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Characterization of fibril reinforced membranes for fuel cells

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Abstract

Characteristics of fibril reinforced membranes developed by Asahi Glass Company are reviewed. PTFE-fibrils <1 μm in diameter are dispersed in ion-exchange membranes uniformly. Mechanical properties, such as tensile strength, tear strength, creep property and compressive property were examined and compared with non-reinforced membranes. Fibril reinforced membranes, even by the addition of a small amount of PTFE-fibrils (2.7 wt.%), show excellent mechanical strength, especially in creep and tear strength. Cell performance is nearly equal to the one using a non-reinforced membrane and cell voltage stays about the same during the cell operation at 80 °C for 3000 h.

Keywords: Fibril reinforced membrane; Polymer electrolyte fuel cell; Mechanical strength; Durability

1. Introduction

Fuel cells are one of the most prospective candidate sources of power for clean electricity generators. Polymer electrolyte fuel cells (PEFCs) are especially expected to be applied to automotive and stationary uses because PEFCs are compact and simple systems. Recently, the pace of development has accelerated year by year.

New energy and industrial technology development organization (NEDO), administered by the Ministry of International Trade and Industry, started the research and development of PEFC as a part of New Sunshine Program in fiscal year 1992. Since then, Asahi Glass Co. Ltd. (AGC) has been in the NEDO's program to develop the membrane technology and investigate the characteristics of membranes [1–5].

A unit of PEFC is made up of a membrane and catalytic electrodes which are attached to both sides of the membrane (Fig. 1). Hydrogen and oxygen are fed to the anode and the cathode, respectively. At the anode, the hydrogen dissociates into two protons with the release of two electrons per hydrogen molecule.

$$H_2 \rightarrow 2H^+ + 2e^- \quad \text{(anode)}$$

The proton passes through the membrane to the cathode. At the cathode, oxygen reacts with the proton, taking up electrons to form water.

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad \text{(cathode)}$$

Chemical energy can be converted to electric energy at high efficiency by PEFC. In this reaction, membranes play an important role.

Required characteristics for membranes are as follows.

- High chemical stability
- High proton conductivity (low resistance)
- Low gas permeability
- High mechanical strength
- Fast transportation of water

Various kinds of membranes have been developed, but perfluorinated membranes such as Nafion® (Du Pont), Aciplex® (Asahi Chemical Industry), Flemion® (AGC) have been mainly used for PEFC due to their high chemical stability. The chemical structure of perfluorinated membrane is as shown in Fig. 2.

Our previous work [5] revealed that the usage of thinner membranes realizes higher proton conductivity. However, non-reinforced thinner membrane does not have enough mechanical strength. We have studied reinforcement technologies using PTFE-fibrils. In this study, the applicability of PTFE-fibril reinforced membranes, 50 μm in thickness, is discussed.

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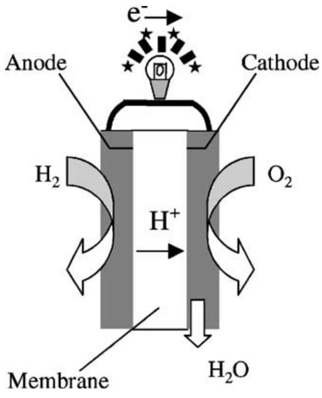
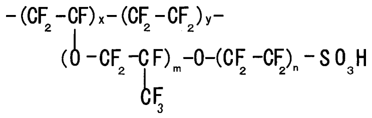


Fig. 1. Principle of PEFC.



$$-(CF_2-\underset{\displaystyle (O-CF_2-\underset{\displaystyle CF_3}{CF})_m-O-(CF_2-CF_2)_n-SO_3H}{CF})_x-(CF_2-CF_2)_y-$$

Fig. 2. Chemical structure of perfluorinated membrane.

2. Results and discussion

2.1. Mechanical properties, gas permeability and resistance

Mechanical properties, hydrogen permeability, ac specific resistance of PTFE-fibril reinforced membranes were examined. We also examined other kinds of non-reinforced perfluorinated membranes as listed in Table 1. Ion-exchange capacity and thickness of membrane are summarized in Table 1.

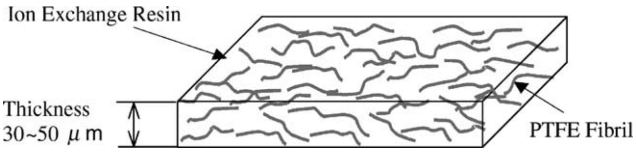


Fig. 3. Structure of the PTFE-fibril reinforced membrane.

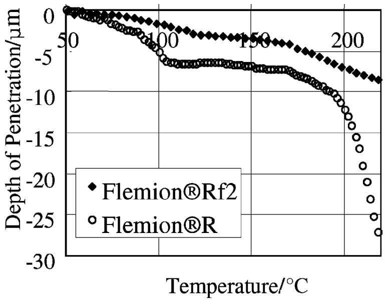


Fig. 4. Compressive behaviors of Flemion®Rf2 and Flemion®R.

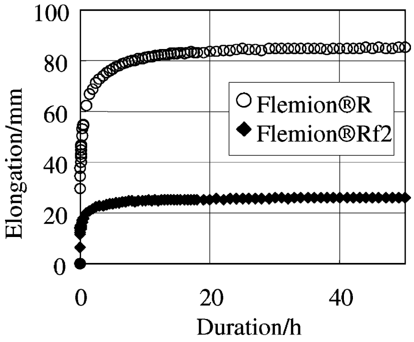


Fig. 5. Creep behaviors of Flemion®Rf2 and Flemion®R (90 °C-95%RH).

Table 1

Ion-exchange capacity and thickness of membranes in this study

Membrane	Ion-exchange capacity (meq g^{-1})	Thickness (μm)	PTFE-fibril content (%)	Remarks
Flemion®Rf2	1	50	2.7	PTFE-fibril reinforced
Flemion®R	1	50	–	AGC's standard membrane in the NEDO's PEFC program
Nafion®112	0.91	50	–	Membrane for comparison

Table 2

Tear strength, tensile strength, hydrogen permeability and resistance of various membranes

Membrane	Tear strength (N mm^{-1})		Tensile strength (MPa)		H_2 permeability coefficient (cm^3 (STP) cm^{-1} s^{-1} cm Hg^{-1})	ac specific resistance (Ω cm)
	MD	TD	MD	TD		
Flemion®Rf2	3.1	16.5	21	10	9×10^{-9}	7–8
Flemion®R	0.5	0.7	18	16	8×10^{-9}	6–7
Nafion®112	0.5	0.9	22	20	7×10^{-9}	6–7

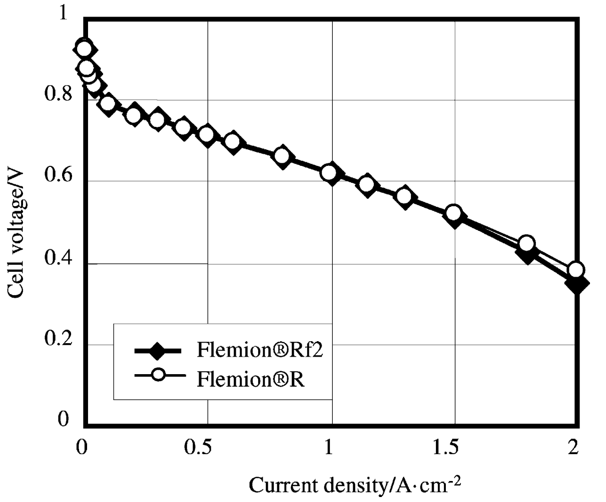


Fig. 6. Cell performance of MEA using Flemion®Rf2 and Flemion®R in a single cell (gas: H_2/air, pressure: 0.15/0.15 MPa, electrode area: 25 cm^2, cell temperature: 80 °C, Pt loading: 0.4/0.4 mg cm^{-2}).

Fig. 3 shows the structure of the PTFE-fibril reinforced membrane. The PTFE-fibrils, <1 μm in diameter, are dispersed in the ion-exchange resin uniformly.

Table 2 shows tear strength, tensile strength, hydrogen permeability, and ac specific resistance of non-reinforced and PTFE-fibril reinforced membranes.

The tear strength value of PTFE-fibril reinforced membrane, namely Flemion®Rf2, is 6–18 times larger than those of the other non-reinforced membranes. The PTFE-fibril can improve the tear strength effectively. The difference of the tear strength values of machine direction (MD) and transverse direction (TD) is due to the orientation of PTFE-fibrils. Hydrogen permeability coefficients and ac specific resistance of PTFE-fibril reinforced membrane are almost equivalent to those of the other membranes since the amount of PTFE-fibril is small.

The compressive behavior of Flemion®Rf2 and R were examined by thermomechanical analysis (TMA) (Fig. 4). The penetration of the needle into Flemion®R

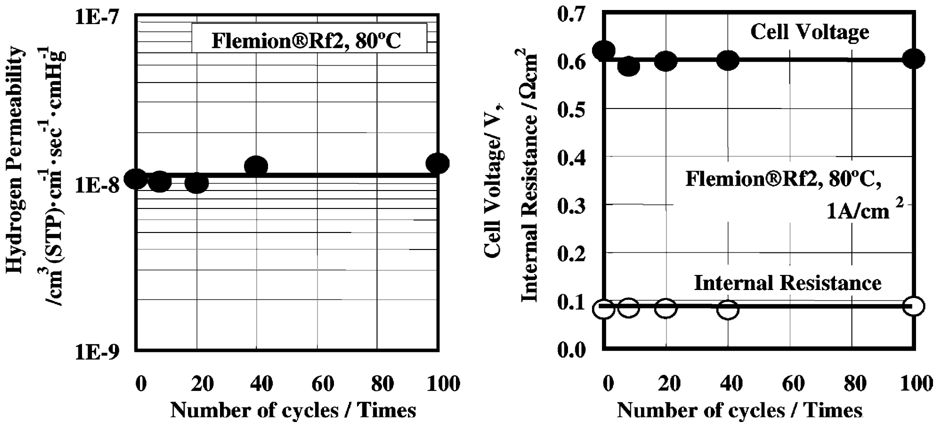


Fig. 7. Influence of environmental cyclic changes on cell voltage and hydrogen permeability of MEA using Flemion®Rf2.

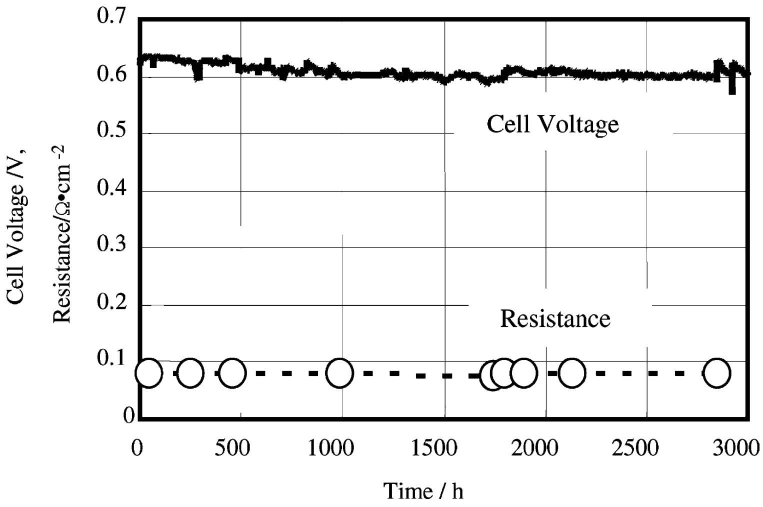


Fig. 8. Life test of MEA using Flemion®Rf2 (gas: H_2/air, pressure: 0.15/0.15 MPa, electrode area: 25 cm^2, cell temperature: 80 °C, Pt loading: 0.4/0.4 mg cm^{-2}, current density: 1 A cm^{-2}).

was observed at temperatures around 90 °C, since perfluorinated resin has the transition point at around this temperature. The PTFE-fibril reinforcement can suppress the penetration of the needle and improve the toughness of the membrane.

Fig. 5 shows the creep behavior of Flemion® membranes at 90 °C–95%RH. The elongation value of the PTFE-fibril reinforced membrane, Flemion®Rf2, after 40 h, is about one-third of that of the non-reinforced membrane, Flemion®R. It was confirmed that PTFE-fibril reinforcement is also effective for improvement in the creep properties, even by the addition of small amount of PTFE-fibril.

2.2. Cell voltage characteristic, environmental cyclic test and durability test

Fig. 6 shows the current–voltage curves of the membrane–electrode assemblies (MEAs) using Flemion®Rf2 and Flemion®R, both of which have the same membrane thickness. The cell performances are nearly equal to the one using a non-reinforced membrane.

Environmental cyclic test for MEAs was carried out using Flemion®Rf2. The changes in cell voltage and hydrogen permeability after the environmental cycle are as shown in Fig. 7. No significant changes were observed up to 100 cycles.

Fig. 8 shows the result of durability test of MEAs at 1 A/cm^2 using Flemion®Rf2. Although the cell voltage showed a gradual decrease for 3000 h of operation, the internal resistance did not change at all. It is concluded that the addition of PTFE-fibrils does not give undesirable effects on both cell voltage and durability.

3. Conclusions

1. PTFE-fibril reinforcement improved the mechanical strength, especially in creep and tear strength of the membrane.
2. Cell performance of MEA using Flemion®Rf2 is nearly equal to the one using a non-reinforced membrane.
3. Cell voltage of MEA using Flemion®Rf2 stays about the same during the cell operation at 80 °C for 3000 h.

4. Experimental

4.1. Tensile strength and tear strength

Tear strength and tensile strength were measured at 25 °C-50%RH in accordance with JIS K7128-1 and JIS K7127, respectively. The dimensions of a test piece for tensile strength measurement were 10 mm × 200 mm, and those for tear strength measurement were 50 mm × 150 mm with a slit of 75 mm in the middle.

4.2. Hydrogen permeability

Hydrogen permeation was evaluated at 80 °C-90%RH. The amount of hydrogen permeated through the membrane was measured using gas chromatography while hydrogen and nitrogen gases flowed on both sides of the membrane, respectively.

4.3. ac Specific resistance

Resistance of membranes was measured at 80 °C-95%RH by the four-probe method as shown in Fig. 9. ac Resistance at 10 kHz in horizontal direction was determined by LCR meter changing the distance between the terminals. After plotting the relationship of terminal distance and ac resistance, the slope of straight line was obtained. Specific resistance was given as the product of the slope multiplied by the cross-sectional area, which was calculated from membrane thickness.

4.4. Compressive properties

The compressive behaviors of the membranes were examined by thermomechanical analysis. While the membrane was heated from room temperature to higher temperatures at the heating rate of 5 °C min^{-1}, the needle of 1 mm diameter was pushed onto the membrane with 2 g load to measure the depth of penetration (Fig. 10).

4.5. Creep properties

Creep properties were measured at 90 °C-95%RH in accordance with JIS K7115. The dimensions of the test

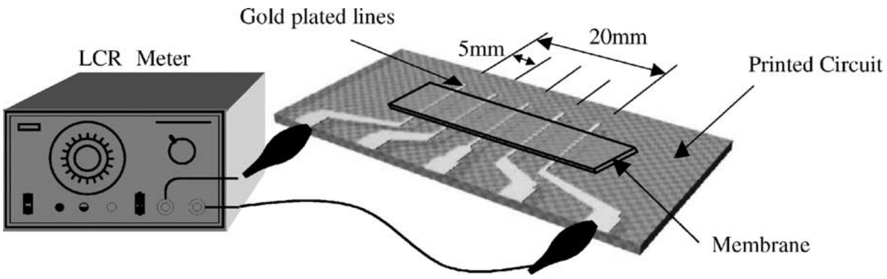


Fig. 9. Schematic illustration of ac specific resistance measurement.

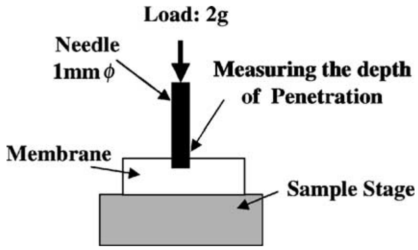


Fig. 10. Measurement of compressive behavior.

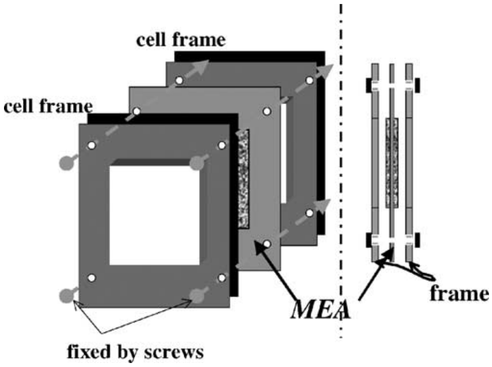


Fig. 11. MEA fixed by cell frames for environmental cyclic test.

piece was 10 mm × 50 mm and elongation was measured with a hanging at the lower part of the test piece.

4.6. *Cell performance*

Cell performance was evaluated using a single cell at 80 °C. Hydrogen and air were fed to the anode and the cathode, respectively (H_2/air utilization: 70%/40%). The area of electrodes were 25 cm^2, and Pt loading was 0.4 mg cm^{-2} on both the electrodes.

4.7. *Environmental cycle test*

Environmental cycle test was carried out for MEA fixed by cell frames (Fig. 11). One cycle consists of the following four steps:

1st step: 80 °C-95%RH for 1.5 h;
2nd step: lowing the temperature from 80 to −40 °C in 2 h;
3rd step: −40 °C for 1.5 h;
4th step: raising the temperature from −40 to 80 °C-95%RH in 1 h.

After cyclic change, cell performance and hydrogen permeability were measured.

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