fibril content, length and radii of PTFE-fibrils or other parameters.

3.3 Preparation

The key to preparing a thin and flat membrane with fibril reinforcement is the uniform dispersion of the fibrils in the matrix and the flatness of the membrane which assures good coating of the electrode layers. In the extrusion process of a film, the filler usually disturbs the flow pattern of the melted polymer and it makes it difficult to extrude a thin film. The conventional extruding process has not materialized a thickness less than 150 μm. Recently Asahi Glass has proposed a new process and the method of preparation is described in the European patent EP1,139,472.[16] As shown in Figure 5, precursor polymer and PTFE powder are kneaded and pelletized followed by extrusion to make a thicker base film. The base film is sandwiched with supporting films and stretched together with supporting films to form a thin cationic film followed by alkali and acid treatment.

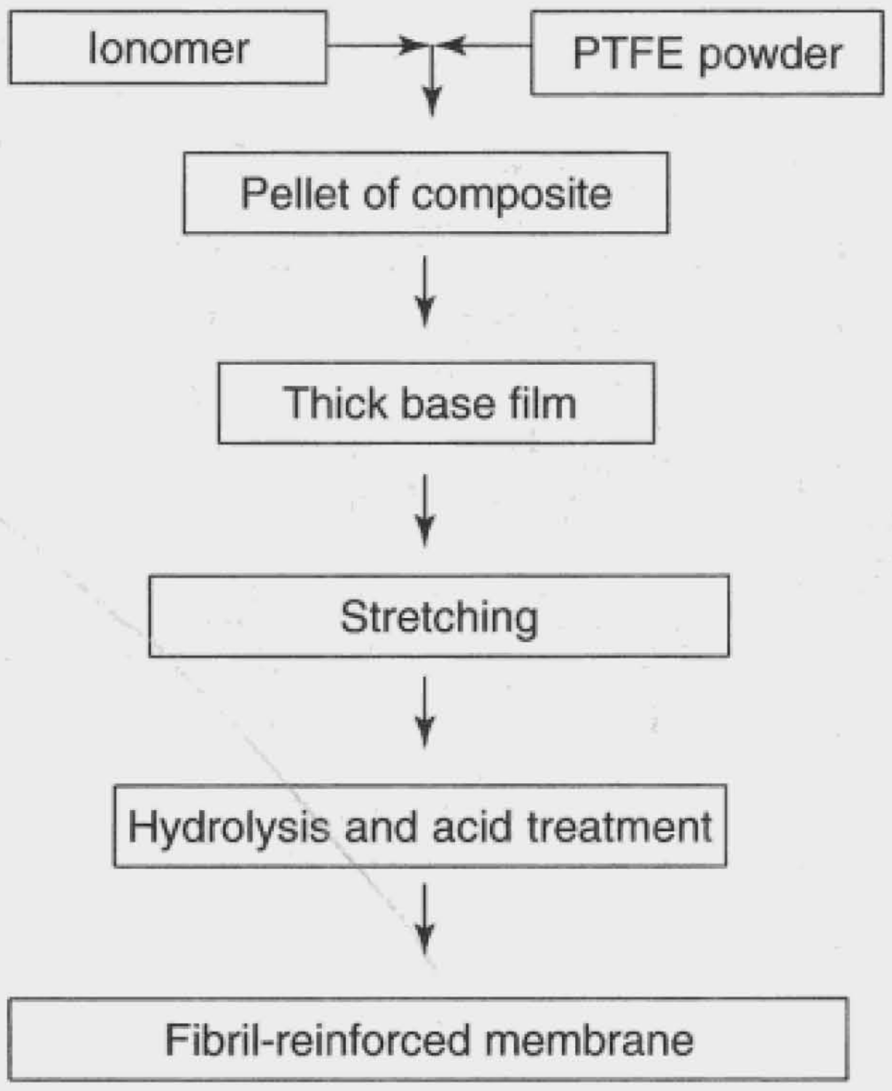

Figure 5. Flow chart of fabrication of PTFE fibril-reinforced Flemion®.

3.4 Properties

The characteristics of the fibril-reinforced membranes are summarized in Table 4. As for alternating current (a.c.) resistance, water uptake and hydrogen permeability, the fibril reinforced Flemion® membrane has values almost equivalent to those of nonreinforced membranes because the addition of PTFE is small. On the other hand, as shown in Table 4 improvement in mechanical properties such as elastic modulus, tear strength and creepage is observed compared with nonreinforced membranes. The fibril-reinforced membrane shows the same cell performance as the nonreinforced membrane with the same thickness as shown in Figure 6. Durability of the fibril-reinforced membrane was evaluated under relatively higher current density using pure hydrogen gas with a laboratory cell

Table 4. Characteristics of the fibril-reinforced Flemion® membrane.

Membrane type	Reinforced 2–3 wt% PTFE fibril	Non-reinforced
AC resistivity (Ω cm)[a]	7–8	6–7
H_2 permeability ($cm^2\ s^{-1}\ cm^{-1}$ Hg)[b]	10×10^{-9}	8×10^{-9}
Elastic modulus ($kg\ mm^{-2}$)[c]	9.3	2.8
Tear strength ($N\ mm^{-1}$)[d]	2.7	0.5
Visco-elasticity ($dyn\ cm^{-2}$)[e]	$5–6 \times 10^8$	$1–2 \times 10^9$
Single cell performance	Excellent	Excellent
Environmental cyclic test	Excellent	Excellent

[a] 80 °C, 95% relative humidity.[16]
[b] 80 °C, humidified at 80 °C.
[c] 85 °C, 95% relative humidity.
[d] 25 °C, 50% relative humidity.
[e] 25 °C, 85% relative humidity.

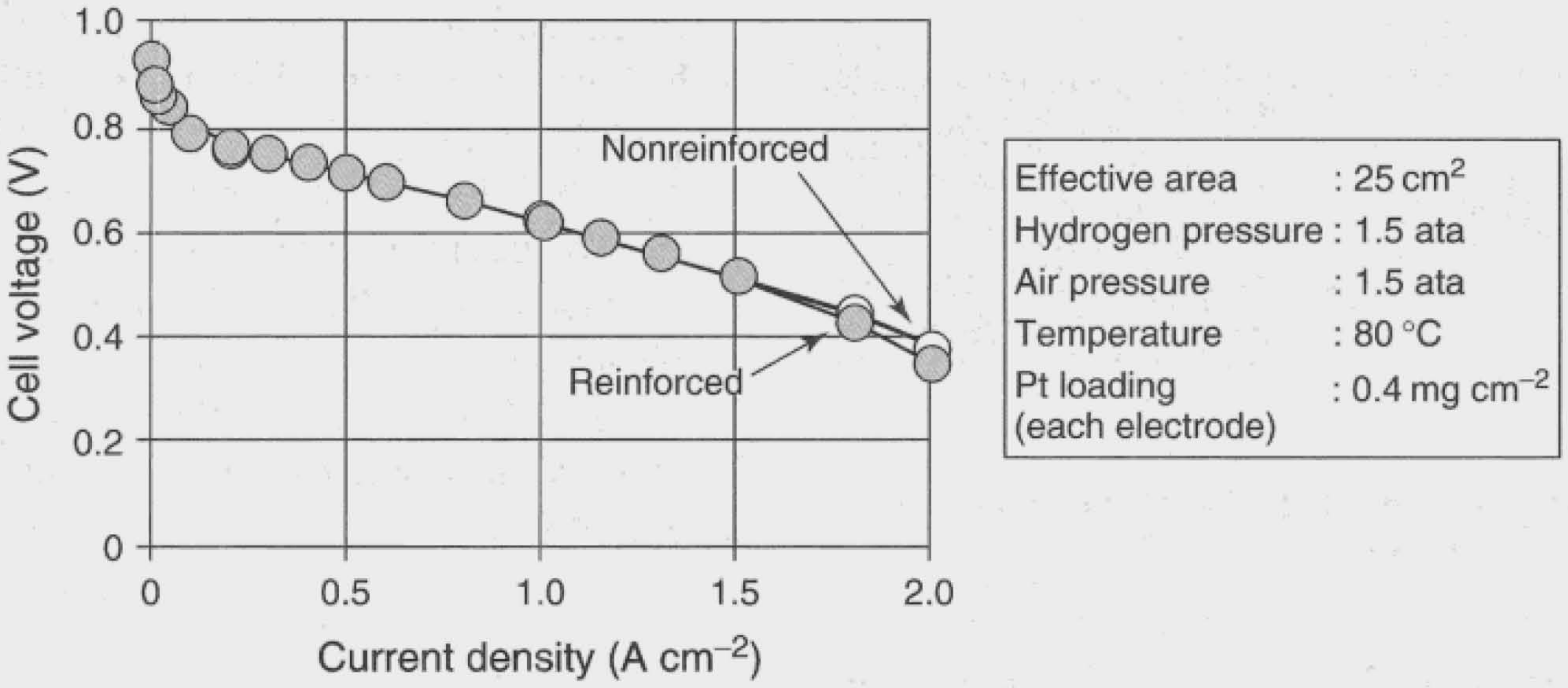

Figure 6. Typical cell performance of fibril-reinforced Flemion®.

having an active area of 25 cm^2. As shown in Figure 7 the cell voltage was stable at 0.6 V for 4 months.

In consideration of the actual operation, the environmental cycle tests were done by changing the operating conditions repeatedly. The details of the test procedure are illustrated in Figure 8.[23–25] This test reveals that the reinforced membrane has good stability both in cell performance and gas permeability (Figures 9 and 10).

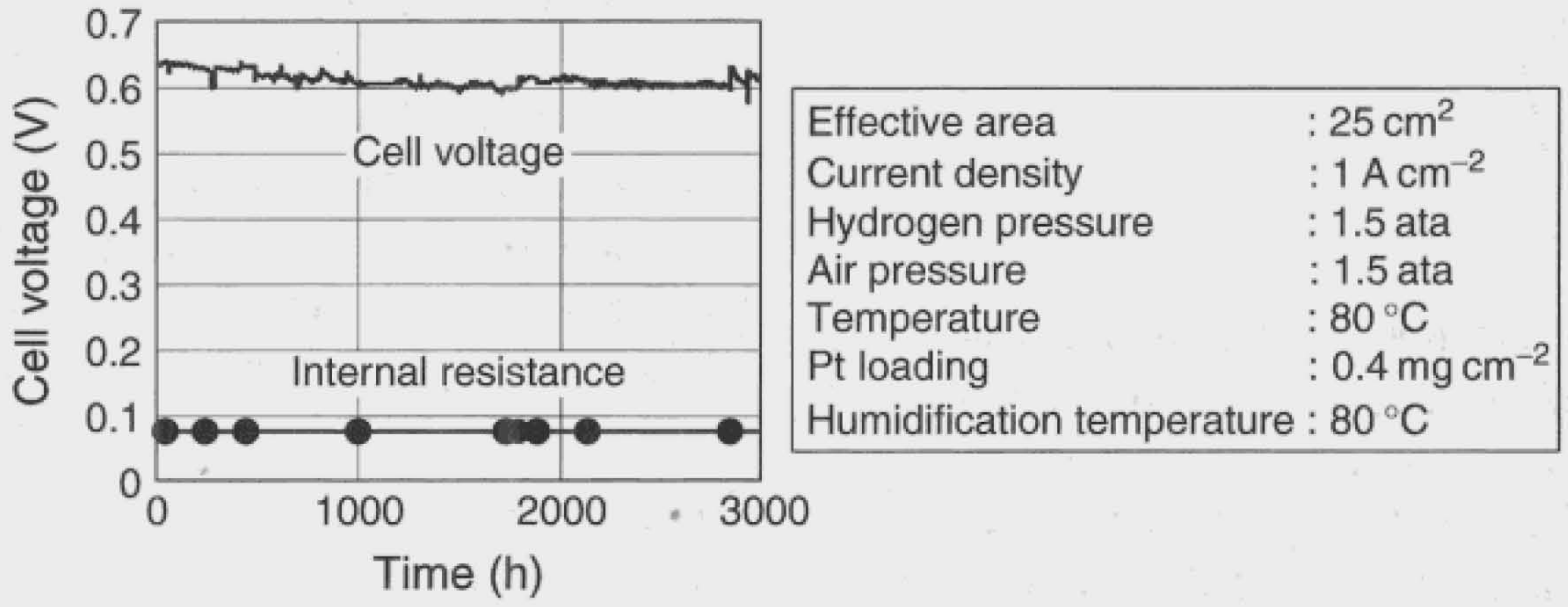

Figure 7. Durability test of fibril-reinforced Flemion®.

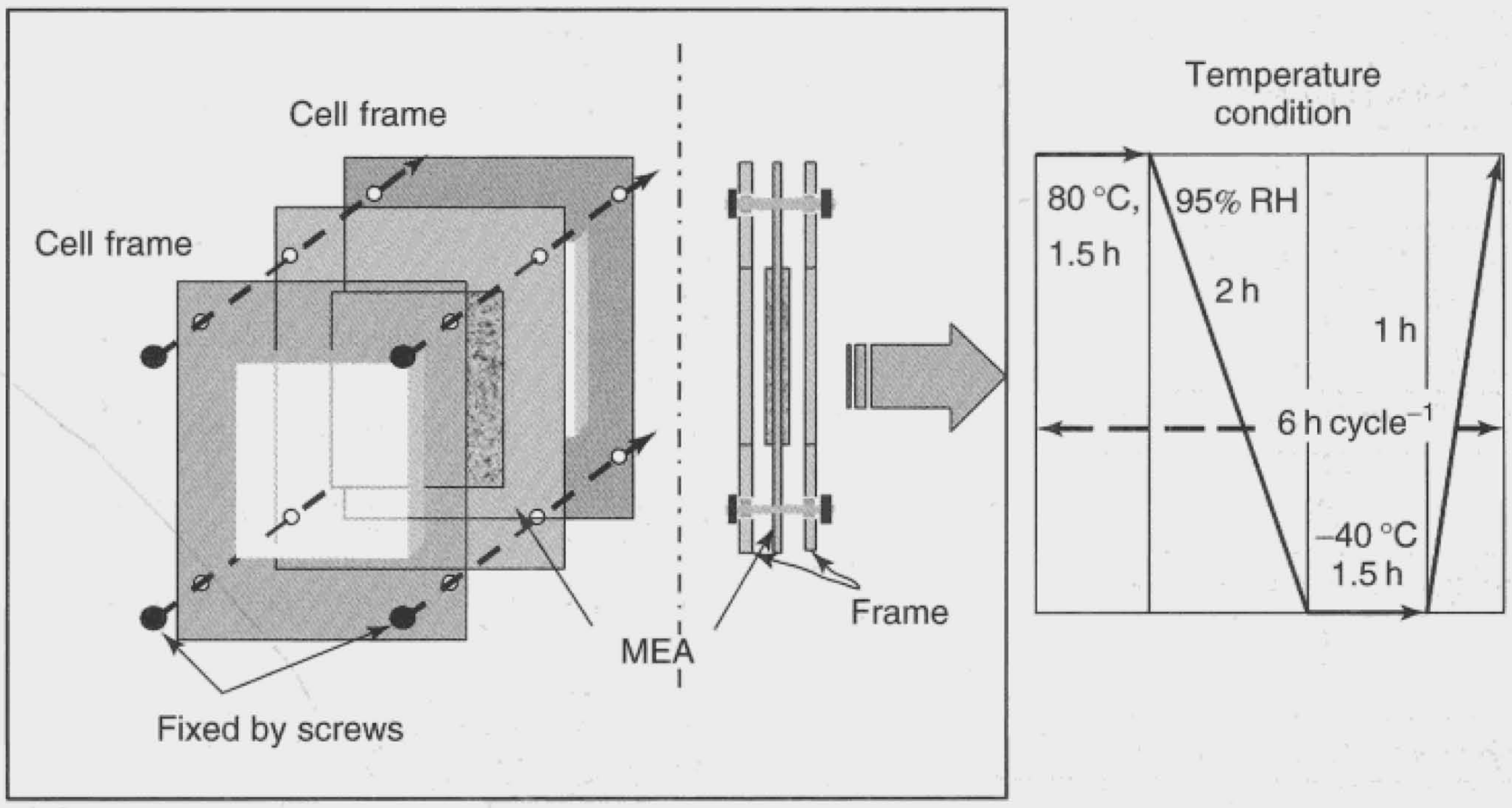

Figure 8. Setup and condition for the cyclic environmental test of the MEA.

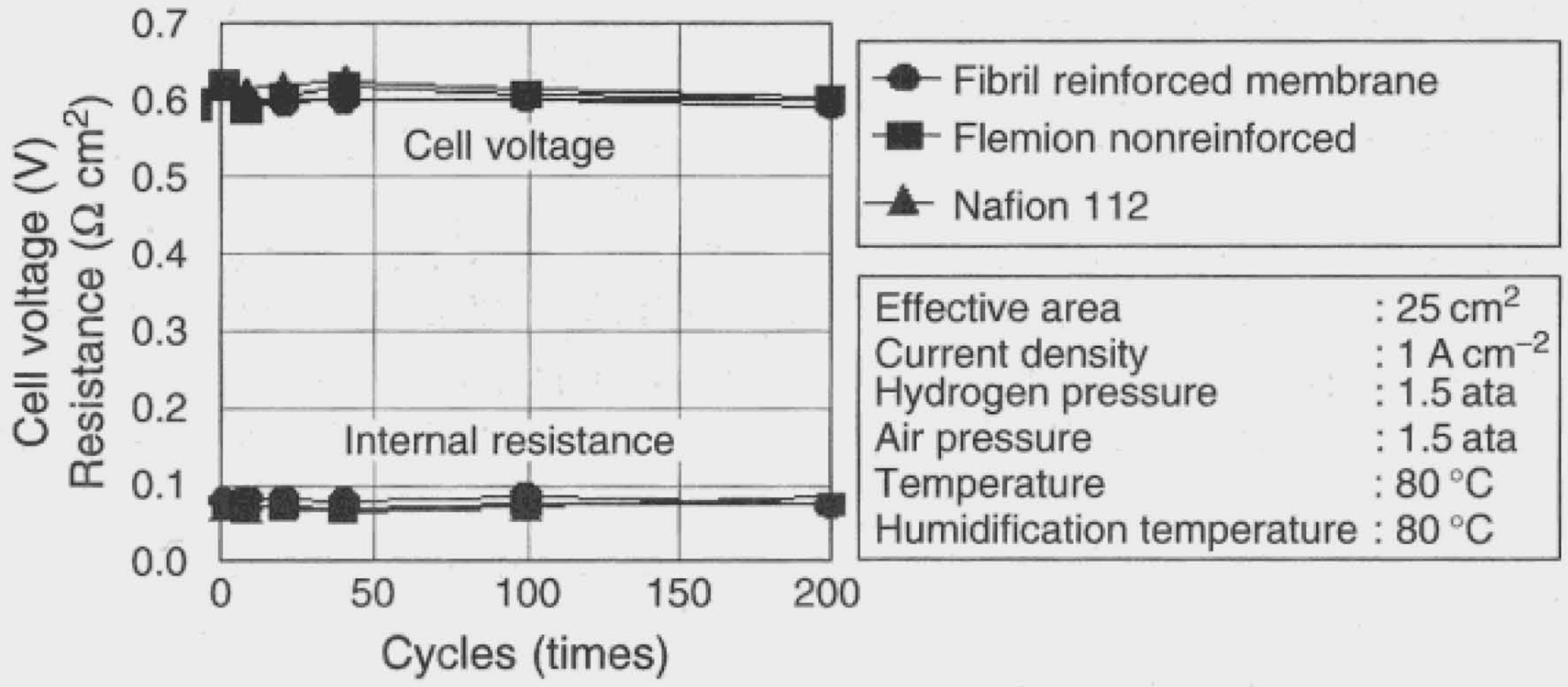

Figure 9. Influence of cyclic change of the environment on cell performance.

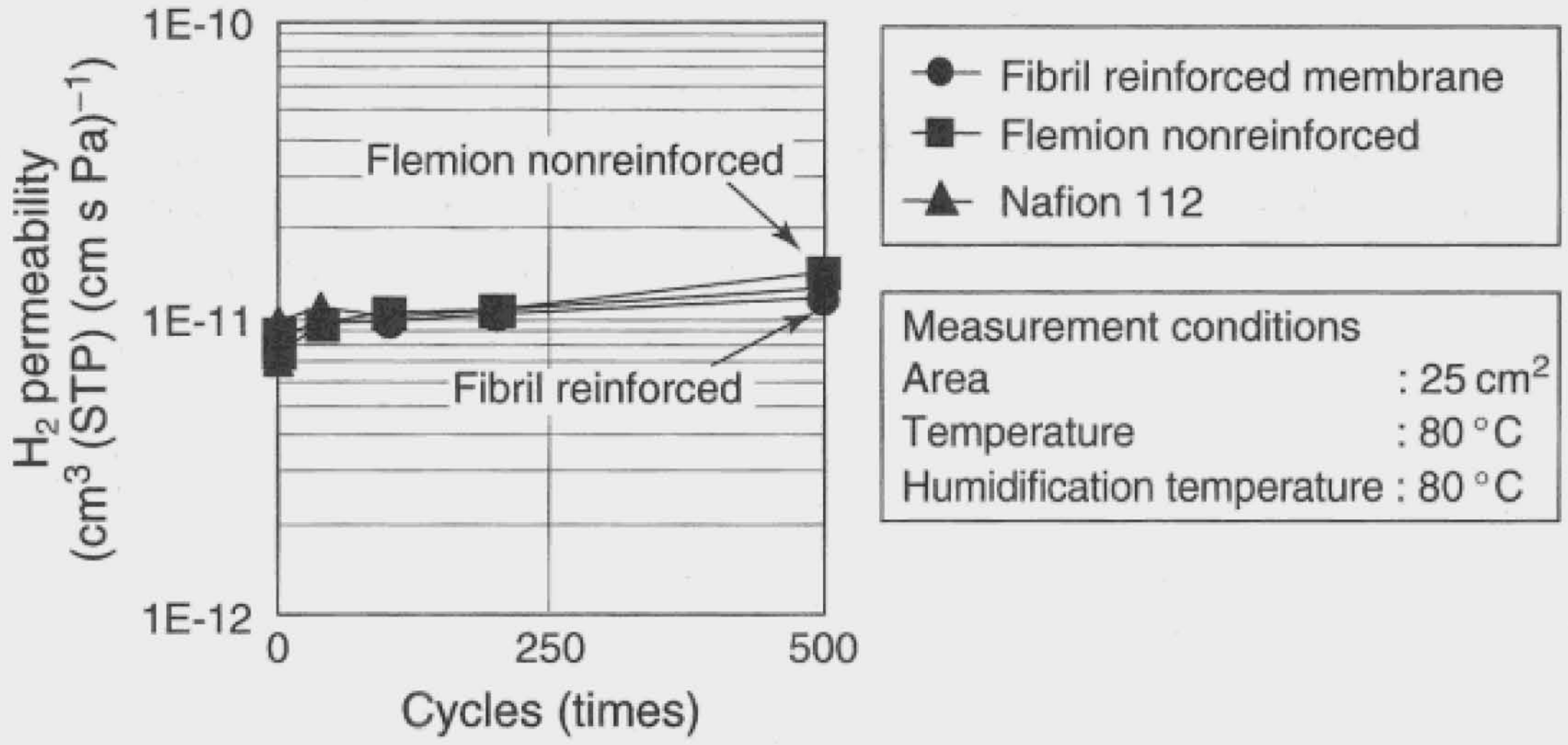

Figure 10. Influence of cyclic change of the environment on H_2 permeability.

4 SUMMARY/OUTLOOK

As typical composite perfluorinated membranes applied to PEMFC, two types of membranes with different reinforcements were reviewed. Gore-select®, reinforced with a porous PTFE sheet, and fibril-dispersed membrane, reinforced with micro-PTFE fibrils, are characterized by their unique preparation methods to make thin membranes. Both membranes provide not only good mechanical properties such as tear strength and dimensional stability but also good electrochemical performance such as low membrane resistance and durability under practical operating conditions.

In the future, PEMFC will be widely used for stationary and automobile applications. Drastic cost reduction and maturity of the technology to enhance its performance and reliability are the essential prerequisites for the widespread use of PEMFCs. The future membrane needs to fulfill various requirements such as good performance, robustness, attractive cost, and ease of handling that is essential for mass production. Furthermore, some other breakthroughs, which will enable the operation of PEMFCs at high temperatures or under extremely dry conditions, are necessary. These thin composite membranes will play more important roles in future fuel cell technology.

REFERENCES

1. H. Dhar, US Patent 5,242,764 (1993).
2. H. Dhar, Programs and Abstracts of Fuel Cell Seminar, San Diego, CA, p. 85 (1994).
3. M. Yoshitake, E. Yanagisawa, T. Naganuma and Y. Kunisa, *Mater. Res. Soc. Symp. Proc.*, **575**, 213 (2000).
4. A. Eisenberg and H. L. Yeager (Eds), in 'Perfluorinated Ionomer Membranes', ACS Symposium Series, No. 180, ACS (1982).
5. W. G. Grot, US Patent 3,770,567 (1973).
6. I. Watanabe, Y. Yamakoshi, H. Miyauchi, S. Tsushima and M. Fukumoto, US Patent 4,072,793 (1978).
7. H. Ukihashi, T. Asawa and T. Gunjima, US Patent 4,218,542 (1980).
8. T. Asawa, *J. Appl. Electrochem.*, **19**, 566 (1989).
9. J. A. Kolde, B. Bahar, M. S. Wilson, T. A. Zawodzinski and S. Gottesfeld, 'Proceedings of the First International Symposium on Proton Conducting Membrane Fuel Cells', The Electrochemical Society Proceedings, PV95-23, p. 193 (1995).

10. B. Bahar, A. R. Hobson, J. A. Kolde and D. Zuckerbrod, US Patent 5,547,551 (1996).
11. B. A. Bahar, R. S. Mallouk, A. R. Hobson and J. A. Kolde, US Patent RE37,307.
12. M. Wakizoe, H. Murata and H. Takei, 'Proceedings of the 3rd International Fuel Cell Conference', Nagoya, p. 121 (1999).
13. M. Yoshitake, E. Yanagisawa, K. Umemura and Y. Kunisa, 'Proceedings of the 3rd International Fuel Cell Conference', Nagoya, p. 125 (1999).
14. M. Tamura, K. Sanekata and Y. Higuchi, Laid Open Japanese Patent Application 6-231779 (1994).
15. Asahi Glass Co., Ltd., 'NEDO PEFC R&D Contractor's Annual Progress Report FY 1999', p. 112 (2000).
16. M. Yoshitake, E. Yanagisawa, N. Yoshida, I. Terada, T. Naganuma, T. Ishisaki and Y. Kunisa, Reports of the Research Laboratory, Asahi Glass Co. Ltd., Vol. 50, p. 67 (2000).
17. Y. Higuchi, I. Terada, H. Shimoda and S. Hommura, US20010026883A1, EP1139472 (2201).
18. W. G. Grot, J. T. Rivers and R. H. Silva, US Patent 4469744 (1984).
19. O. Savadogo, *J. New Mater. Electrochem. Systems*, **1**, 47 (1998).
20. Mitsubishi Electric Co. Ltd., 'NEDO PEFC R&D Annual Report FY 1996' (in Japanese).
21. H. Fujimoto, M. Aimu and K. Tabata, 'Proceedings of the 8th FCDIC Fuel Cell Symposium', Tokyo, (in Japanese), p. 36 (2001).
22. L. E. Nielsen, 'Mechanical Properties of Polymers and Composites', Marcel Dekker, New York (1975).
23. E. Yanagisawa, Y. Kunisa, T. Ishisaki, I. Terada and M. Yoshitake, Proceedings Volume of International Symposium on Fuel Cells for Vehicles, Nagoya, p. 172 (2000).
24. Asahi Glass Co., Ltd., Report of the NEDO's PEFC R&D Program, p. 130 (2000).
25. M. Yoshitake, E. Yanagisawa, I. Terada, H. Shimoda, S. Hommura, T. Ishisaki and Y. Kunisa, 'Proceedings of the 1st European PEFC Forum', Lucerne, p. 109 (2001).