

Study of Seal Structure of High-differential-pressure Water Electrolysis Cell

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ABSTRACT

A study was conducted of a method of realizing airtightness for high-pressure hydrogen in an electrolysis cell using high differential pressure water electrolysis, a high-pressure (35 MPa) hydrogen production technology. When conducting high differential pressure water electrolysis in an electrolysis cell using a proton exchange membrane, the maintenance of airtightness against high-pressure hydrogen via the membrane, an elastic part, represents an issue. To resolve this issue, the effect of the use conditions of the membrane on changes in the thickness of the membrane was studied. The results indicated that it was necessary to set the holding loads in the cells so as to help ensure that the surface pressure of the membranes maintaining airtightness around the cathode space was greater than the pressure of the high-pressure hydrogen, and to select the hardness of the seal parts with consideration of the gaps occurring due to the state of wetness or dryness of the membrane. Evaluation of the durability of a high differential pressure water electrolysis stack applying the findings of this study verified that airtightness was maintained over the long term.

1. Introduction

Using hydrogen as fuel and emitting only water, the fuel cell electric vehicle represents the ultimate clean car. The provision of infrastructure for the supply of the hydrogen used as fuel by fuel cell electric vehicles is an important factor in promoting their more widespread use. As one means of supplying hydrogen, Honda has proposed the Solar Hydrogen Station (SHS), at which fuel cell electric vehicles can be filled with hydrogen produced by water electrolysis using electricity generated by solar cells.

In the initial phase of its development, the SHS stored the hydrogen produced by water electrolysis under pressure for supply to vehicle hydrogen tanks, using a mechanical compressor. However, this method presented the issue that the power consumed by the mechanical compressor reduced operating efficiency^{(1),(2)}.

The development of a high differential pressure water electrolysis technology that pressurizes hydrogen at the same time as electrolyzing water increased system efficiency by 25% and reduced volume by 60% against the system using the mechanical compressor⁽³⁾. The SHS2, a second-generation hydrogen station using this technology, has been demonstrated in Japan and U.S.⁽⁴⁾.

The characteristics demanded of the electrolytic unit used in this high differential pressure water electrolysis

can be classified into electrolysis performance, ability of sustaining differential pressure, and airtightness performance. Of these, the results of tests concerning electrolysis performance and ability of sustaining differential pressure have already been reported⁽⁵⁾. With regard to airtightness performance, the system uses a combination of elastic parts, a proton exchange membrane (PEM) and O-rings, in order to realize a structure that seals in high-pressure hydrogen. This is the same airtight structure that is standard for fuel cells that have an internal pressure close to atmospheric pressure, and for water electrolysis at atmospheric pressure. However, the thickness of the PEM varies in response to pressure on the membrane or the state of wetness or dryness of the membrane. This property represents an issue for the seal structure in high differential pressure water electrolysis. It is therefore necessary for the O-rings, one of the seal parts, to maintain the seal even in conditions under which the thickness of the PEM changes.

In response to this issue, this paper will discuss research that measured the changes in the thickness of the PEM under moist, high-pressure conditions to clarify its behavior in an actual operating environment, and that studied the conditions necessary for the holding loads in the cells and the O-ring sealing parts. The ability of a stack manufactured with consideration of the results of these studies to maintain airtightness was verified in durability tests.

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2. Characteristics of High Differential Pressure Water Electrolysis

2.1. Structure of High Differential Pressure Water Electrolysis Cell

2.1.1. Basic principle and airtight structure

The basic principle of high-pressure water electrolysis is electrolysis of water using a PEM. If the flow of hydrogen, the product of the electrolysis, in the downstream direction is controlled, pressure will increase as the volume of hydrogen produced increases. By comparison with equal pressure systems, in which pressure increases simultaneously at both the cathode and the anode, differential pressure systems increase pressure only at the cathode, making it possible to reduce the size of the unit. A differential pressure system was therefore adopted in the present research. Figure 1 shows a schematic diagram of a high differential pressure water electrolysis cell.

In this cell, the PEM does not simply separate the cathode space and the anode space, but together with the O-ring seals in the outer circumference of the electrolysis section, also plays a role as a part that maintains the airtightness of the water electrolysis cell. This high differential pressure water electrolysis cell structure has the same structure as a normal atmospheric pressure water electrolysis cell using a PEM, but a higher holding load is employed in order to seal in the high-pressure hydrogen.

2.1.2. Electrode holding structure

It is necessary for the holding force pushing on the electrodes in the electrolysis cell to be greater than the repulsion force due to internal pressure. As an example, if the surface area of the bottom of the cathode space is assumed to be 100 cm², at a hydrogen pressure of 35 MPa, the repulsion force is 350 kN. There are two methods of generating this holding force: A method that uses the elasticity of metal in the form of the axial force of springs or bolts [Fig. 2(a)], and a method using a piston [Fig. 2(b)], in which the piston is pushed down by the high-pressure hydrogen produced by water electrolysis to provide the holding force. Elastic parts are also employed

in the cylinder in the piston method in order to help ensure the necessary holding force at atmospheric pressure and the contact surface pressure at the electrolytic surfaces necessary for electrolysis to occur⁽⁵⁾. In the method shown in Fig. 2(a), when the pressure of the product hydrogen increases, the force holding the electrodes declines as a result of the repulsion force produced by internal pressure. This makes it necessary to initially set an excessive holding load. By contrast, in the method shown in Fig. 2(b), which uses a piston, the holding force increases in proportion with internal pressure, and it is therefore possible to set the minimum necessary initial load. Figure 3 shows the holding power in relation to internal pressure and the changes in the surface pressure of the seal section of the PEM sandwiched between the anode and cathode parts. As Fig. 3(a) shows, in order to maintain a specified PEM surface pressure when the hydrogen is under high pressure, the surface pressure of the PEM is high from the stage of low hydrogen pressure. Because of this, the PEM undergoes a high degree of static deformation, and because the load produced by the elastic parts declines, it is necessary to set the initial load at an even higher level. Imparting this type

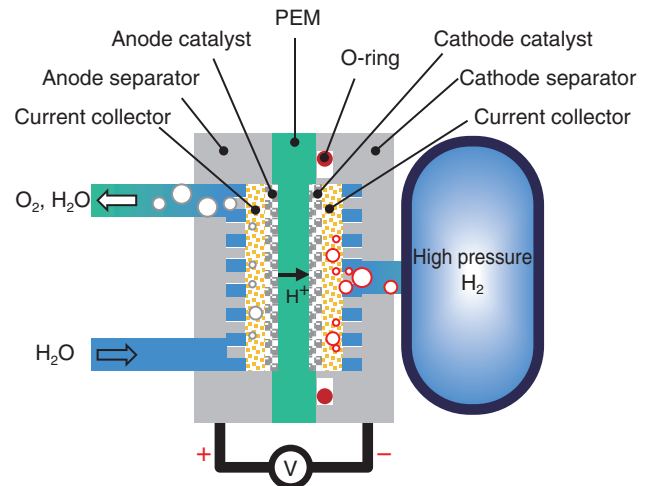


Fig. 1 Schematic of high-differential-pressure water electrolysis cell

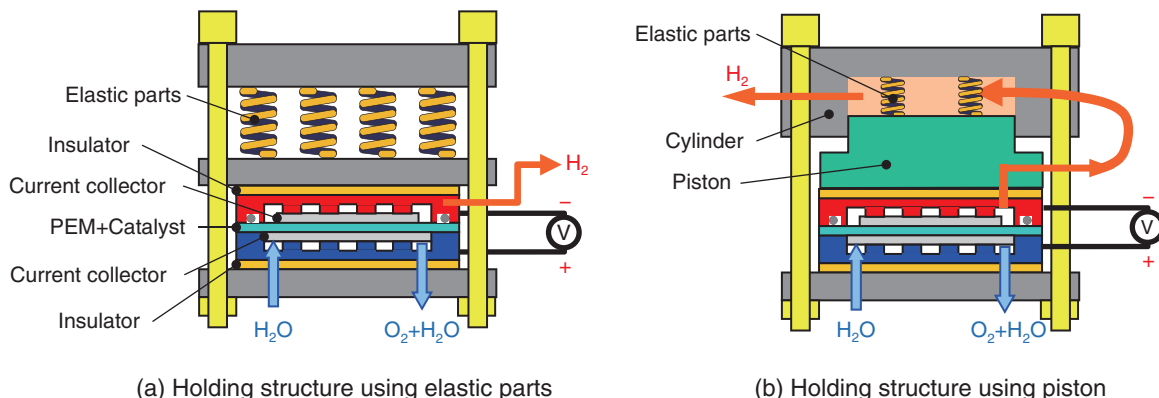


Fig. 2 Holding structure of electrolysis cell

of load necessitates the use of large springs as the elastic parts, increasing the size of the unit. By contrast, in the system shown in Fig. 3(b), the surface pressure of the PEM is appropriate irrespective of the hydrogen pressure. For this reason, the present research employed the piston method, as shown in Fig. 3(b).

2.2. Study of Airtightness

In the structure of the high differential pressure water electrolysis cell, the PEM, together with the O-rings, fulfills the role of maintaining airtightness. O-rings are normally used as seals between solid, non-deformable parts. In this structure, however, because the PEM with which the O-rings make contact deforms under loads, the characteristics of the PEM affect airtightness. The fluorine-based PEM used in the present development has a comparatively low elastic modulus, and therefore deforms easily, and its swelling ratio when it absorbs water is also high. In order to maintain airtightness, it is therefore necessary to study the appropriate load settings and evaluate changes in the thickness of the PEM in response to load and conditions of wetness and dryness.

2.2.1. Study of holding load in cell

In order to impart the optimum surface pressure to the PEM in both the electrolysis section and the seal section of the electrolysis cell, it is essential to set the optimum diameter for the piston that generates the holding load. The load generated by internal pressure is determined by the pressurized area of the piston. If the diameter is large, the piston will be capable of generating a large load, but this would increase the size of the unit and might result in excessive increase in the surface pressure of the PEM. Because of this, it is necessary to set the appropriate load with the aim of realizing the minimum necessary size.

The holding load on the piston is expressed by Eq. (1).

$$F_{pis} = S_{pis} \cdot P_H + F_{sp} \quad (1)$$

F_{pis} : Piston holding load (N)

S_{pis} : Piston pressurized area (mm²)

P_H : Hydrogen pressure (MPa)

F_{sp} : Load generated by elastic parts in cylinder (N)

The necessary surface pressure for electrolysis to occur

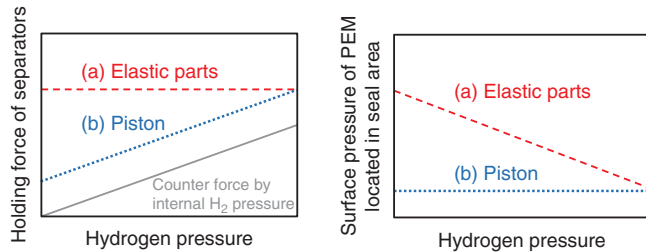


Fig. 3 Comparison of holding force of separators and surface pressure of PEM located in seal area

in the electrolysis section is 5 MPa, as determined from contact resistance and membrane resistance⁽⁵⁾. This surface pressure is imparted to the entire range of the effective surface area of the PEM based on the setting of F_{sp} , without consideration of the hydrogen pressure.

2.2.2. Study of specifications of seal parts

Standard criteria for the selection of O-rings as seals are provided by JIS⁽⁶⁾, but because the O-rings will be in contact with PEM in the case of the high differential pressure water electrolysis configuration, a special selection criterion is necessary. This is the gap produced by the change in the thickness of the membrane due to the amount of expansion that occurs when there is a difference in the state of wetness and dryness of the PEM in the seal section. Figure 4 shows channels for the flow of hydrogen in the exterior of the electrolysis section when the cells are layered. These are areas in which it is assumed that extrusion of the O-rings. The seals on these channels are also formed by the PEM and O-rings. In these areas, the PEM swells at the inner sides of the O-rings due to the water content of the product hydrogen. However, at the outer sides of the O-rings, the PEM is exposed to the air and is therefore dry, resulting in the occurrence of gaps in the outer sides of the O-rings due to differences in membrane thickness, as shown in Fig. 5. It is therefore necessary to select the O-rings used in these areas with consideration of these gaps.

With regard to the twin issues of setting the holding load in the cells and responding to the gaps that form in the O-rings, the change in the state of the PEM under high pressure – a phenomenon unique to high differential pressure water electrolysis – is a factor in the settings for the seal structure. The clarification of the changes in the

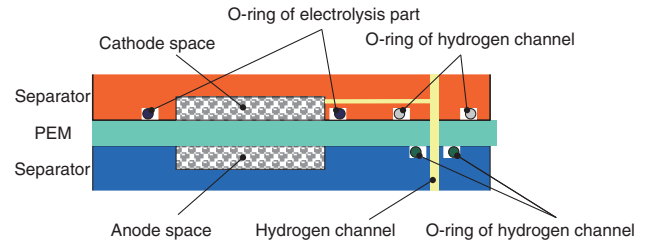


Fig. 4 Schematic of hydrogen channel designed on outside of electrolysis part

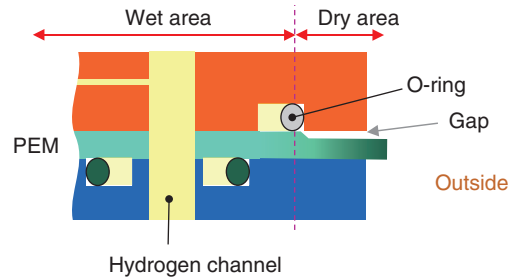


Fig. 5 Generation of gap by dryness of PEM of seal area

thickness of the PEM membrane under actual operating conditions helped to resolve these issues. The airtightness of a stack in which the outcomes of these studies were applied was verified in long-term durability tests.

3. Test Methods

3.1. PEM Compression Characteristic Test

Compression tests were conducted to study the thickness change characteristic of the PEM under moist, high-pressure conditions. The sample PEM was immersed in water prior to the test and allowed to swell until saturation. It was then pressed using an indenter of a specified surface area, and displacement and load were measured. The strain characteristic of the device was measured in advance, and the measured values were corrected on this basis. The atmosphere for the measurements was based on conditions for electrolysis; the temperature range was 35° to 80°C, and the humidity was set at 95% RH in order to maintain the moist state of the PEM. Pressure was applied repeatedly to the sample, and it was immersed in 25°C water in order to rehydrate, following which the amount of displacement in the membrane was measured.

3.2. Electrolysis Test using Piston-type High Pressure Water Electrolysis Cell

Figures 6(a) and 6(b) show schematic diagrams of electrolysis cells. To verify the optimum setting of piston load, changes in the PEM were studied based on behavior during electrolysis for pistons with two different pressurized areas (S_{pis}): In (a), S_{pis} is equal to the surface area of the bottom of the cathode space, S_H , the minimum setting; while in (b), S_{pis} corresponds to S_H plus S_{seal} , the surface area of the seal section.

The basic structure of the electrolysis cell was the same as that of an atmospheric-pressure cell, and the body of the cell was constructed of a titanium alloy. The spring load inside the piston was set to produce the 5 MPa surface pressure necessary for electrolysis under high pressure. The stiffness of the supporting column connecting the upper cylinder and the bottom section was set to help ensure that

the deformation produced by the repulsion force generated by the product hydrogen did not affect the spring load inside the piston. A fluorine-based electrolytic membrane was used for the PEM, and a Ru-Ir-Fe complex oxide catalyst was used at the anode and a platinum black catalyst was used at the cathode. Sintered metal current collectors were used at both electrodes.

Electrolysis voltage, E_{we} , during high differential pressure water electrolysis was used as the indicator in evaluating electrolysis performance. This parameter is found using Eq. (2)⁽⁷⁾.

$$E_{we} = E_0 + \frac{RT}{2F} \ln \frac{P_1}{P_2} + ir \quad (2)$$

E_0 : Theoretical operating voltage (V)

T : Absolute temperature (K)

R : Gas constant (J/mol · K)

P_1 : High-pressure side hydrogen partial pressure (MPa)

P_2 : Low-pressure side hydrogen partial pressure (MPa)

ir : DC resistance voltage (V)

F : Faraday constant (C/mol)

The second term in the equation corresponds to the potential arising from the difference in hydrogen concentration in a gas concentration cell.

3.3. Durability Tests of Stack Structure

The high differential pressure water electrolysis stack was subjected to durability operation using the test apparatus shown in Fig. 7 in order to verify its durability. The stack was put through continuous high differential pressure electrolysis, and was operated with repeated pressure increase and decrease: Pressure was increased, maintained at 35MPa, and decreased to atmospheric pressure. Current efficiency, calculated from the flow rate of the hydrogen produced by the stack, can be used as a numerical indicator of seal performance. Current efficiency is calculated using Eq. (3). This parameter was calculated based on measurements of the amount of hydrogen produced per hour by high differential pressure electrolysis, taken using a gas meter.

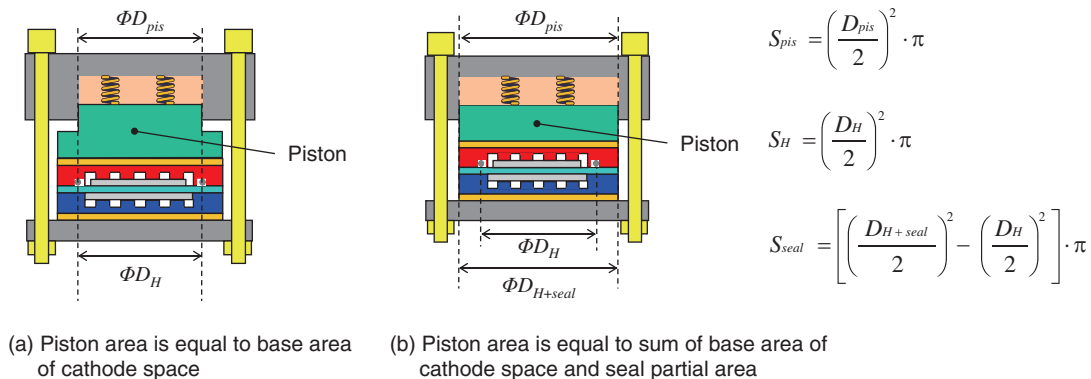


Fig. 6 Structure of piston type high-differential-pressure water electrolysis cells

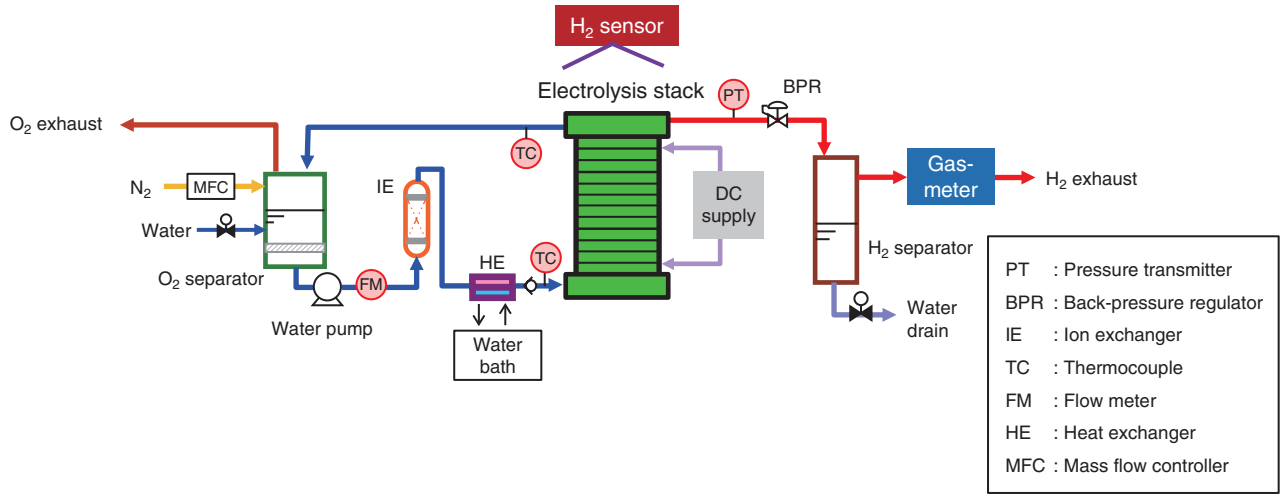


Fig. 7 Evaluation system of electrolysis stack

$$\eta_A = Q \cdot \left(\frac{I_{WE} \cdot 3600}{F} \cdot \frac{1}{2} \right)^{-1} \times 100 \quad (3)$$

η_A : Current efficiency (%)

Q : Amount of hydrogen produced (mol/hr)

I_{WE} : Electrolysis current (A)

A hydrogen sensor was positioned close to the stack, and verified that there were no leaks of hydrogen to the exterior.

4. Results and Considerations

4.1. Setting Cell Holding Load

4.1.1. PEM compression characteristic

When the PEM employed in the high differential pressure water electrolysis cell is compressed under high pressure, its thickness declines. This is due to the compression of the base material and the expulsion under high pressure of the water that has swollen the membrane due to the constant presence of water as an electrolyte at the anode. Figure 8 shows the results of measurements of the

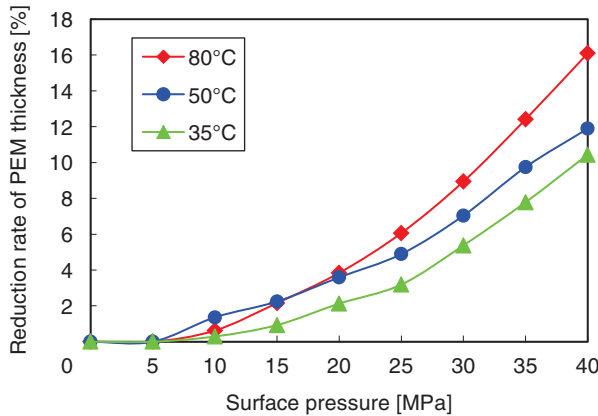


Fig. 8 Reduction rate of PEM thickness to surface pressure

rate of decline in thickness in response to the application of surface pressure to the PEM under moist conditions, taken using a compression tester. The degree of displacement changes significantly at close to 5 MPa, irrespective of the measurement temperature, and increases as surface pressure increases.

4.1.2. Evaluation using electrolysis cells

Figure 9 shows changes in cell voltage against the pressure of the hydrogen produced in electrolysis tests of the electrolysis cells shown in Fig. 6. In the results shown as (a), for the cell with a piston pressurized area corresponding to the area of the bottom of the cathode space, cell voltage increases rapidly from close to 15 MPa; in the results shown as (b), for the cell with a piston pressurized area corresponding to the area of the piston in (a) plus the surface area of the seal section, the cell voltage almost conforms to the electrolysis voltage calculated using Eq. (2). The increase in cell voltage shown in (a) is due to a decline in the contact surface pressure between the current collector and the catalyst at the electrolysis surface⁽⁵⁾.

The factors behind this decline in surface pressure will

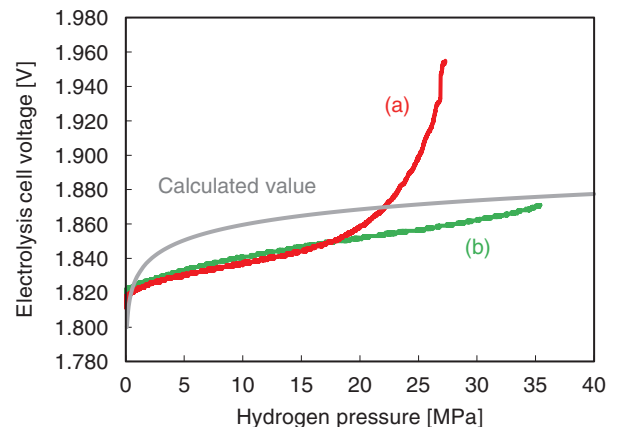


Fig. 9 Comparison of electrolysis cell voltage change

be considered from the perspective of the surface pressure of the section of the PEM acting as a seal on the external circumference, designated P_{seal} . P_{seal} is expressed by Eq. (4), using the piston load found by means of Eq. (1), the repulsion force generated by the high-pressure hydrogen, and the surface area of the seal.

$$P_{seal} = (S_{pis} \cdot P_H + F_{sp} - S_H \cdot P_H) / S_{seal} \quad (4)$$

In the results shown as (a) in Fig. 9, $S_{pis} = S_H$, and Eq. (4) therefore becomes Eq. (5), with P_{seal} becoming constant at 5 MPa due to the setting of F_{sp} .

$$P_{seal} = F_{sp} / S_{seal} = 5 \text{ [MPa]} \quad (5)$$

Because $S_{pis} = S_H + S_{seal}$ in the result shown as (b) in Fig. 9, Eq. (4) becomes Eq. (6), with P_{seal} varying as a linear function of hydrogen pressure.

$$P_{seal} = (S_{seal} \cdot P_H + F_{sp}) / S_{seal} = P_H + 5 \text{ [MPa]} \quad (6)$$

Figure 10 shows the surface pressure of the PEM in the cathode space, including the electrolysis section, and the seal section at the outer circumference for configuration (a) and configuration (b) in Fig. 9. In configuration (a), the difference in pressure between the cathode space and the seal section increases with increasing internal pressure. When this occurs, the thickness of the membrane in the cathode space including the electrolysis section declines in comparison to the thickness of the membrane in the surrounding seal sections, as shown schematically in Fig. 11. The reduction of contact surface pressure on the electrolysis surface resulting from this produces an increase in cell voltage. This phenomenon does not occur in

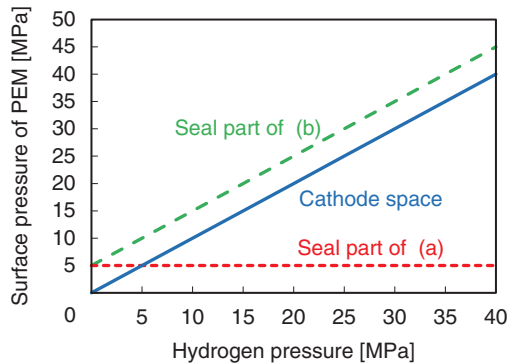


Fig. 10 Comparison of PEM surface pressure of cathode space and each seal part of (a) and (b)

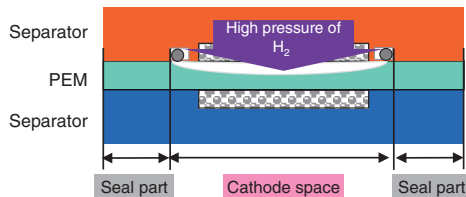


Fig. 11 Modification situation of PEM at time of high pressure in electrolysis cell (a)

configuration (b), because the surface pressure of the PEM in the seal section is set higher than the surface pressure of the PEM in the cathode space.

This type of pressure difference produces O-ring deformation of the type shown in Fig. 12, which can act as a factor in reducing seal performance. This is because, when the PEM surface pressure on the exterior of the O-ring is lower than the hydrogen pressure in the cell, a force acts on the O-ring to push it towards the exterior.

Based on the considerations above, it can be seen to be necessary to set the piston load so as to help ensure that the surface pressure of the seal section of the PEM is greater than the pressure of the product hydrogen. In other words, it is necessary for the pressurized area of the piston, S_{pis} , to be greater than the sum of the surface area of the bottom of the cathode space, S_H , and the surface area of the seal section, S_{seal} .

4.2. Wetness and Dryness of PEM and Selection of Seal Parts

Section 4.1. discussed the reason for seeking to realize uniform compression deformation of the PEM in the high-pressure gas section and the surrounding seal sections. However, it is also necessary to select seal parts with consideration of the differences in membrane thickness occurring when there are differences in the state of wetness and dryness of the PEM.

Figure 13 shows the rate of change in the thickness of

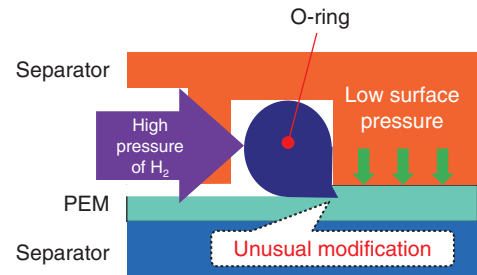


Fig. 12 Sectional view of seal portion

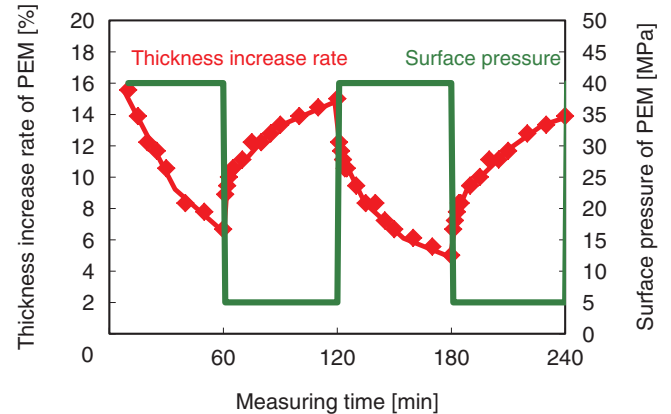


Fig. 13 Change of thickness increase rate of PEM to surface pressure change in humidification conditions

the membrane against a dry membrane when the surface pressure of the membrane is repeatedly alternated between the figure when electrolysis is not being conducted (5 MPa) and the figure when electrolysis is being conducted (40 MPa) under humid conditions. These results indicate that while the thickness of the membrane begins to decline simultaneously with the application of high pressure, because the speed of displacement is comparatively slow, specific conditions exist at the commencement of high-pressure operation under which the difference in thickness between the membrane when wet and when dry is at its maximum. Under these conditions, a maximum gap of 15% occurs in the membrane thickness. It is known that the maximum allowable gap is determined by the pressure on the O-rings and their hardness level. As allowable levels for planar seals at an internal pressure of 35 MPa, 20 μm is recommended for A80 seals and 55 μm for A90 seals⁽⁸⁾. For a membrane thickness of 100 μm , the gap would correspond to 15 μm , and an A80 seal could be used; for a membrane thickness of 200 μm , the gap would correspond to 30 μm , and it would be necessary to use an A90 seal.

4.3. Results of Durability Tests of Stack Structure

In order to obtain the necessary supply of hydrogen for the SHS2, it is necessary to layer the electrolysis cells to form a stack configuration. Based on the study of the characteristics of the PEM and the setting of the piston load and selection of the O-ring specifications described above, a stack of layered electrolysis cells was designed, and its durability was evaluated using the durability test set-up shown in Fig. 7. Because the volume of hydrogen measured will maintain a fixed value if airtightness is maintained during durability operation, measurement of changes in the volume of hydrogen flowing in the system can be used to judge whether an airtight structure has been realized in the high differential pressure water electrolysis stack.

Figure 14 shows current efficiency, an indicator of the volume of hydrogen produced, and hydrogen concentration as measured by a hydrogen sensor positioned close to

the stack under conditions of 10000 hr of continuous electrolysis, with the pressure cycle electrolysis repeated 330 times. A loss of approximately 5% in current efficiency as the hydrogen passed through the PEM and passed the anode existed from the initial stages of operation, but this figure remained constant throughout the durability test; in addition, no hydrogen leaks were detected by the hydrogen sensor. These results demonstrate that the electrolysis cells maintain airtightness over the long term even when layered in a stack configuration.

5. Conclusion

A study of the airtightness of high differential pressure water electrolysis cells, a high-pressure (35 MPa) hydrogen production technology, produced the following results.

- (1) The necessary holding load was obtained by using a piston, the cell holding structure, with a surface area greater than the sum of the surface areas of the bottom of the cathode space and the seal parts used in the outer circumference.
- (2) Airtightness was maintained by setting the hardness of the O-rings with consideration of gaps occurring due to the state of wetness or dryness of the PEM.

Tests verified the long-term airtightness of a stack manufactured based on the findings of the study.

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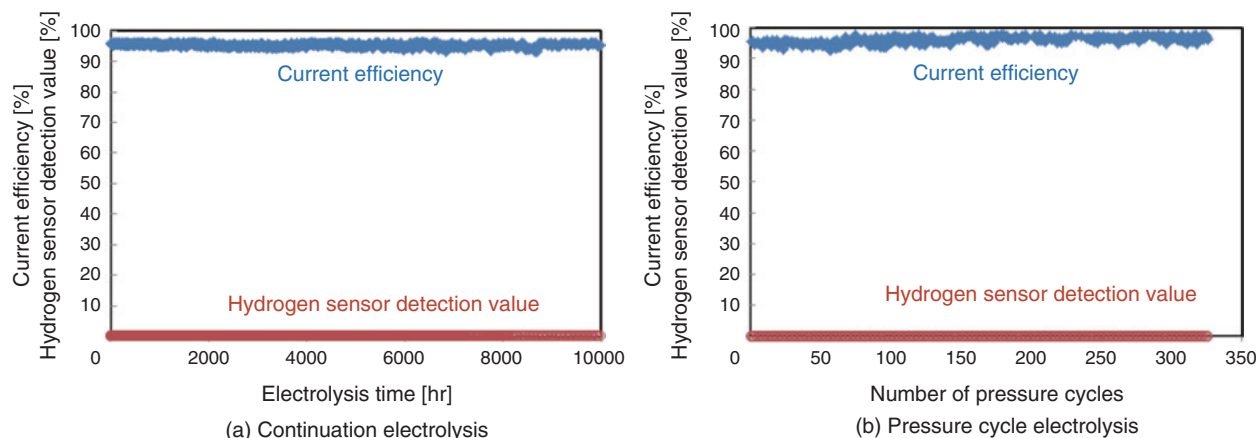


Fig. 14 Change of current efficiency and hydrogen sensor detection value at time of stack durable electrolysis

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