ThreeBond
TECHNICAL NEWS

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New Series of Fuel Cell Sealing Compounds – ThreeBond 1152/1153

Introduction

Major topics about automotive industry these days include reduction in total emission of CO_2 as an all-out incentive to arrest global warming, development of alternative energy sources as countermeasures against the depletion of petroleum resources, and controlling regulations to check air pollution becoming increasingly intensified in urban areas. The requirements to meet the situation are the utilization of alternative energy sources, efforts for energy saving and to obtain higher energy efficiency, and the materialization of low emission vehicles (automobile engines).

Fuel cell is attracting much attention as a promising new energy source as it can provide high energy efficiency and is ecofriendly as well. In particular, polymer electrolyte fuel cells are hopefully expected as a new power source for the next-generation vehicles as these cells can work at relatively low temperatures and also permit to materialize downsized cars with higher power because of their high current density.

Convinced of great potential of the polymer electrolyte fuel cell as a new vital power source for the next-generation vehicles, at Three Bond we have been focusing our efforts on the research and development of materials that can perfectly seal hydrogen, which is the fuel for these cells, and the establishment of their sealing methods.

The performance characteristics and features of fuel cell sealing compounds ThreeBond 1152 and 1153 (“TB1152/1153”) are described below.

Contents

1. The Principle of Fuel Cell and Its Classification

Fuel cell battery is a new system to generate electric power by means of the chemical reaction of oxygen (O_2) to hydrogen (H_2) that is obtained by reforming gasoline, natural gases or the like and is used as main fuel (see Fig. 1). As compared to the existing internal combustion engines such as gasoline and diesel engines, this new system can provide a higher generating efficiency that ranges between 30% and 60%. Besides, it practically emits no CO_2 and other exhaust gases, drawing therefore much attention as an environment-friendly, next-generation power generating system.

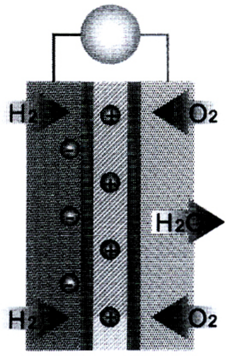


Fig. 1 The principle of fuel cell

The fuel cells currently in course of development can be classified into the following groups according to the type of electrolyte to be used: phosphonic acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and polymer electrolyte fuel cell (PEFC), as shown in Table 1 below. Of these, development competition is heating up especially with the polymer electrolyte type (PEFC) for automotive application, home use and as portable power source. This is because the PEFC type can be smaller and lighter than others are, in addition that it can work at relatively low temperatures within a range between 70°C and 100°C.

2. Construction of Fuel Cell (PEFC)

A polymer electrolyte fuel cell battery is a stack of various cells. Each stacked cell is comprised of a membrane and electrode assembly (MEA), which consists of an electrolytic membrane carrying platinum catalysts on both sides, sandwiched between a fuel electrode plate and an air electrode plate, two separators having reaction gas feed channels, and the respective sealing compound layers. (See Fig. 2.)

Hydrogen (H_2) and oxygen (O_2) are supplied to this stack from outside to induce a series of reactions reverse to electrolysis so that current is produced in the external circuit. These reactions can be expressed by the following formulae:

Fuel plate: $H_2 \rightarrow 2H^+ + 2e^-$
Air plate: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Total reaction: $H_2 + 1/2O_2 \rightarrow H_2O$

In general terms, a d.c. voltage of around 0.7 volts can be obtained per cell. So energetic efforts are being concentrated on developing a stack that can generate several kW to 200 kW using about 100 fuel cells.

3. Required Performance Characteristics of Fuel Cell Sealing Compound

As described above, the electromotive force of a fuel cell is obtained by means of the chemical reaction between oxygen (O_2) and hydrogen (H_2), which is the reaction gas, supplied externally. Since hydrogen (H_2), particularly when used as fuel gas, is colorless, odorless, flammable gas with small molecular weight, it can easily leak even from a very fine clearance and is readily ignitable even with a very small spark in a wide range of mixing. Because of these characteristics of the hydrogen (H_2) as fuel gas, a sealant that can provide almost perfect gas barrier is required between cells.

Table 1 Classification of Fuel Cells

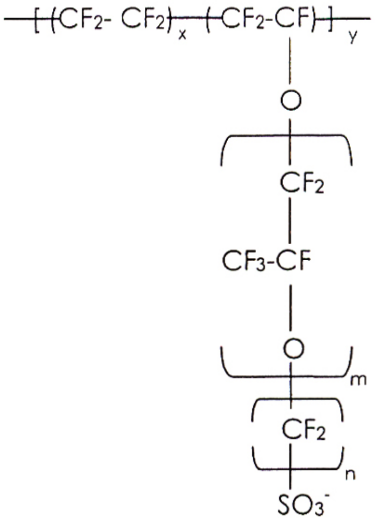
	(PAFC) Phosphonic Acid Fuel Cell	**(MCFC)** Molten Carbonate Fuel Cell	**(SOFC)** Solid Oxide Fuel Cell	**(PEFC)** Polymer Electrolyte Fuel Cell
Electrolytic membrane	Phosphate water solution	Li-Na carbonate	Zirconia ceramic	Polymeric membrane
Working temperature range	200˚C	650~700˚C	900~1000˚C	70~100˚C
Fuel	Reformed hydrogen (natural gas, etc.)	Natural gas, LP gas	Natural gas, LP gas	Pure hydrogen, refomed hydrogen
Generating efficiency	35~45%	45~60%	45~65%	30~40%
Characteristics	Works at relatively low temperatures.	Provides high generating efficiency.	Provides high generating efficiency.	Works at low temperatures; downsizing possible.
Main applications	Cogeneration; decentralized power source	Substitutes for large-scale thermal power plants; cogeneration	Substitutes for medium-scale thermal power plants; cogeneration	Automotive power source; home cogeneration; Portable power source

An ionic-conductive polymer membrane (cation exchange membrane) is used as electrolyte in a polymer electrolyte fuel cell. This membrane has a chemical structure as shown in Fig. 3: it consists of the principal chain of fluorocarbon resin with the side chain of sulfonic acid radicals (SO_3^-) that allows addition of protons (H^+).

This polymeric membrane becomes proton-conductive only after it absorbs water, permitting connection between sulfonic acid radicals. Because of this fact, it is necessary to humidify the reaction gas so that the membrane's conductivity of protons can be maintained. For this reason a polymer electrolyte fuel cell must be operated at around 100°C, a temperature level that can keep the membrane wet. The inside of the cell, on the other hand, is exposed to strong acid (pH 1~2) by the influence of the side-chain sulfonic acid radicals.

The sealant or sealing compound for a polymer electrolyte fuel cell must therefore own a low moisture permeability to prevent leakage of water vapor required for working of the membrane. Additionally, this characteristic must be combined with acid resistance, moisture resistance and heat resistance in relation to the above-mentioned working conditions.

Also, the less the ionic elution (especially, heavy metal ions), the better the sealing compound. This is because ions eluted from sealing compound attack the aforementioned polymer membrane's sulfonic acid radicals, adversely affecting its proton-conductivity. Secondly, the eluted ions deactivate the platinum catalysts provided on the membrane which function to oxidize hydrogen and reduce it to oxygen. Both of these ionic actions could decrease the electromotive force of each of the cells composing the whole fuel cell system (battery), leading to a functional deterioration of the whole system. A sealing compound allowing the least possible ion elution is therefore desired.



Nafion[8] m≧1, n=2, x=5-13.5, y=1000

Fig. 3 Chemical structure of fluorocarbon ion exchange membrane

To obtain direct current voltage from each component cell, electrical insulation must be provided between its separators. It is further desirable that these separators be made of some rubber elastic material so that they can absorb shocks and vibrations, considering applications of the fuel cell (and consequently, its sealing compound) to vehicles and portable batteries.

Summarizing the above, the essential characteristics required for a fuel cell sealing compound can be described as follows:

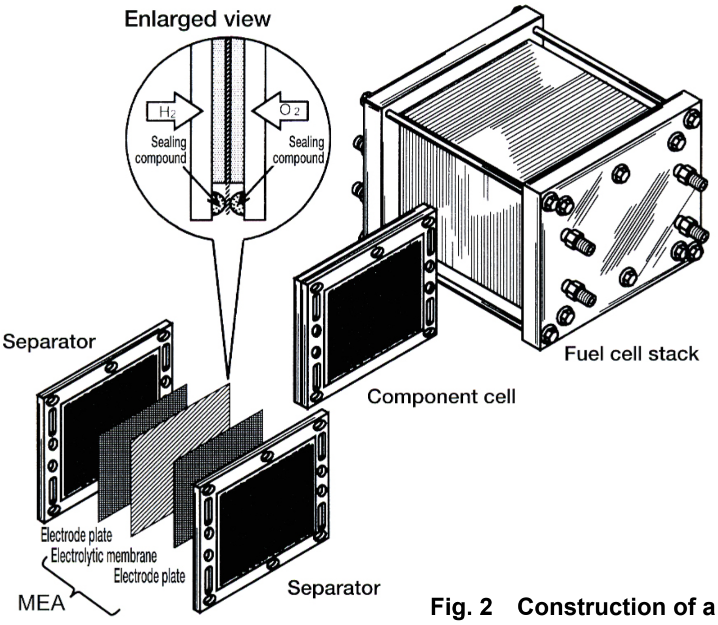


Fig. 2 Construction of a fuel cell (PEFC)

* High level of gas barrier capability… For sealing of hydrogen (H_2) and oxygen (O_2) gases.
* Low moisture permeability… To let the polymer membrane work in saturated vapor and keep the inside of the cell wet.
* Acid resistance… To protect the inside of the cell from exposure to strong acid, which occurs when the polymer membrane functions in saturated vapor.
* Moisture resistance… Because the inside of the cell is saturated with vapor while the polymer membrane is functioning.
* Heat resistance… Because of the working conditions of the polymer membrane.
* Low ion elution… To maintain the polymer membrane's proton-conductivity and also keep the platinum catalysts provided on the membrane active.
* Electrical insulation… To prevent short circuit between cells.
* Rubber elastic body… To absorb vibrations and impacts.
* Others … Resistance to coolant, and methanol resistance (this in anticipation of a modified methanol or direct methanol fuel cell -DMFC-).

4. Leak Mechanism and Comparison of Gaskets

According to the definition by the JIS (Japanese Industrial Standard), a gasket is "any of such objects that is used to prevent leakage of internal fluid by inserting it between contact surfaces of pipes or equipment devices or by bolting or tightening it by other methods." There are three types of leakage (see Fig. 4):

(i) Leakage along contact surface … Fluid leaks from between gasket and flange faces.
(ii) Osmotic leakage (In-layer leakage) … Fluid leaks through the gasket.
(iii) Breakdown leakage (Burst leakage) … Fluid leakage occurs due to the burst of the gasket.

In terms of material, gaskets can be classified into two: solid and liquid gaskets.

The sealing performance of the solid type gasket is mainly discussed based on the compression righting moment (restoring force) of the gasket itself when subjected to a clamping force, and the principal concern is the level of its set. Leakage along contact surface also is an issue of vital importance to be taken into consideration for this type of gasket as its close contact with the joint surfaces plays a part in its compression set. The advantages of a solid gasket include easy removal and availability of relatively thick gaskets, thus providing good sound insulation and vibration proofing.

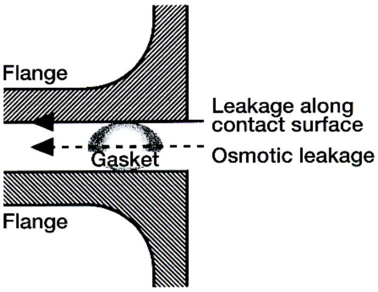


Fig. 4 Types of leakage

The liquid type gasket, on the other hand, is very effective in sealing performance because, being a fluid, it can penetrate into uneven spots of the contact surfaces and also, it can get into close contact with the surfaces. There are two types of liquid gaskets: wet type formed-in-place gasket (FIPG) and dry type cured-in-place gasket (CIPG).

4.1 FIPG (Formed-in-place Gasket)

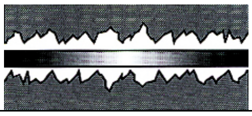
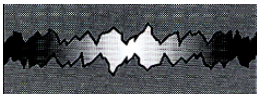
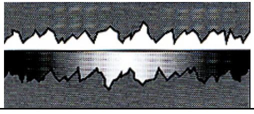
Liquid gasket material is applied to sealing surfaces (flange faces) and the faces are brought into contact while the applied material still remains unhardened. The material is then subjected to hardening. Because the liquid faithfully follows the profile of the face, practically it does not require a high precision of flange faces. Additionally, being a bonding seal, its sealing performance is reliable, and flange width and thickness can be reduced.

4.2 CIPG (Gured-in-place Gasket)

Unhardened liquid gasket material is applied to sealing surfaces and is then heated for hardening. As this type is directly applied to parts surfaces and cured in place, it does not require molds that are needed for ordinary molded gaskets. However, the sealing performance of CIPG mainly depends on the shape, clamping pressure and compression set in the same way as with a solid gasket. Special attention must be paid to the accuracy in the shape of application beads because the material is hardened as is as applied. Shown in Table 2 are the characteristics of liquid gaskets (FIPG and CIPG) in comparison with those of solid type.

What is important here is that supposing that the sealing performance of the gasket material is fully displayed, sealing width and thickness can be reduced as the level of its barrier capability against the medium to be sealed is higher. This is of vital importance for selection of the best sealing compound for a fuel cell because it needs to seal hydrogen (H_2) and oxygen (O_2) gases whose molecular weights are very small and which are wet. A smaller seal also contributes to increasing the generating efficiency of a fuel cell, which will in turn do much toward downsizing of the whole system.

Table 2 Comparison of Characteristics

	Solid gaskets	Liquid gaskets	
		FIPG (Formed In Place Gasket)	CIPG (Cured In Place Gasket)
Sealing method	Double face contact 	Double face adhesion 	One face contact, one face adhesion 
Dimensional precision for sealing compound	High	Low	High
Flange face precision	High	Low	High
Surface pressure	High	Low	High
Compression set	Required	Not required	Required
Removability	O	×	O
Line production	×	O	O

Solid gaskets (including CIPG) greatly depend on the rigidity and pressure of the contact surface. Because of this, creeps are produced from immediately after they are mounted, causing the sealed surface pressure to decrease. These creeps are especially conspicuous at points that are subjected to heat and where internal pressure fluctuates frequently, which usually lead to torque decrease that is the most possible cause of leakage. For a fuel cell battery, particularly, full consideration is required to these creeps in the design of sealing points because the battery consists of a stack of tens to hundreds of cells.

5. Features of TB1152/1153

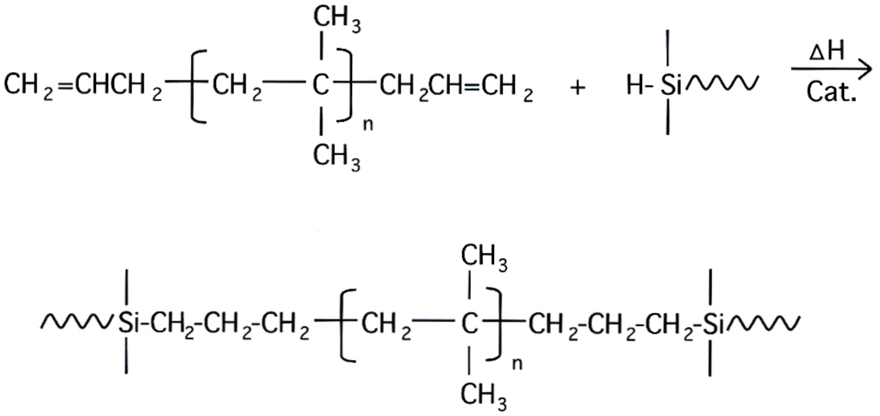
We have been successful in developing fuel cell sealing compounds TB1152 and TB1153 after years of investigation and research in materials that can meet the performance characteristics required for the above-mentioned two types of sealing gaskets.

TB1152 and TB1153 consist of telechelic polymer (main component) whose principal chain is polyisobutylene having anyl groups at ends. The finished sealing compound is formed by additional polymerization and bridging of curing agent that contains SiH radicals (see Fig. 5). Heating in the presence of catalysts performs this forming. Table 3 shows the respective properties and general characteristics of these sealing compounds.

It is known that usually, gas permeability of rubber becomes lower as its molecular rotations become difficult and molecular interactions become intensified. This is because molecular movement is restrained.

Polyisobutylene, which is the main component of TB1152/1153, has a C-C chain in its principal base. Compared with the siloxane chain of silicone, the C-C chain is shorter in intermolecular distance and smaller in free volume. Because of these properties, it can provide higher performance of gas barrier and lower moisture permeability while it is soft and flexible as silicone. (See Photo 1.)

Fig. 6 shows the relative comparison of the results of hydrogen (H_2) gas permeability test (JIS K 7126) and water vapor permeability experiment (JIS Z 0208) between additional type common silicone sealant and TB1152/1153 hardened sheets (1-mm thick).



$$CH_2{=}CHCH_2\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right]_n CH_2CH{=}CH_2 + H-\overset{|}{\underset{|}{Si}}\sim\sim \xrightarrow[Cat.]{\Delta H}$$

$$\sim\sim\overset{|}{\underset{|}{Si}}-CH_2-CH_2-CH_2\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right]_n CH_2-CH_2-CH_2-\overset{|}{\underset{|}{Si}}\sim\sim$$

Fig. 5 Curing mechanism of TB1152/1153

Compared with existing silicone sealing compounds commonly in use, the hydrogen (H_2) gas permeability of TB1152/1153 is 1/20 and its water vapor permeability is around 1/100, showing that TB1152/1153 are incomparably excellent in gas barrier performance.

TB1152/1153 also provide high resistance in various physical conditions: the results obtained from dumb-bell physical property testing show that their tensile strength has not dropped in any of resistance test conditions: acid resistance (Fig. 7), moisture resistance (Fig. 8), heat resistance (Fig. 9), and heat-cold cycle resistance (Fig. 10). This means that TB1152/1153 can retain stable rubber-like physical properties for an extended period of time.

Likewise, there has been no significant fluctuation in their hydrogen (H_2) gas permeability (see Figs. 11 through 14), proving that their gas barrier capability is highly reliable.

Finally, the measurement results of ions eluted from these sealing compounds are shown in Table 4. As can be seen in the table, no ionic elution (especially, heavy metal ions) has been observed, meaning that they will not cause any significant damage to the electrolytic membrane, which is the heart of the polymer electrolyte fuel cell (PEFC).

TB1152 is designed for use with FIPG, and TB1153 with CIPG so that each type can meet the stack variations and different manufacturing processes as may be required by fuel cell manufacturers. TB1153 (for CIPG) has higher levels of physical properties of sealing agent than those of TB1152 (for FIPG) so as to increase its compression set characteristic and improve its sealing feature against compression. Shown in Photos 2 and 3 are the application images of the respective sealing compounds.

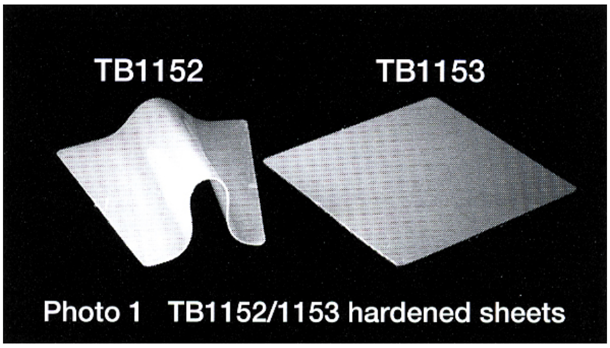


Photo 1 TB1152/1153 hardened sheets

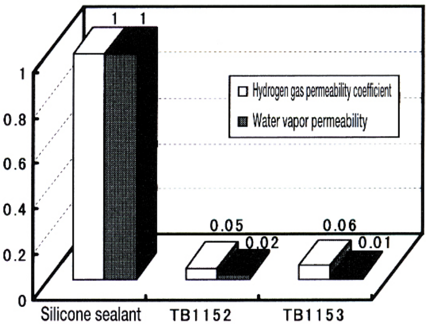


Fig. 6 Hydrogen (H2) gas permeability coefficients and water vapor permeability (Relative comparison)

Table 4 Measurement Results of Eluted Ions

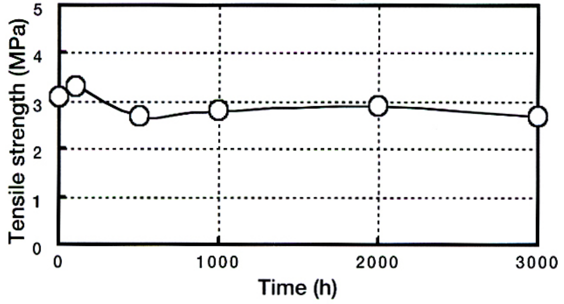
Extracting conditions: pH = 1; H_2SO4 aqueous solution; at 100˚C for 100 hrs

Ion type	Result	Ion type	Result
Mg	ND	Cu	ND
Al	ND	Zn	ND
Si	ND	Ag	ND
Cr	ND	Cd	ND
Mn	ND	Sn	ND
Fe	ND	Hg	ND
Ni	ND	Pb	ND

*ND: Not Detected

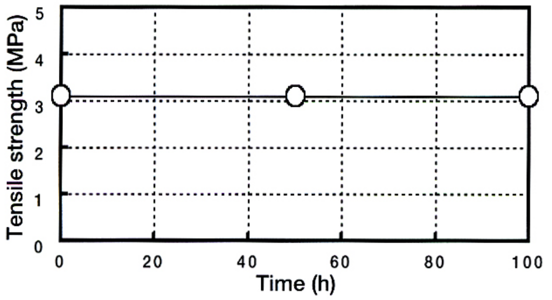
Table 3 General Properties of TB1152/1153

	Unit	TB1152 (for FIPG)	TB1153 (for CIPG)	Test method
Appearance	–	Milky white	Gray	3TS-201-01
Viscosity	Pa·s	828	1110	3TS-210-03
Specific gravity	–	0.93	1.00	3TS-213-02
Glass transition point	˚C	-67.2	-67.4	3TS-501-04
Hardness	A	35	54	3TS-215-01
Tensile strength	MPa	3.0	4.1	3TS-320-01
Elongation	%	315	140	3TS-320-01
Characteristic volume resistivity	Ω·m	2.6×10^{14}	3.7×10^{14}	3TS-401-01
H_2 gas permeability coefficient	$mol·m/m^2·s·Pa$	7.2×10^{-15}	9.6×10^{-15}	JIS K 7126
Water vapor permeability (40˚C × 95%RH)	$g/m^2/24h$	3.5	0.21	JIS Z 0208
25% compression set (120˚C × 100h)	%	35	19	JIS K 6262



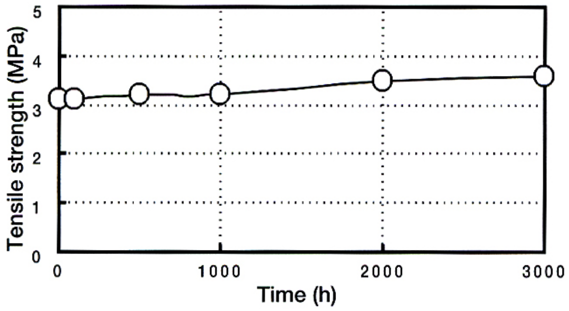
Sample: TB1152
Test conditions: at 100℃; pH = 1; H_2SO_4 aqueous solution

Fig. 7 Acid resistance (Tensile strength)



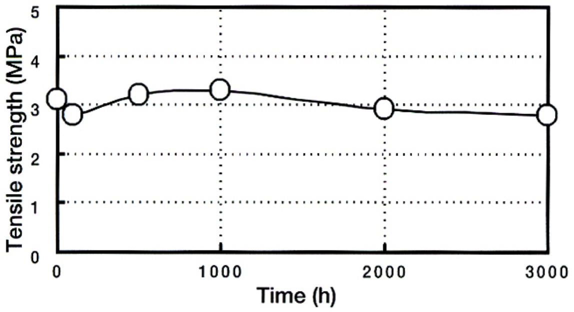
Sample: TB1152
Test conditions: at 110℃×100%RH

Fig. 8 Moisture resistance (Tensile strength)



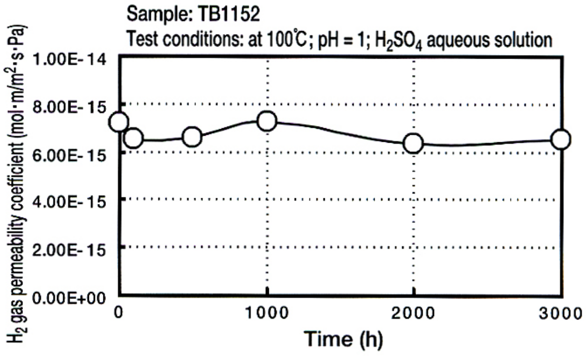
Sample: TB1152
Test conditions: at 100℃

Fig. 9 Heat resistance (Tensile strength)



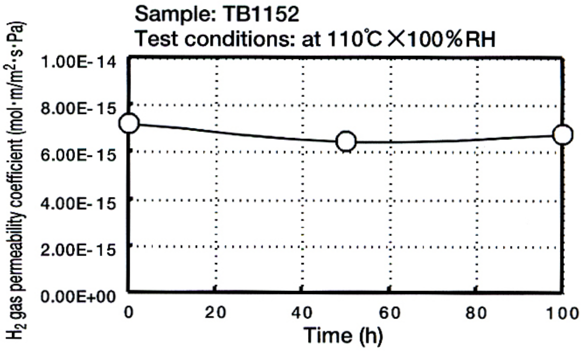
Sample: TB1152
Test conditions: at −30℃×2h⇔100℃×2h

Fig. 10 Heat-cold cycle resistance (Tensile strength)



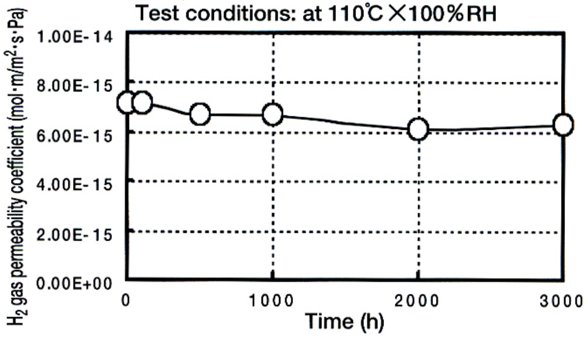
Sample: TB1152
Test conditions: at 100℃; pH = 1; H_2SO_4 aqueous solution

Fig. 11 Acid resistance (H_2 gas permeability coefficient)



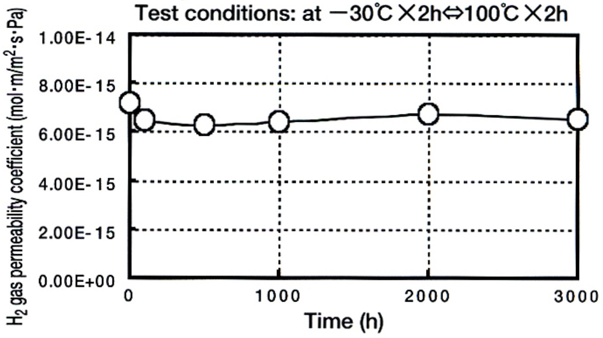
Sample: TB1152
Test conditions: at 110℃×100%RH

Fig. 12 Moisture resistance (H_2 gas permeability coefficient)



Sample: TB1152
Test conditions: at 110℃×100%RH

Fig. 13 Heat resistance (H_2 gas permeability coefficient)



Sample: TB1152
Test conditions: at −30℃×2h⇔100℃×2h

Fig. 14 Heat-cold cycle resistance (H_2 gas permeability coefficient)

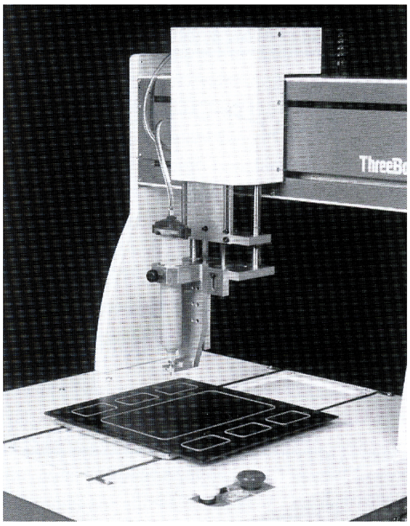


Photo 2 Application image of TB1152

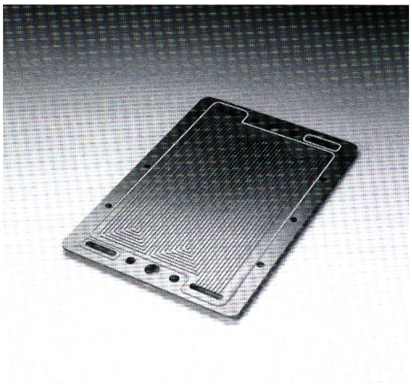


Photo 3 Application image of TB1153 for CIPG on a dummy separator

6. Epilogue

The recent news report that vehicles equipped with polymer electrolyte fuel cell battery (PEFC) will be launched even this year (2003) although in limited quantity. Because of its high potential, its applications to notebook personal computers, mobile phones, PDAs and other portable devices are also in study, and therefore, heat-up of development competition and technological breakthrough are anticipated.

Making the most of our long-experienced sealing technologies and also taking advantage of our newly developed TB1152/1153, we will challenge for establishing more sophisticated hydrogen gas sealing technology so that we can contribute to the development and spread of fuel cells much more actively.

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