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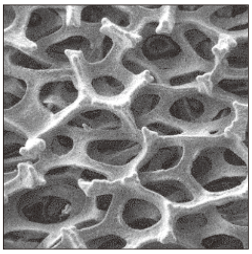

Application of Porous Metal Celmet to AEM Water Electrolyzers

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Anion exchange membrane (AEM) water electrolysis offers the low-cost and high-efficiency hydrogen production compared to conventional methods and has attracted significant attention. The authors developed a layered nickel (Ni) Celmet, which is a product of Sumitomo Electric Toyama Co., Ltd., for the application of porous transfer layers (PTLs) in AEM water electrolyzers. This paper evaluates its physical properties and electrolysis performance, and demonstrates its applicability to water electrolysis cells without flow channels in bipolar plates.

Keywords: AEM water electrolysis, Celmet, porous metal, porous transfer layer (PTL), bipolar plate

1. Introduction

The use of hydrogen is spreading in various fields, such as fuel cells, hydrogen gas turbines, and hydrogen boilers, as a new alternative energy carrier to petroleum. Notably, hydrogen can be produced through water electrolysis using electricity generated from a renewable energy source in place of fossil fuels. Hydrogen produced in this way is called “green hydrogen” and is expected to serve as a core technology for a decarbonized society since it does not emit carbon dioxide.(1), (2)

There are various forms of water electrolysis used, and they have been weighed in terms of technological characteristics, applicable targets, and economic efficiency. Among these forms, anion exchange membrane (AEM)*1 water electrolysis, which uses AEMs as the diaphragms, has been attracting attention recently. This system operates in an alkaline environment, offering the advantage that non-precious metal catalysts can be used. As a result, it lowers hydrogen production costs and is also effective in the efficient use of precious metal resources. Further, when compared with alkaline water electrolysis, which operates in the same alkaline environment, AEM water electrolysis has the advantage that it can achieve higher current densities, permitting more efficient hydrogen production in more compact systems. Although AEM water electrolysis excels in both economic and operational performance as described above, it still suffers problems with durability and other properties. Research institutions around the world are promoting research and development to solve these problems.

A typical AEM water electrolysis cell is shown schematically in Fig. 1. Catalyst layers are arranged on both sides of the AEM, where water electrolysis reaction progresses. Porous substrates called “porous transfer layers (PTLs)”*2 are placed outside the catalyst layers. These PTLs are required to be highly porous to ensure adequate transfer of a solution to the catalyst layers while discharging smoothly the gas generated. Located further outside are bipolar plates*3 with flow channels cut on them. These plates conduct electricity to the PTLs and transfer the gas discharged from the layers.(3)

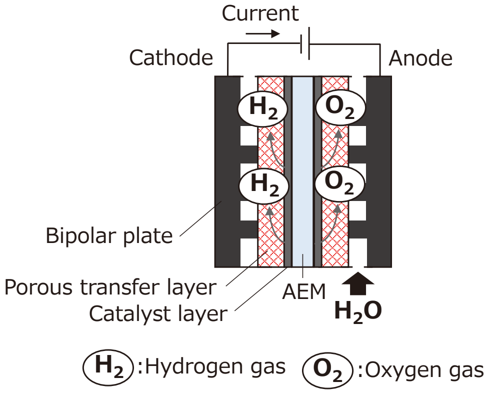

Fig. 1. AEM water electrolysis cell

Celmet made by Sumitomo Electric Toyama Co., Ltd. is a porous metal sheet with a three-dimensional network structure and a porosity of 90% or more. Due to its high porosity, this product is used for various components, including current collectors for nickel (Ni) hydrogen cells, current collectors for fuel cells,(4), (5) and catalyst carriers.(6) Since a three-dimensional network structure was considered suitable for PTL, we began a study on the application of Ni Celmet to PTLs.

In addition to high porosity, many other characteristics are required of PTLs. Table 1 summarizes the characteristics required of typical PTLs, the physical properties necessary for achieving these characteristics, and their evaluation indicators. The first characteristic is the transferability of a solution or gas, which is the reason that PTLs are required to be highly porous. To meet this requirement, PTLs must allow a fluid to pass through in their thickness direction. The second characteristic is the catalyst retainability of the surface. If the surface is significantly irregular, the catalyst will sink into the depressions and reduce its effective amount. Therefore, the surface must be highly smooth with a minimum number of irregularities. The third characteristic required of PTLs is protection of the AEMs from damage. This characteristic is thought to be achieved by combining several factors, such as minimizing protrusions, rounding them, and using a soft frame. These characteristics could not be achieved by just applying Celmet to PTLs. After inquiring into the thickness of Celmet and its combination, we developed a Celmet suitable for the PTLs of AEM water electrolyzers. This paper discusses the various characteristics and electrolytic performance of the Celmet developed.

Table 1. Characteristics required of PTLs

Characteristics required		Physical properties necessary for achieving the required characteristics	Evaluation indicators
1	Transportability of liquid and gas	It is easy for a fluid to pass through in the thickness direction.	Pressure loss
2	Catalyst retainability	The surface is extremely smooth.	Surface roughness Sa
3	AEM protectability	The layer contains a minimum number of protrusions, the framework is soft, and so on.	Short-circuit pressure

2. Experimental Method

2-1 Fabrication of layered Celmet

Generally, porous metal sheets improve surface smoothness as they are rolled thinly. However, the density of the frame increases at the same time, causing pressure loss*4 to increase. Therefore, it has been very difficult to achieve high surface smoothness and a low pressure loss at the same time. In this study, we conceived an idea of achieving these characteristics on the front and rear surfaces of the PTL (Fig. 2). Specifically, we obtained high surface smoothness by locating a thinly rolled Celmet with a small pore size on the surface while being in contact with the AEM. On the bipolar plate side, a thickly rolled Celmet with a larger pore size was placed to obtain a low pressure loss.

Fig. 2. Conceptual diagram of layered Celmet

Celmet is made by conductively treating a polyurethane foam*5 substrate, electroplating it, and then baking off the polyurethane foam by heat treatment. In this process, the pore size of Celmet can be changed by changing the pore size of the polyurethane foam. In this study, we prepared two types of Celmet, one with a large pore size and the other with a small pore size, and overlaid one on the other to fabricate a layered Celmet (Fig. 3). The overall thickness was adjusted to 0.30 mm, the standard thickness of typical PTL.

In this study, we performed the evaluations described in Sections 2-2 to 2-6 to check the performance of the layered Celmet that was developed for use as PTL. For comparison, we also prepared Ni felt, which is commonly used as PTL. Measuring the characteristics of both substrate samples by the same method and comparing the results made it possible to comparatively evaluate the layered Celmet developed.

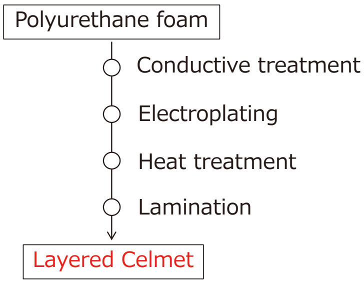

Fig. 3. Layered Celmet fabrication process

2-2 Pressure loss measurement method

We prepared a fixture, which is illustrated schematically in Fig. 4. When air is fed into the fixture at a predetermined rate from the surface of the PTL through an air supply tube, the air passes through the PTL and is discharged from the rear surface. Using this fixture, we measured the pressures when air was fed with and without a PTL and defined the difference between the two measured values as the pressure loss.

The diameter of the air supply tube was 20 mm. The air flow rate was adjusted within the range of 0 to 0.8 L/min. Since this flow range was equivalent of the amount of gas generated on the hydrogen generation side when electricity is applied in the current density range of approximately 0 to 40 A/cm², this air flow rate was considered to cover the actual operating conditions.

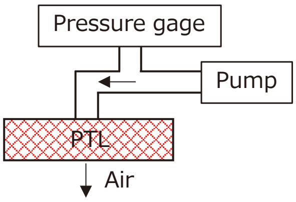

Fig. 4. Pressure loss measurement fixture

2-3 Surface roughness measurement method

We evaluated the surface roughness of the PTL in terms of Sa.*6 Although the catalyst retainability of the sheet surface was thought to correlate with the contact area with the AEM, we used Sa in this study as a substitute due to the difficulty in quantifying the contact area. A laser microscope (VK-X100 made by Keyence Corporation) was used for the measurement. The Sa was measured at 5-fold magnification in 10 random fields of view on the substrate surface, and the average of the measured values was taken as the Sa of the substrate.

2-4 Short-circuit pressure measurement method

Figure 5 shows schematically the measurement fixture. In this study, we used a 0.05 mm thick PTFE*7 sheet in place of an AEM because the AEM is weak and difficult to handle. This sheet was punched to create a 25 × 25 mm size opening, and a PTL cut to the same size was fitted into the opening. Then, another PTFE sheet was placed on top and brought into contact with the PTL. It was then vertically sandwiched between two pairs of a metal plate and insulating material, and a vertical load was applied to the structure. Until the load was applied, the upper metal plate and PTL had been separated by the PTFE sheet and completely insulated from each other. However, as the load was increased, the PTFE sheet was damaged by the surface frame of the PTL, causing a short circuit between the upper metal plate and PTL. The pressure at this point is called the short-circuit pressure. Since the higher the short-circuit pressure is, the harder it is to damage the PTFE sheet, it can be used as an indicator of the damage resistance of the AEM. The measurement was repeated five times, and the average of the measured values was taken as the short-circuit pressure of the substrate.

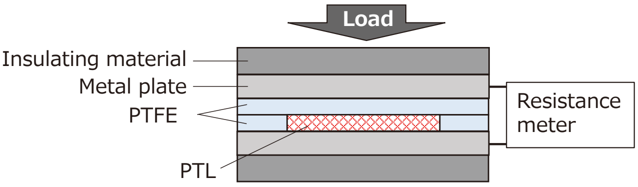

Fig. 5. Short-circuit pressure measurement fixture

At the time of short-circuit pressure measurement, the Vickers hardness*8 of the porous frame was also measured. In the measurement, the substrate was first embedded in epoxy resin*9 and then polished to expose the cross-section of the frame. Following the above, a diamond indenter with a tetrahedral tip was pressed against the frame for 10 seconds at a reasonable test load. In this process, since the resin surrounding or behind the frame could potentially affect the measurement results, multiple test loads were considered, and the load that minimized the variation in measured values for every sample was selected. Finally, the lengths of the two diagonals of the indentation remaining after removal of the test load were measured with an optical microscope. The Vickers hardness was determined by substituting the average length into the following equation.(7)

$$\text{Vickers hardness (HV)} = 0.1891 \times F/d^2 \quad \cdots\cdots\cdots\cdots\cdots (1)$$

F: test load [N]
d: average length of the diagonals of indentation [mm]

2-5 Method for measuring electrical resistance in thickness direction

A substrate was cut to 25 × 25 mm and sandwiched between two gold-plated stainless plates of the same size. After a load was applied to this laminated body, the electrical resistance between the gold-plated stainless plates was measured. This measurement was repeated five times, and the average was taken as the electrical resistance in the thickness direction of the substrate. The pressure to be applied was selected within the range of 0 to 10 MPa. Pressures in this range could be exerted on the PTL when the water electrolysis cell is tightened and by the gas generated.

2-6 Electrolysis voltage measurement method

We evaluated electrolysis using an AEM electrolysis cell we designed. Carbon paper*10 was used for the cathode PTL, while a layered Celmet and Ni felt were used for the anode PTL. With regard to catalysts, we used a Pt catalyst for the cathode and an IrOx catalyst for the anode. A method known as CCS*11 was used to apply these catalysts on the substrate. Prior to the main electrolysis, the specimen was preconditioned by applying a constant current to it for a predetermined period of time. In the main electrolysis, the electrolysis voltage was plotted at the point where the specimen was held at each current density for three minutes. In this study, we used two types of water electrolysis cells: one with flow channels carved into the bipolar plate and the other without flow channels in the plate (Fig. 6). Cells with flow channels are usually used for AEM water electrolysis, but this method has shortcomings: cutting flow channels is costly, and pressure from the counter electrode causes the PTL to fall into the channels and reduces electrolytic performance. In this study, we also evaluated a cell without flow channels to eliminate these shortcomings. It is generally known that a cell without flow channels prevents the generated gas from being discharged outside the cell and significantly reduces the electrolytic performance. However, since a layered Celmet exhibited a low pressure loss, this material was expected to function adequately without flow channels.

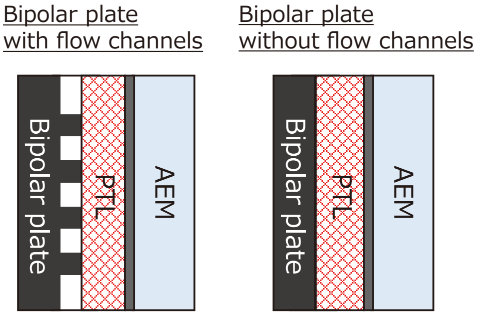

Fig. 6. Two types of water electrolysis cells that were evaluated in this study

3. Measurement Results and Analysis

3-1 Pressure loss

The pressure loss measurement results are shown in Fig. 7. At every flow rate, the layered Celmet demonstrated significantly lower pressure loss than the felt. Figure 8 shows a SEM*12 image of the low pressure loss surface (on the bipolar plate side) of the layered Celmet, in order to analyze the measurement results. This figure shows that, in the Celmet, interconnected pores derived from the polyurethane foam are interconnected in both the thickness and in-plane directions. It is considered that the Celmet reduced the pressure loss by enabling the fluid to flow smoothly through these interconnected regions.

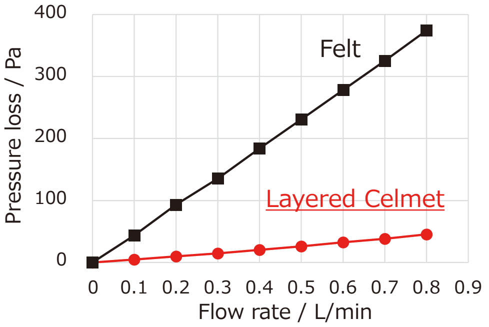

Fig. 7. Pressure loss measurement results

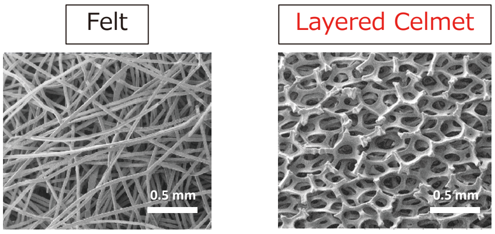

Fig. 8. A SEM image of the surface (on bipolar plate side)

3-2 Surface roughness

Subsequently, we measured the surface roughness Sa of the layered Celmet and felt, using a laser microscope. For the layered Celmet, its Sa of the smoother side (on the AEM side) was measured. The Sa of the felt was 28 µm, while that of the layered Celmet was 13 µm, verifying that the latter was significantly smoother than the former. High smoothness of the layered Celmet is accounted for by the structure of its frame. As shown in Fig. 3, the base polyurethane is burned off in the production process, leaving a hollow frame. As a result, when rolled with a rolling press,*13 the frame itself on the outermost surface is crushed, thereby enhancing further the surface smoothness (Fig. 9). A SEM image of the surface also shows that the frame on the surface of the layered Celmet was crushed and formed a smooth surface (Fig. 10).

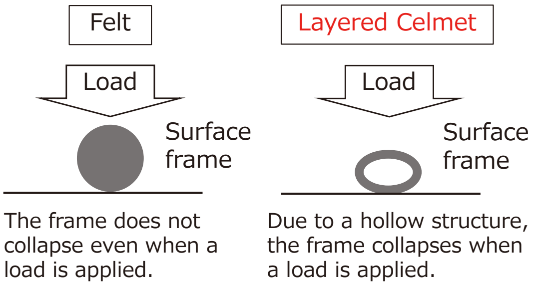

Fig. 9. Difference in the structural deformation of a frame when rolled

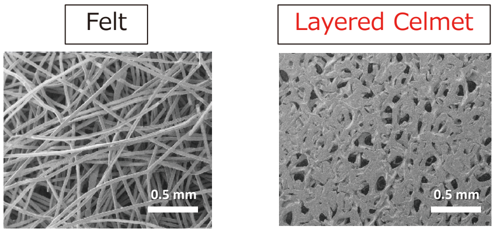

Fig. 10. A SEM image of the surface (on AEM side)

3-3 Short-circuit pressure

The evaluation result for the short-circuit pressure is shown in Fig. 11. The short-circuit pressure of the layered Celmet was more than double that of the felt. This means that the former is less likely to damage the AEM than the latter.

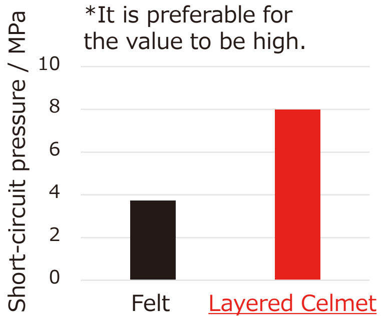

Fig. 11. Short-circuit pressure measurement results

There are two possible reasons that the layered Celmet exhibits high short-circuit pressure. One is that the layered Celmet is highly smooth with a minimum number of protrusions that will damage the membrane, as discussed in Section 3-2, or a large area of contact with the AEM disperses the pressure. The other one is that since the layered Celmet undergoes a high-temperature heat treatment process, as shown in Fig. 3, its grain size increases and reduces the hardness of the frame. To verify this reason, we measured the Vickers hardness of the frame. The results are shown in Fig. 12. As estimated above, the hardness of the layered Celmet was lower than that of the

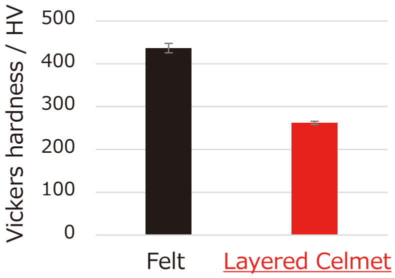

Fig. 12. Vickers hardness measurement results

felt. We concluded that the combined action of these properties of the layered Celmet led to the difference in short-circuit pressure that was revealed in this study.

3-4 Electrical resistance in thickness direction

We measured the electrical resistance of the substrate in its thickness direction in the pressure range of 0 to 10 MPa. The results are shown in Fig. 13. This figure shows that, at every pressure, the electrical resistance of the layered Celmet was lower than that of the felt. The possible reason is that since the felt contains many interfaces between its fibers, integration of the contact resistance of these interfaces increases the electrical resistance. In contrast, all frames of the layered Celmet are interconnected, and this reduces the resistance.

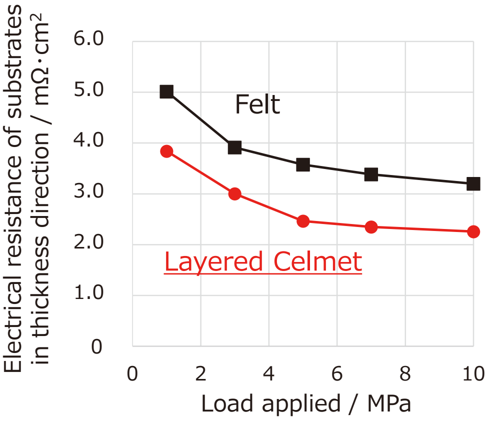

Fig. 13. Electrical resistance in thickness direction

3-5 Electrolysis voltage

Finally, the results of electrolysis voltage measurement are shown in Figs. 14 and 15. Although the actual values of electrolysis voltage measured have been withheld, they can be directly compared since the vertical axes of these figures are graduated on the same scale.

Figure 14 shows the electrolysis evaluation results for a water electrolysis cell with flow channels in the bipolar plates. It was confirmed that the electrolysis voltage of the layered Celmet was lower than that of the felt on both the low and high current density sides. These results were thought to be attributable to high catalyst retention and low pressure loss of the layered Celmet, respectively. Figure 15 shows the electrolysis evaluation results for a water electrolysis cell without flow channels in the bipolar plates. The felt further increased the electrolysis voltage in the high current density region. This was considered to be attributable to the fact that the porous transport layers alone could not vent the generated gas outside the cell, and this reduced the effective reaction area. On the other hand, it was confirmed that electrolysis voltage of the layered Celmet increased very little. This result suggested that the gas can be discharged sufficiently by using layered Celmet even if no flow channel is cut in the bipolar plates.

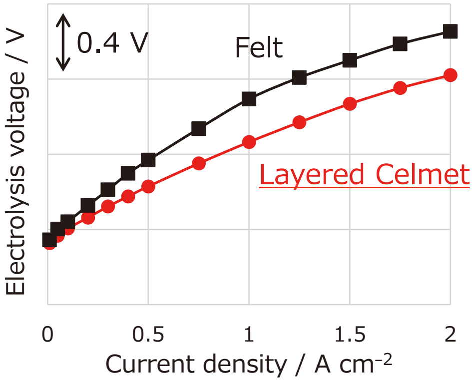

Fig.14. Electrolysis voltage measurement results for bipolar plate with flow channels

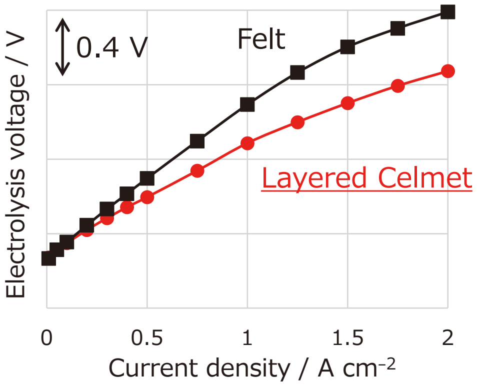

Fig. 15. Electrolysis voltage measurement results for bipolar plate without flow channels

4. Conclusion

In this paper, we evaluated the layered Celmet we developed for use as the PTLs of AEM water electrolyzers and confirmed that the new material provides superior performance when used for porous transfer layers. We also evaluated the performance of a water electrolysis cell with no flow channel cut in the bipolar plates, and the results have suggested that the use of layered Celmet enables the cell to function satisfactorily without a flow channel.

Currently, we are receiving many inquiries for Celmet for AEM water electrolysis applications. In the future, we will promote studies on the application of Celmet so that we will be able to recommend to users the Celmet structure most suitable for their cell structure and catalyst.

- Celmet is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

Technical Terms

*1 Anion exchange membrane (AEM): A membrane that selectively permeates anions.

*2 Porous transfer layer (PTL): A porous material that serves as a reaction site for water electrolysis by transferring the reaction liquid and gas.

*3 Bipolar plate: A plate-like structure that conducts an electric current and distributes the reaction liquid and gas in an electrochemical device.

*4 Pressure loss: A phenomenon where the pressure of a fluid is reduced by the resistance generated when the fluid flows through a pipe.

*5 Polyurethane foam: A foamed material produced by adding a foaming agent during polyurethane synthesis. Polyurethane foam is used as a heat-insulating or cushioning material.

*6 Arithmetic average surface height Sa: The average of the absolute values of surface irregularities. It is used as an evaluation indicator of surface roughness.

*7 PTFE: A type of fluororesin having superior insulation performance and slipping property.

*8 Vickers hardness: A measure of the hardness of a material. The surface of the material is pressed with an indenter with a tetrahedral tip to measure and quantify the deformation resistance of the material.

*9 Epoxy resin: A resinous material containing an epoxy base. Due to its heat-hardening property, this material is used for various purposes, including embedment of substrates.

*10 Carbon paper: A papyraceous conductive material composed of carbon fibers.

*11 CCS: The abbreviation for Catalyst Coated Substrate, a method for coating a catalyst on a porous transfer layer. This method is distinguished from Catalyst Coated Membrane, a method for coating a catalyst on a membrane.

*12 SEM: The abbreviation for Scanning Electron Microscope, a device for observing the surface of a material by detecting the secondary electrons or reflection electrons which are discharged when the material is irradiated with electron beams.

*13 Rolling press: A processing method that compresses materials into shape using rollers. It is used to make the thickness and density of the materials uniform.

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