

Development of 70 MPa Differential-pressure Water Electrolysis Stack

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ABSTRACT

In order to accommodate the increased fuel tank storage pressure of fuel cell vehicles to 70 MPa, measures were taken to enable hydrogen stations that use Honda's proprietary differential-pressure water electrolysis technology to support higher pressures. Specifications capable of enduring long-time operation at 70 MPa were established by using a sealing structure with a high-pressure hydrogen channel in the center of the cell. In addition, the break mechanism of the proton exchange membrane was clarified, and specifications capable of sustaining the differential pressure were set. A high-pressure water electrolysis stack based on this know-how was manufactured and compared with existing hydrogen stations that use a mechanical compressor, and it was confirmed that the electric power needed to produce hydrogen compressed to 70 MPa was reduced by approximately 30%. Moreover, the water content of the hydrogen was reduced by 60% compared to that of hydrogen compressed to 35 MPa, which reduced the dehumidification energy needed for use as hydrogen fuel for fuel cell vehicles.

1. Introduction

Honda is continuing development of fuel cell vehicles (FCV) that use hydrogen as an energy source to address the two issues of reduction of CO₂ emissions and depletion of fossil fuels. Efforts are being made to increase the FCV fuel tank storage pressure from 35 MPa to 70 MPa to extend FCV cruising ranges and increase user convenience. However, there are also calls to manufacture the hydrogen used as fuel from renewable energy without using fossil fuels as much as possible. Therefore, proving tests are under way worldwide for solar hydrogen stations that use solar cells as the input power source to help expand the hydrogen supply infrastructure in parallel with FCV development⁽¹⁾⁻⁽⁴⁾. In addition, smart hydrogen stations, which are the first known stations to combine all elements from hydrogen production to the dispenser in a single package, have been operated in Saitama City and Kitakyushu City since 2014^{(5), (6)}. These hydrogen stations use Honda's proprietary differential-pressure water electrolysis technology that integrates water electrolysis and hydrogen pressurization functions, and realize a more compact, space-saving size compared to existing stations that use a mechanical compressor (Fig. 1). However, the existing differential-pressure water electrolysis stacks used in these stations have 35 MPa specifications, so measures are needed to support 70 MPa.

Figure 2 shows a schematic of differential-pressure water electrolysis. The water electrolysis reaction at high pressure

is the same as that at normal pressure, and is the water electrolysis reaction using a proton exchange membrane (PEM). In addition, electrochemical hydrogen pressurization methods operate on the principle of setting only the cathode to high pressure to obtain high-pressure hydrogen. Therefore, unlike methods that use a mechanical compressor, there is no vibration noise and motor rotation noise during hydrogen pressurization, realizing excellent quietness, and there is also no friction loss or motor loss, increasing efficiency. However, the cell structure should provide both electrochemical reactor and high-pressure hydrogen vessel functions, so a sealing structure is considered necessary to prevent external gas leaks. At the same time, the structure should have water supply performance and gas exhaust performance that do not impede the water electrolysis reaction. During the course of research on differential-pressure water electrolysis at 35 MPa, the authors established a structure that satisfies water electrolysis performance, differential-pressure sustaining performance, and external sealing performance^{(7), (8)}. Development typically has the goal of realizing differential-pressure water electrolysis with a pressure difference on the order of about a dozen MPa⁽⁹⁾, and there are no known reports of obtaining 70 MPa hydrogen by differential-pressure water electrolysis without using a mechanical compressor.

This study investigated a structure that realizes 70 MPa differential-pressure water electrolysis, manufactured an actual stack using that structure, and evaluated the performance.

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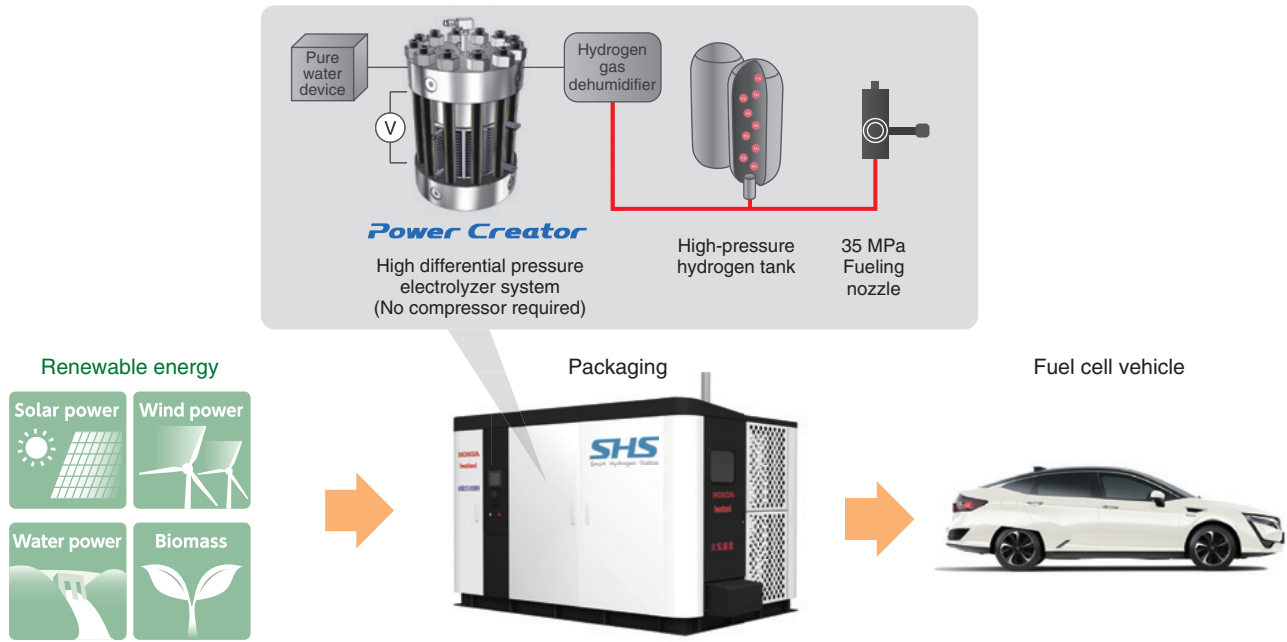


Fig. 1 Concept of Honda original smart hydrogen station

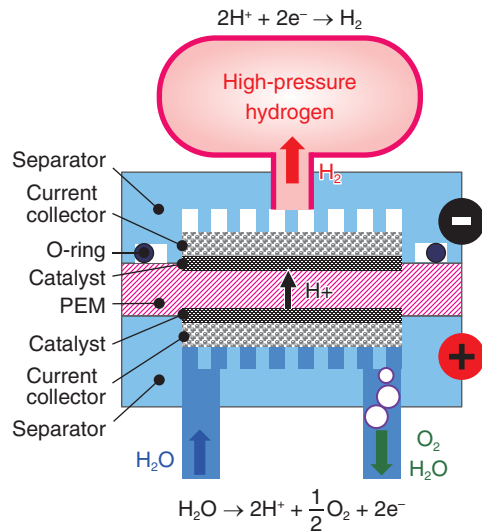


Fig. 2 Overview of high differential pressure water electrolysis

2. Approach toward Construction of Differential-pressure Water Electrolysis System that Supports 70 MPa

2.1. Understanding of Differential-pressure Sustaining Mechanism

In differential-pressure water electrolysis, the differential pressure is sustained by the PEM, so the PEM needs pressure resistance capable of enduring the differential pressure between the target hydrogen pressure and the anode-side

pressure. This pressure resistance is provided by the anode current collector, so the current collector itself should not deform and should also suppress PEM deformation relative to the pores on the current collector surface. Therefore, to help ensure that the membrane does not break even if differential pressure of 70 MPa is produced on the PEM, it is necessary to understand the minimum membrane thickness capable of sustaining this differential pressure and to clarify the differential-pressure sustaining mechanism.

2.2. Establishment of 70 MPa Sealing Structure

Figure 3(a) shows the conventional 35 MPa sealing structure, and Fig. 4 shows the location where different membrane thickness occurs due to the difference of dry-wet in the conventional structure. In the conventional structure, the PEM is exposed to the outside air, and different membrane thickness occurs between the part next to the high-pressure hydrogen channel that is kept in the wet state by the water content of the generated hydrogen and the part outside the O-rings. As shown in Fig. 5, this difference in dry-wet membrane thickness is greater at 70 MPa than at 35 MPa. Generally speaking, in order to seal with an O-ring, the design should clasp the O-ring in the installation gap and help prevent O-ring extrusion. This gap needs to be reduced as the pressure received by the O-ring increases, but the allowable gap is not specified at the high pressure of 70 MPa⁽¹⁰⁾, so likewise there should be no gap in order to help achieve 70 MPa sealing durability. Therefore, a structure with the high-pressure hydrogen channel parts [parts 7 and 8 in Fig. 3(b)] in the center of the cell was devised as shown in Fig. 3(b). In this structure, no part of the PEM is exposed to the outside air, so there is no concern

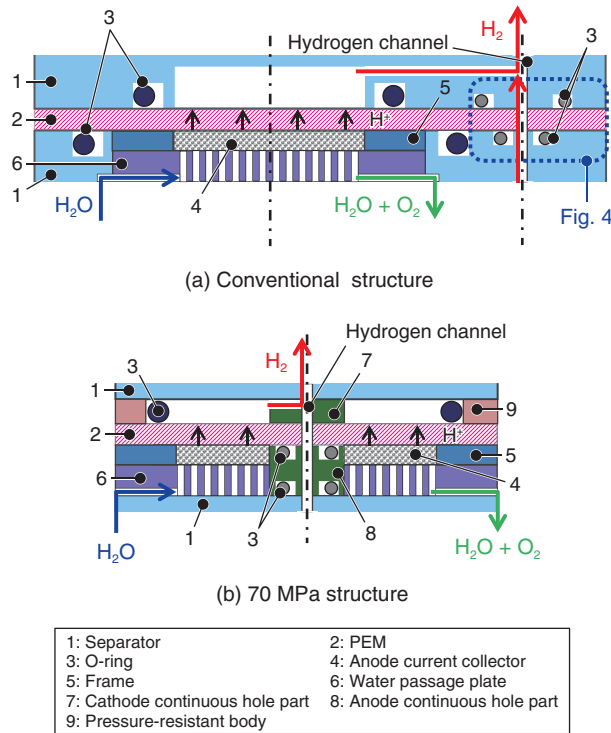


Fig. 3 Schematic of conventional and 70 MPa sealing structures

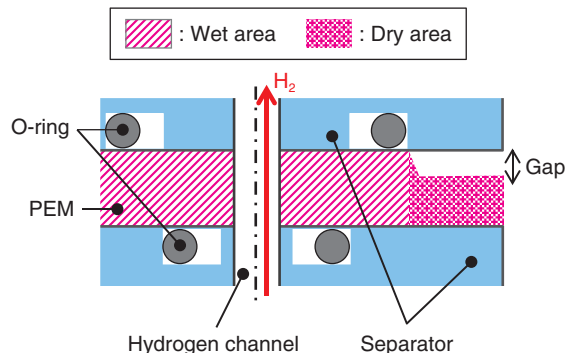


Fig. 4 Enlarged view of PEM dry-wet area in conventional sealing structure

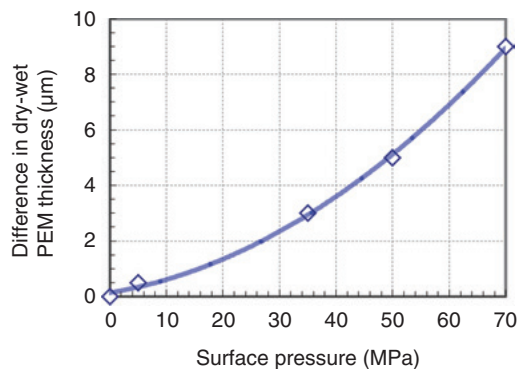


Fig. 5 Relation between surface pressure and difference in dry-wet PEM thickness (50°C, 100 μm)

of O-ring extrusion due to different dry-wet membrane thickness. Next, it was necessary to demonstrate durability to confirm that this sealing structure secures pressure resistance at 70 MPa and that there is no damage to the cell parts.

3. Experimental Method

3.1. Method for Understanding Minimum PEM Thickness

Figure 6 shows a cross-sectional view of the cell used to investigate a 70 MPa pressure-resistant structure. As described above, the structure has a hydrogen channel in the center of the cell, the current collector supports the PEM, and the O-ring provides the sealing function. A constant surface pressure is applied to the cell by a spring inside the piston, and the overall cell was manufactured in accordance with the design guidelines for high-pressure hydrogen vessels. The nitrogen gas used in the test was pressurized in steps using a gas pressurization compressor, and it was confirmed that pressures up to 70 MPa can be sustained. In addition, it was also confirmed whether there was damage to the O-ring that provides sealing performance and to the current collector parts. The test temperature for the pressure resistance test was set to 80°C, and this temperature was maintained by circulating hot water within the cell. The PEM thickness used in the test was reduced in steps starting from 200 μm to determine the minimum membrane thickness at which the differential pressure can be sustained. Based on these results, the cross-section of the PEM after the test was observed in locations with different membrane thickness to examine the mechanism by which differential pressure can be sustained.

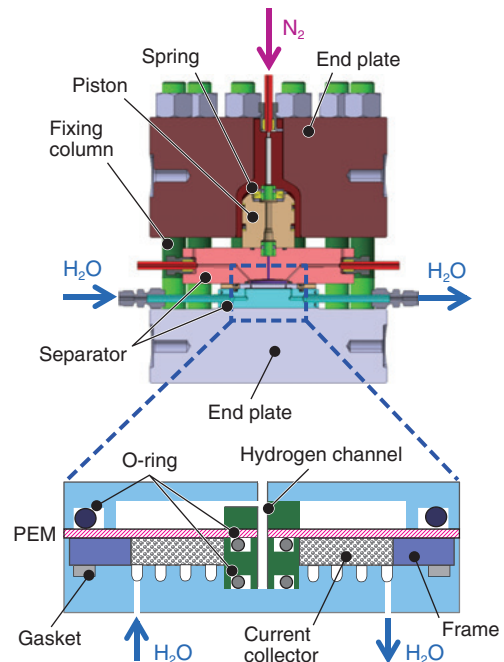


Fig. 6 Structure of 70 MPa pressure-resistant cell

3.2. Structural Durability Test Method

Figure 7 shows the evaluation system used in the 70 MPa cell structure durability test. A pressure cycle test that repeats pressurization to a maximum of 85 MPa and pressure reduction to normal pressure was performed with the target of 1000 cycles as the durability mode. The reason for this is that the solar hydrogen station currently being verified in Japan performs start-stop approximately 100 times per year⁽⁴⁾, so the target was set to the number of start-stop times for 10 years. The test medium was incompressible water, and the test was performed using an air-driven hydraulic pump with sufficient pressure resistance to make it easier to check for leaks and to shorten the durability test. Pressurization and reduction was performed by adjusting the valve output of the pressure regulator and the flow regulator beforehand and turning the solenoid valve on and off with a timer. In addition, from the viewpoint of safety, relief valves were installed before the high-pressure filter and after the pressure regulator. The temperature during the durability test was set to the maximum stack operating temperature of 65°C. Cell structure durability was evaluated by performing the above-mentioned nitrogen gas sealing test (25°C) at 70 MPa. The nitrogen permeation amount from the high-pressure side to the opposite side was collected by the water replacement method, and durability was judged by comparing the amount before and after the durability test.

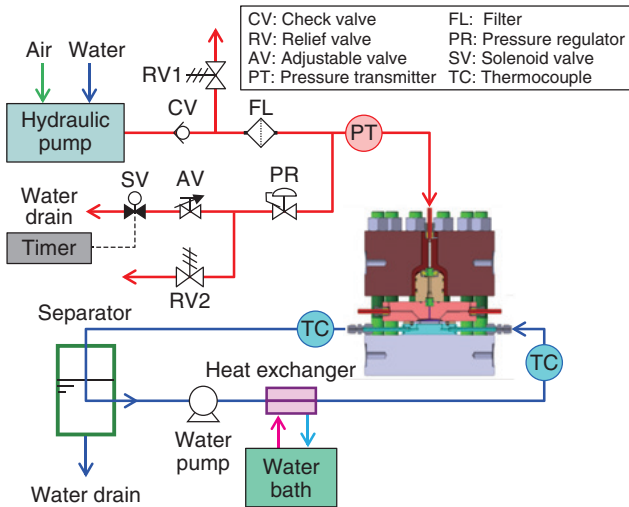


Fig. 7 Evaluation system of hydraulic durability test

4. Results and Discussion

4.1. Differential-pressure Sustaining Mechanism and Needed Membrane Thickness

Figure 8 shows the difference in differential-pressure sustaining performance at different PEM thicknesses. A differential-pressure of 70 MPa could be sustained at a

membrane thickness of 60 μm or more, but at 50 μm the membrane broke four minutes after reaching 70 MPa, and at 30 μm the membrane broke immediately after reaching 50 MPa. In addition, after the test with a membrane thickness of 60 μm , it was found that there was no damage to the PEM, O-ring or current collectors, and that the structure with a high-pressure hydrogen channel in the center can satisfy both the differential-pressure sustaining and the sealing structure functions.

The membrane cross-section at each membrane thickness was observed after the above test. Figure 9 shows schematics of the differential-pressure sustaining condition and the membrane break condition. This shows that in the condition where the membrane broke, the entire membrane was in the tensile state relative to the current collector pores, but at a membrane thickness that sustained the differential pressure, the membrane maintained the compression state relative to the current collector pores. This clarified that in order to secure durability at 70 MPa, it is necessary to determine the minimum membrane thickness necessary to sustain the differential pressure, and also the

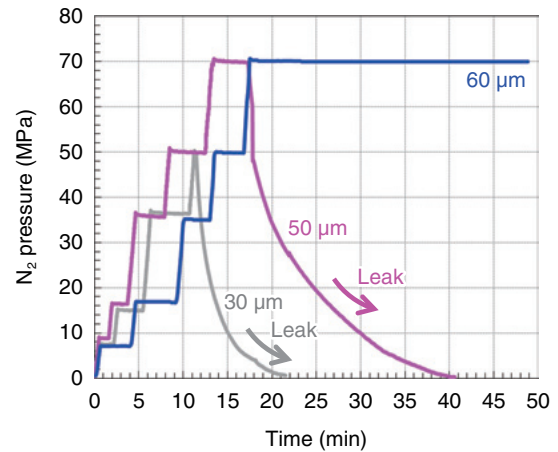


Fig. 8 Pressure sustaining characteristic by PEM thickness difference (80°C, N_2)

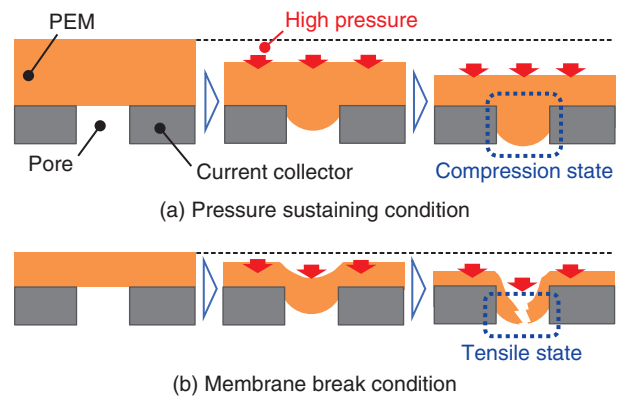


Fig. 9 Schematic of PEM cross section at pressure sustaining and membrane break conditions

Table 1 N₂ permeation amount before and after hydraulic durability test (25°C, N₂)

Measurement point	PEM permeation amount of N ₂ (cm ³ /min/cm ²)*
Before durability test	0.046
After 1000 cycles	0.046

* Average value of 3 times

amounts by which the membrane thickness decreases due to deformation at the current collector pores and due to compression creep. Therefore, PEM deformation to the pores was obtained by converting the pore volume into the membrane thickness, and was calculated to be 20 μm . In addition, PEM compression creep was determined by obtaining the property of the PEM alone, and it was found that 20 μm should be estimated. These results clarified that a PEM thickness of 100 μm or more satisfies the durability requirement.

4.2. Results of Structural Durability Test

Figure 10 shows the temperature and pressure profile in the hydraulic pressure rising and reduction durability test. The pressure rising and reduction test was performed for 1000 cycles at approximately 25 s per cycle. Table 1 compares the amount of nitrogen gas permeating to the opposite side at the start of the hydraulic pressure cycle test and after 1000 cycles in the 70 MPa sealing test. There was no difference in the nitrogen permeation amount before and after the durability test, which proved that this structure can endure extended use in terms of both differential-pressure sustainment and sealing structure performance. In addition, there was no damage to the PEM, O-ring or current collectors after the durability test, which also confirmed the durability of the parts.

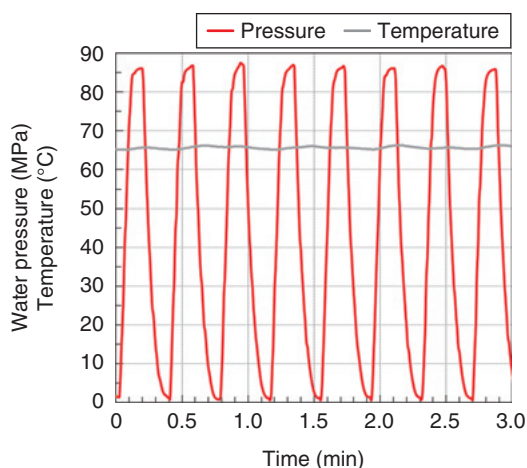


Fig. 10 Water pressure and temperature profile in hydraulic durability test

5. Evaluation of 70 MPa Stack Performance

5.1. Performance Evaluation Items

It is necessary to confirm whether changing the cell structure affects the electrolysis performance in a 70 MPa stack. Therefore, this was verified by comparing the difference in the electrolysis voltage during high-pressure water electrolysis with that of the conventional 35 MPa stack. In addition, the compressor power consumed by existing 70 MPa hydrogen stations and the pressurization energy needed by high-pressure water electrolysis were compared, and the advantage of differential-pressure water electrolysis was verified.

Meanwhile, in order to use hydrogen generated by 70 MPa high-pressure water electrolysis as hydrogen fuel for FCVs, the hydrogen quality should be as specified by SAE J2719⁽¹¹⁾ and ISO 14687-2⁽¹²⁾, and the water concentration should be less than 5 ppm. In the water electrolysis reaction, water accompanies the protons moving within the PEM, so the generated hydrogen always contains some water. The energy needed to remove the water contained in the hydrogen in a subsequent process can be estimated by quantitatively determining this amount of water, so this is important for system design. Therefore, the amount of water contained in hydrogen generated by high-pressure water electrolysis was measured in the manufactured 70 MPa stack.

5.2. Stack Performance Evaluation Method

The PEM used in the test had a membrane thickness of 100 μm , and used an Ru-Ir complex oxide catalyst as the anode catalyst and a platinum black as the cathode catalyst. These catalysts were hot-pressed to both surfaces of the PEM to manufacture the stack used in the test. Figure 11 shows the evaluation system used to evaluate the performance of the manufactured 70 MPa differential-pressure water electrolysis stack. Hydrogen permeating

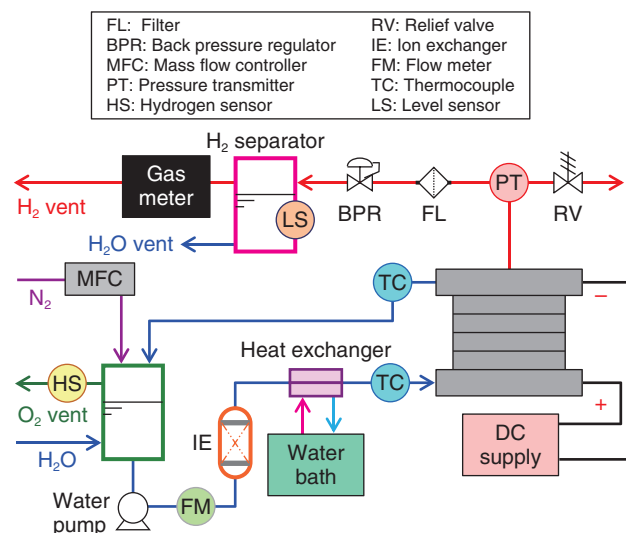


Fig. 11 Evaluation system of electrolysis stack

from the opposite electrode during high-pressure water electrolysis is included in the oxygen side, so for reasons of hydrogen safety, the test was performed by diluting with nitrogen at the oxygen-water separator and measuring with a hydrogen sensor to make sure that the hydrogen concentration was sufficiently low.

The test conditions adjusted the temperature to the stack operating temperature of 60°C using the temperature of the water circulating through the stack. The water quality was pure water, and the current density was set to 1.2 A/cm². Stack performance was evaluated by comparing the calculated and measured values of the electrolysis voltage needed to raise the pressure to 70 MPa, and by performing I-V measurement with different current values at each pressure to compare the cell voltage at different pressures. In addition, the amount of hydrogen produced was measured using a wet gas flow meter after lowering the pressure to normal pressure with the back pressure regulator. Furthermore, the amount of water permeating to the high-pressure hydrogen side during high-pressure water electrolysis was obtained by adding the rate of increase in the water level of the hydrogen-water separator on the hydrogen side and the amount of saturated vapor contained in the generated hydrogen.

5.3. Results of Stack Performance Evaluation

The know-how described above related to differential-pressure sustaining performance, sealing performance, and water electrolysis performance was used to manufacture a 70 MPa differential-pressure water electrolysis stack. Figure 12 shows a photograph of the exterior.

Figure 13 shows a graph comparing the electrolysis voltage needed to raise the pressure to 70 MPa with that of the conventional 35 MPa stack. These results clearly show that the pressurization curve up to 35 MPa matches that reported thus far. This demonstrates that the changes



Fig. 12 Photograph of 70 MPa differential-pressure water electrolysis stack

Table 2 Electrolysis voltage for 70 MPa compression

	Electrolysis voltage for 70 MPa compression (mV)
Calculated value	78
Measured value	120

in the cell structure between the 70 MPa stack and the conventional 35 MPa stack do not have an adverse effect on water electrolysis performance. In addition, Table 2 compares the measured value with the calculated value of the electrolysis voltage E_{WE} needed for high-pressure water electrolysis as derived when ir is zero in Eq. (1)⁽¹³⁾. The reason why the measured value is 42 mV larger than the calculated value is assumed to be due to the increase in the direct-current resistance component resulting from the rise in PEM resistance when the PEM is highly compressed.

$$E_{WE} = E_0 + \frac{RT}{2F} \ln \frac{P_1}{P_2} + ir \quad (1)$$

E_{WE} : Electrolysis voltage measured value [V]

E_0 : Theoretical electrolysis voltage [V]

R : Gas constant [J/(K·mol)]

T : Absolute temperature [K]

F : Faraday constant [C/mol]

P_1 : Hydrogen partial pressure on high-pressure side [MPa]

P_2 : Hydrogen partial pressure on low-pressure side [MPa]

ir : Direct-current resistance voltage [V]

Based on these results, Table 3 compares the amount of power needed to compress 1 kg of hydrogen to 70 MPa with that of existing hydrogen stations⁽¹⁴⁾. These results show that the hydrogen pressurization energy needed by differential-pressure water electrolysis is less than that for any currently operated hydrogen station, and that power consumption can

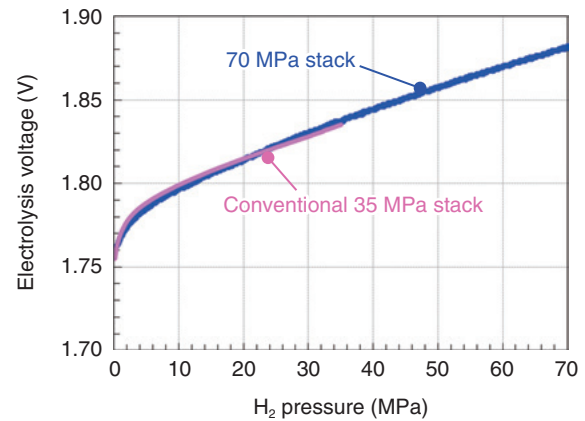


Fig. 13 Hydrogen compression curve of 70 MPa stack and conventional 35 MPa stack (60°C, 1.2 A/cm²)

Table 3 Comparison of energy consumption for hydrogen compression

Manufacturer (Location)	Energy consumption for Hydrogen compression (kWh/kg-H ₂)
Honda 70 MPa stack	3.71
JHFC (Asahi, Yokohama)	6.44
JHFC (Daikoku, Yokohama)	4.54
JHFC (Senju, Tokyo)	4.82

be reduced by approximately 30% compared to the amount of power consumed by a mechanical compressor.

Figure 14 shows the graph obtained by performing I-V measurement at each pressure and using Eq. (2) below to obtain the voltage efficiency (HHV conversion). The I-V slope at 70 MPa is larger than that at 35 MPa, and this is presumed to be due to an increase in the direct-current resistance component [*ir* term in Eq. (1)] accompanying the increase in PEM resistance. As a result, the obtained voltage efficiency is 78% at 70 MPa and 1.2 A/cm². This is lower than the voltage efficiency of 81% at 35 MPa, but also higher than the initially predicted 75%, so better than expected efficiency was obtained.

$$\eta_v = \frac{E_0}{E_{WE}} \times 100 \quad (2)$$

η_v : Voltage efficiency [%]

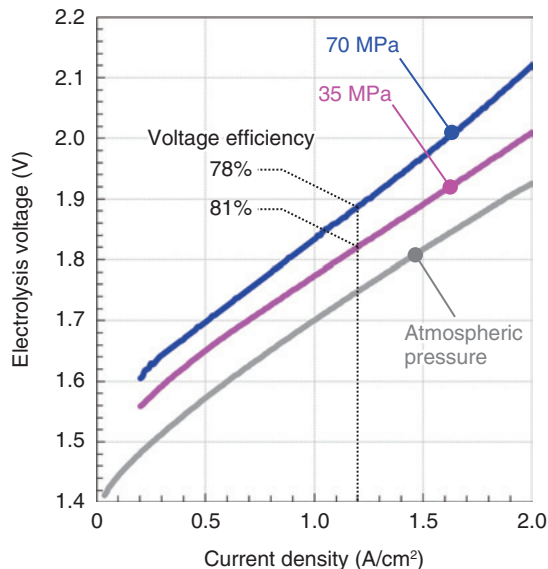
Fig. 14 Effect of H₂ pressure on I-V curve (60°C)

Figure 15 shows the transition in current efficiency due to pressure. Current efficiency indicates the production rate of hydrogen generated relative to the force current, and is calculated from Eq. (3). It was found that the current efficiency decreases as the pressure increases, but the rate of decrease lessens at higher pressures of 35 MPa or more. Current efficiency was initially thought to decrease in inverse proportion to the pressure, so 75% had been assumed⁽⁷⁾, but the results showed that current efficiency of 83% was achieved at 70 MPa.

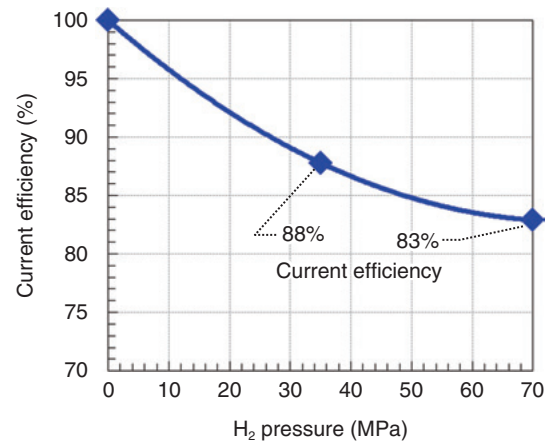
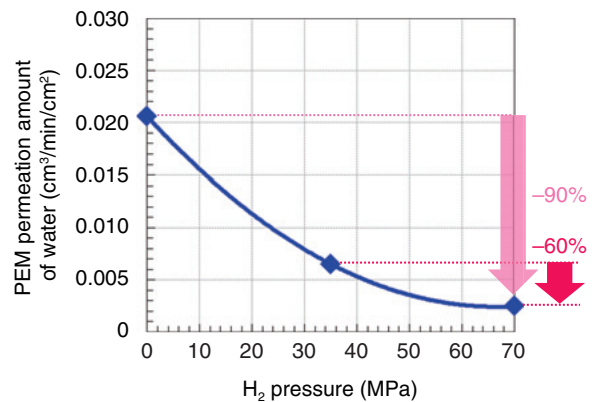
$$\eta_A = Q \cdot \left(\frac{I_{WE} \cdot 3600}{F} \cdot \frac{1}{2} \right)^{-1} \times 100 \quad (3)$$

η_A : Current efficiency [%]

Q : Amount of hydrogen generated [mol/hr]

I_{WE} : Electrolysis current [A]

Figure 16 shows the relationship between the pressure and the amount of water permeating to the high-pressure cathode. This shows that the amount of water decreases as

Fig. 15 Effect of H₂ pressure on current efficiency (60°C, 1.2 A/cm²)Fig. 16 Effect of H₂ pressure on PEM permeation amount of water to cathode (60°C, 1.2 A/cm²)

the pressure increases, and at 70 MPa is 60% less than that at 35 MPa, and 90% less than that at normal pressure. This indicates that the water content of the generated hydrogen decreases, which suggests that the internal volume of the high-pressure hydrogen-water separator can be reduced, and that the energy required for dehumidification can also be reduced compared to that at 35 MPa. This provided prospects for additional system simplification.

6. Conclusion

A pressure-resistant structure for a 70 MPa differential-pressure water electrolysis stack was investigated and durability tests of this structure were performed. As a result, the following conclusions were obtained.

- (1) The membrane thickness limit capable of sustaining a differential-pressure of 70 MPa was determined, and the mechanism by which differential-pressure can be sustained by the PEM was clarified.
- (2) The sealing structure with a high-pressure hydrogen channel in the center used by a 70 MPa stack was proven to have durability capable of enduring the equivalent of 10 years of operation.

A 70 MPa differential-pressure water electrolysis stack that takes into account the above know-how was manufactured and the performance was verified. The following results were obtained.

- (1) Use of 70 MPa differential-pressure water electrolysis successfully reduced the electric power needed to generate hydrogen compressed to 70 MPa by approximately 30% compared to that for existing hydrogen stations that use a mechanical compressor.
- (2) The water content of the generated 70 MPa hydrogen was 60% lower than that at 35 MPa, so the energy required for dehumidification decreases, providing prospects for further simplifying the system.

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