8. Task 8 Development of Hydrogen Production Technology

8.1 Research and Development Goals

This study is directed to establish hydrogen production technology in electrolysis of water by means of Solid Macromolecular Electrolyte Method that is expected to be more efficient and less costly than traditional hydrogen production methods. In the fiscal year 2001 as third year of WE-NET 2nd stage, along with the development of large area electrolysis cell lamination (electrolysis area:2,500cm^2 10 cells) and continuous operation of the electrolyte for commercialization of, production technology, manufacturing of electrolysis cell (electrode area 1,000cm^2 ,25cells) for hydrogen refueling station in connection with the Task 7 (the development of hydrogen refueling station) will be implemented.
And, also, a few different type of high temperature resistant molecule electrolyte membrane to be usable in high temperature will be manufactured and evaluated its ion conductivity and electrolysis performance of the membrane.

Outline of this report is presented below.

8.2 Results in fiscal year 2001

8.2.1 Development of Hydrogen Production Technology by Electroless Plating

8.2.1.1 Targets of Research & Development Work

1.1 Improvement of the long-term durability
1.2 Study of optimization of the cell construction
1.3 Development of large-area cell stacking technology
1.4 Experimental production of the cell stack for hydrogen refueling station

8.2.1.2 Improvement of the long-term durability

Considering its practical operation, we conducted a long-term durability evaluation using the water electrolysis cell stack. The result is shown in Fig.8.2.1-1. As shown in the figure, there was little decrease of energy efficiency even after 400 cycles of operation starts and stops and it was also confirmed that energy efficiency of about 90% could be kept at operating temperature of 373K even after 400 cycles of starts and stops. Fig.8.2.1-2 shows appearance of 10 cells layered stack used for this electrolysis test. We decided to adopt the equivalents of the cells used in this durability test to the electrolysis stack for hydrogen refueling station.

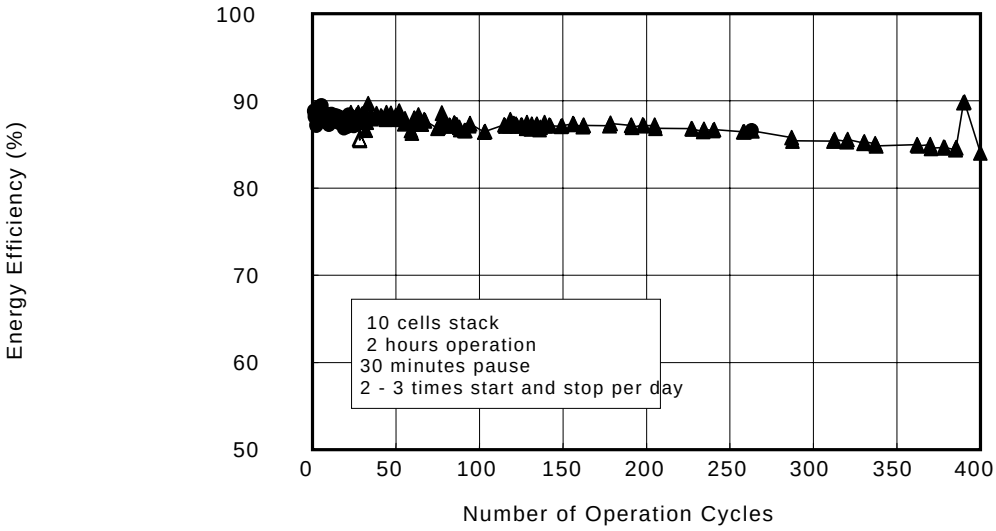


Fig.8.2.1-1 10-cells stack electrolysis test results, 1,000cm² cells

＜Test conditions＞

・Cell area size: 1,000cm² (10 cells)

・Operating pattern: Electrolysis 2Hr/Pause 30min.

・Operating conditions: Temp.353K/Press.0.7MPa

・Current density: 1A/cm²

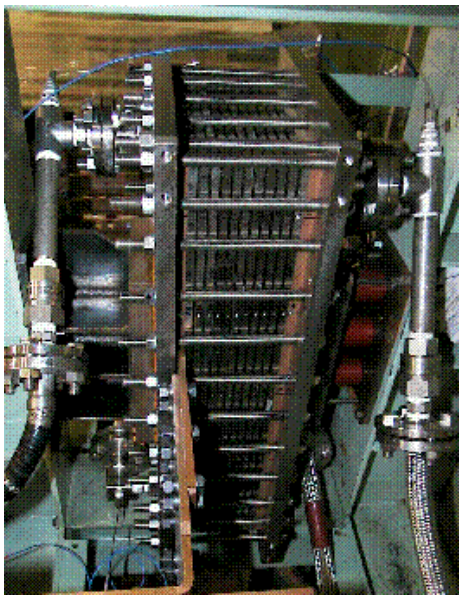


Fig.8.2.1-2 Appearance of electrolysis test using 10 cells layered stack

(Cell electrode area size: 1,000cm²)

8.2.1.3. Study of optimization of the cell construction

Based on the flow analysis results of the water distribution (header part) from the separator and the layered cell stacks, we designed and trially made a 2,500 cm² separator, and 1,000cm² separator for H_2 refueling station, as well as cell stacks for both of them, to conduct their evaluation tests.

8.2.1.4. Development of large-area cell stacking technology

For the evaluation test of 2,500cm^2 cell stack, we enhanced our test facilities by newly adding a D.C. current power source (DC50V-7, 500A spec.), etc. We produced and assembled the 2,500cm^2 cell stack using the same production method for the cell stack for H_2 refueling station.

Fig.8.2.1-3 shows the membrane electrode assembly as produced and Fig8.2.1-4 the appearance of the separator. The cell showed a very good catalyst support condition to the electrolyte membrane without showing appearance of non-uniformity.

Regarding the 2,500cm^2 cell, we produced and evaluated 2-cells stack. Fig.8.2.1-5 shows the view of the experiment and Table8.2.1-1 the test results. The targeted energy efficiency of over 90% could be achieved as in the case of the 1,000cm^2 cell stack.

Fig.8.2.1-3 Membrane electrode assembly (entire view)
(cell electrode area size: 2,500cm^2)

Fig.8.2.1-4 Separator (entire view)

Fig.8.2.1-5 (2 cells stack,2500cm²)

Table 8.2.1-1 Test results of 2-cells layered stack (cell area size: 2,500cm²)

Item	Specification
Cell area size	2,500cm²
Number of cells	2
Electrolysis temp.	353K
Current density	1A/cm²
Current efficiency	98.8%
Energy efficiency	91.1%

8.2.1.5 Experimental production of cell stack for H_2 refueling station

The cell stack for the H_2 refueling station uses 25 cells of 1,000 cm² layered per stack, and this cell stack has been installed for two units of the station system. Appearance of the 25-cells stack is shown in Fig. 8.2.1-6. Also, the system electrolysis pressure has been set at 0.6MPaG, and the system configuration is such that no further gas compressor is required after the gas production.

The PEM water electrolysis hydrogen production system for H_2 refueling station was installed at Shikoku Research Institute Inc. (in Takamatsu City, Japan) in December 2001, and its operational adjustment and its initial performance test have been conducted since January, 2002. Results of its initial performance test are given in Table 8.2.1-2. As shown in the table, achievements of its initial target performances as the water electrolysis unit could be successfully confirmed.

We are planning to have test operation connecting metal hydride, high pressure gas compressor, and dispenser to verify the adaptability for H_2 refueling station.

Specification of the 25 cells layered stack

Cell area size : 1,000cm^2

Layered cells/stack : 25 cells/stack

Electrolysis press. : 0.6MPaG

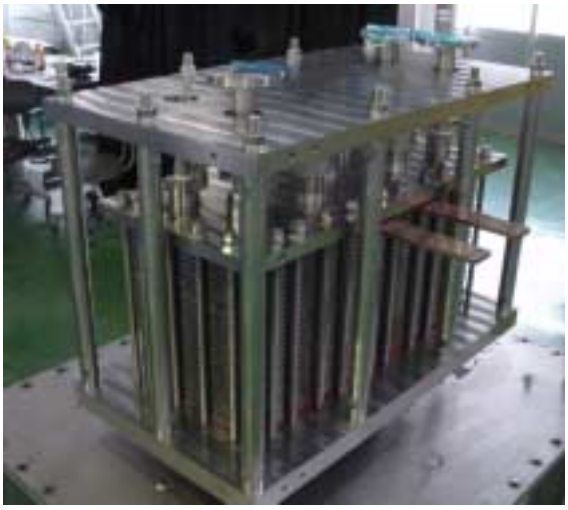


Fig.8.2.1-6 1,000cm^2、25 cells stack

Table8.2.1-2 Results of initial performance test of PEM water electrolysis system for H_2 refueling station

Item	Specification	Test results (normal)	Test results (max.)
H_2 production rate	20/30Nm^3/h (Nor./Max.)	20.6Nm^3/h	30.3Nm^3/h
Current density	1.0/1.5A/cm^2	1.0A/cm^2	1.5A/cm^2
Pressure	0.5MPa G	0.507MPa G	0.522MPaG
Energy efficiency	＞90% (at normal)	90.3%	85% (Reference value)
Dew point	＜－213K	－213K	－213K
Oxygen conc.	＜10ppm	1ppm	1ppm

Test conditions

Cell area size; 1,000cm^2

Numbers of cells/stacks; 50 cells (25 cells×2 stacks)

Electrolysis temperature; 354K

8.2.1.6. Conclusion

In the first half of this fiscal year, we devoted our research and developmental efforts especially to optimization of the specification for the cell stacks for H_2 refueling station as well as their production technology.

As a result, we could achieve the successful results of development of the PEM water electrolysis type H_2 production system as shown in this paper by tackling development of 1,000cm^2-cell stack which could be available for practical operation in terms of its performance and durability. We are now in the stage of our evaluation of the initial performances of the cell, stack and system unit through production of the water electrolysis cell stacks and their assembly into the PEM water electrolysis type H_2 production system for H_2 refueling station.

In future, we will advance the system verification as the H_2 refueling station to conduct its adaptability assessment.

With regard to 2,500cm^2 cell stack, we could also verify its targeted performance by experimentally producing the cell stack through utilization of our know-how on the 1,000cm^2 cell stack for H_2 refueling station. In future, we intend to utilize those successful results to advance practical use of this cell stack.

8.2.2 Development of Hydrogen Production Technology by Hot Press Method

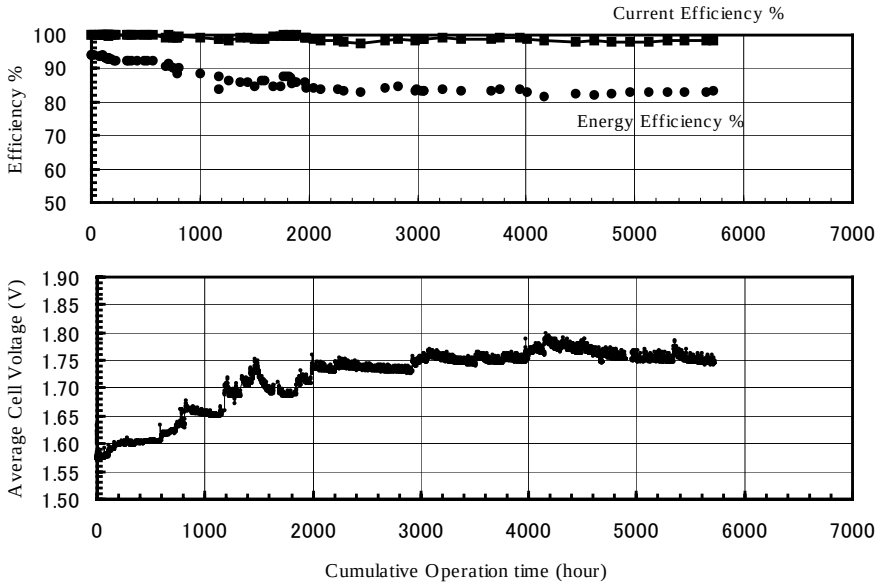
This is to develop manufacturing technology of a large-scale electrolytic cell utilizing solid high molecule electrolytic membrane. A large-scale electrolytic cell with 10 cell- laminated electrolytic cell manufactured in the previous year was tested for continued operation. Further, improved production technology for the large-scale electrolytic cell and operation technology under high pressure and temperature were developed. Following results are noteworthy.

8.2.2.1. Result of Continued Operation Test for a Large Scale Electrolytic Cell with 10 Cell-Laminated Electrolytic Cell

A large-scale electrolytic cell with 10 cell- laminated electrolytic cell manufactured in the end of the year 2000 was tested for continued operation. The accumulated test duration was extended to approximately 5,700 hours. The operation history of the test is shown in Fig. 8.2.2-1.

As observed, the initial energy efficiency was 94% but it started to drop after 1100 hours when average electrolytic pressure of the cells rose all of sudden. Thereafter the efficiency kept dropping as the electrolytic pressure kept rising. Currently the energy efficiency is in the level of 84%.

A sudden increase of electrolytic pressure at 1100 hour operation is considered as a result of deterioration of electrolyte water quality.



Operating condition : 80℃, Atmospheric pressure

Fig8.2.2-1 History of Electrolysis Operation Test in the 2,500cm², 10-Cell Stack Electrolyzer

8.2.2.2 Development of Manufacturing Technology of Large Scale Membrane Electrode Assembly

With the purpose of improvement in stabilizes production quality of a large scale cell, further improvement in production method of MEA (Membrane Electrode Assembly) was implemented in this year. Specific emphasis was made in the following aspects.

(1) Improvement in catalytic layer production procedure.

In the catalytic layer production of a large scale MEA, following two aspects are important for production stabilization, which were thoroughly reviewed.

① Deviation of catalytic suction.

Deviation of catalytic suction is caused by insufficient hydrophilitic treatment of membrane filter used for production of catalytic layer. Relationship among the amount of solvent added during hydrophilitic treatment, homogeneous catalytic suction and the repeatability was studied, and the optimum mixing ratio was attained so that catalytic layer without deviation in the catalytic suction was made produced.

② Damage of MEA and sealing defective (Review of strainer frame dimensions.).

Review of strainer frame dimensions was made to protect from MEA damage and sealing defective. On the electrolytic membrane adjacent to the edges of the catalytic layers, there observed phenomena in the mechanical shortcomings such as emergence of wrinkles caused by dimensional change when MEA hot water expanded. It was presumed that MEA damage and sealing defective were caused by too close a position or direct contact of seal packing to edges of catalytic layers. Thus, analyzing dimensional deviations when MEA hot water expanded, optimum dimensions of the frame for catalytic layer formation(the frame for strainer) not to interfere with sealing area were developed.

(2) Improvement in assembly procedure of MEA free from assembly defect and wrinkling.

When a large scale MEA is hot-pressed, fine wrinkles on the electrolytic surface around edges in the lengthwise were generated. These wrinkles result in MEA defective in the production process or damage of the membrane. In view of expected longer life of the cells, such wrinkles should be minimized. The cause of the wrinkles was found to be the heterogeneous pressure applied during hot-pressing. Some countermeasures were developed not to generate heterogeneous pressure application. As the result, wrinkles particularly around boundaries of catalytic layers and electrolytic membranes were significantly reduced.

(3) Research of internal characteristic distribution of a large scale cells.

On a large scale cell produced being incorporated to above descried improvements, internal deviations of the cell characteristics was studied. A part of the prototype large scale cell, 50 cm^2 in size, was cut off for the analysis. It was confirmed that there was no difference in the extent of deviation of electrolytic characteristics comparing to the whole cell as a unit.

8.2.2.3 Improvement in characteristics of power feed assembly on the anode side

It was noted in the prototype manufacturing of the large scale power feed assembly in the previous year that the cause of deviated thickness was the deflected loading plate of the horizontal pressing machine. Thus it was intended to improve the problem in the particular area by modifying the design of the loading plate, which was the plate directly press the material.

A spherical supporting plate was considered and applied. But there was no improvement in the deviation of the thickness. Then, a liner was inserted around circumference of the spherical supporting plate. The result was almost the same as without the liner in general, however, there was a certain improvement in the deviation of the thickness in the widthwise of power feed assembly comparing to the last year output. This achievement was the result of improvement in the stability of an angle of the plate thickness of the power feed assembly. This was considered a significant improvement for production of multi layer lamination of cells.

8.2.2.4 Development of High Pressure and High Temperature Operation Technology

(1) Test for High Pressure and High Temperature Electrolysis of Large Scale Cell

High pressure tests for a large scale laminated electrolytic cell with two sets of cells with 2500cm^2 area each were conducted at 80℃ temperature and the heat balance was calculated. The test units are shown in Fig 8.2.2-2 and Fig.8.2.2-3. Result of heat balance calculation based on electrolysis characteristic under high pressure is shown in Table 8.2.2-1, from which it was confirmed that there was no need of supplemental heating unit to maintain temperature in the electrolytic cell as long as the pressure was more than 0.2Mpa at 80℃ temperature. It was also found that the energy efficiency of 90% was maintained under atmospheric pressure but it dropped under high pressure due to increased electrolytic pressure.

Table 8.2.2-1 Computation results of heat balance

Operating pressure	Average cell voltage	Usable energy	Heat balance in electrolyzer cell	
MPa	V	W	W	
0	1.605	2108.2	63.6	Deficiency in heat considering released heat
0.2	1.619	2178.2	1353.6	Excess in heat
0.4	1.628	2223.2	1544.7	Excess in heat
0.6	1.643	2298.2	1676.5	Excess in heat
0.8	1.659	2378.2	1786.5	Excess in heat

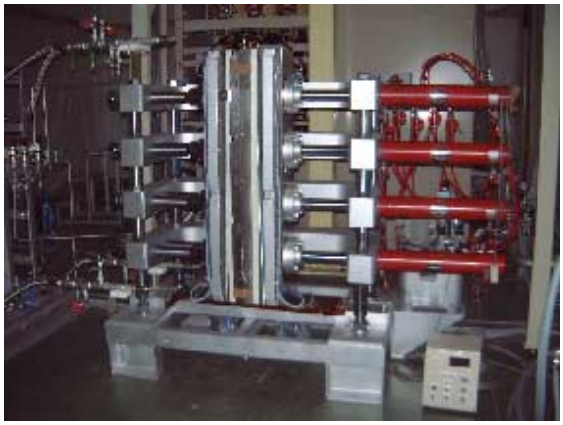


Fig.8.2.2-2 Compression Unit of Electrolyzer and 2-Cell Stack

Fig.8.2.2-3 Water/Gas Supply/Discharge Unit in Test Stand

(2) Evaluation of Characteristics for High Pressure/Temperature Operation of Electrolytic Cell with 200cm² Area Cells.

In order to examine high pressure/temperature conditions, tests for the electrolytic cell with two units of 200cm² area cell were conducted under the constant temperature 80℃ but under various pressures, namely atmospheric, 0.4Mpa and 0.7Mpa. The result of the characteristic is shown in Fig. 8.2.2-4. As noticed, as the operating pressure increases, cell voltage increases and energy efficiency decreases. In the case of current density 1A/cm², the cell voltage was 1.56V and the energy efficiency was 94% under atmospheric pressure, while the voltage was 1.62V and the energy efficiency was 90.5% under 0.7Mpa pressure condition.

Further the tests proceeded under a constant operating pressure 0.7Mpa but under varied temperature, namely 80℃, 100℃ and 120℃. Fig. 8.2.2-5 shows the relation between cell voltage and electrolytic temperature at the current density 1A/cm². As noticed, as the temperature increases, the electrolytic voltage decreases and the

energy efficiency increases.

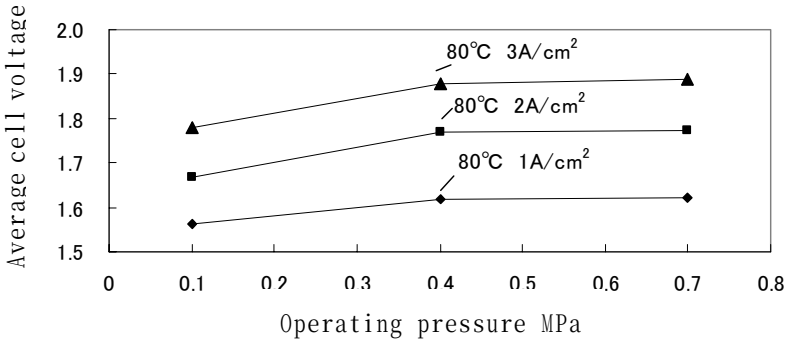


Fig.8.2.2-4 Charactaristics of Cell voltage vs. Operating pressure at 1A/cm²,2A/cm² and 3A/cm² in 200cm²-Cell

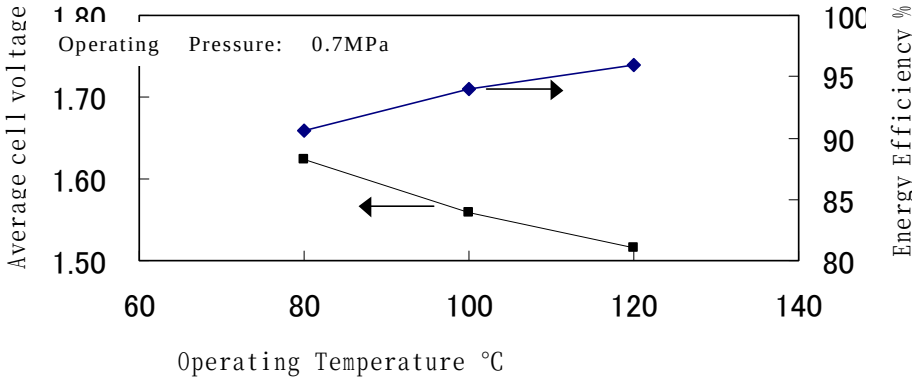


Fig.8.2.2-5 Charactaristics of Cell voltage and Energy efficiency vs. Operating temperature at the operating pressure 0.7MPa in 200cm²-Cell

5. Endurance Test of Small Cell

Endurance test of the small cell had been conducted in the two aspects. One was for smoothness of the cell surface as electrical feed material and another was the life of the cell itself. In order to improve smoothness of the cell surface, introduction of new materials and improvement of a material by means of additives had been studied. In the current year, influence of gaps generated when the cell was formed by pressing and evaluation of two kinds of new material were studied.
Study was made in the following aspects.

(1) Cell No. 3 : Titanium Fine Fiber Sintered Plate.(There were gaps from pressing)
Currently the test duration of the cell No. 3 has been passed over 1500 hours. It was proved that this cell had the highest stability in characteristics among

those produced in 2001. Smoothness on the feed surface processed by pressing must be in the high grade.

(2)Cell No. 4: Titanium Ultra Fine Fiber Sintered Plate.
(Fiber diameter φ20μm. It was intended without pressing.)
Cell No. 4 was tried with an intention to eliminate pressing process, however a short circuit was noted after 500 hours of continuous test of the small cell. The unit was examined in detail and it was found that Ry (Rmax) value of the surface roughness of the feed material supplied by Company A was no better than conventional titanium fine fiber sintered plate. On the other hand, surface roughness of the titanium ultra fine fiber sintered plate, a feed material proposed by Company B consisting of the same fiber with diameter φ 20μm, was found to be better in grade comparing to one supplied by Company A. The test is planned in the future.

(3)Cell No. 5: Titanium Spherical Powder Sintered Plate.
(The new material and the processing method were evaluated.)
Because of spherical powder of the element, the feed material made of Titanium spherical powder sintered plate should have better smoothness without showing sharp bosses on the surface. It was wondered if internal cleanliness was improved by means of platinum spattering plating comparing to conventional electrolytic plating which had been applied to titanium powder sintered plate made in the year 2000. But in the actual operation, majority of the influence was apparent on the part of the quality of the circulating water that was affected by the cell voltage. In the future, the cause of the increased cell voltage needs to be studied considering quality of the circulating water and deterioration of the cell material.

8.2.3 Development of High Temperature Resistant Molecule Electrolytic

Membrane

In order to newly develop a high molecule electrolytic membrane with improved conductivity and mechanical properties, three kinds of membrane were synthesized. They were developed by adding optimized amount of PBI on the composite primarily made of sulfonic acid etherketone molecule. Those membranes were given to National Institute of Advanced Science and Technology (AIST) for performance evaluation.

High molecule membrane 13752-52 (delivered on 9/2001) and 13752-63 (delivered on 4/12/2001) were derived from FSPEEK synthesized by optimum sulfonation method to enable precise control of the extent of sulfonation. High molecule membrane 13752-52 (delivered on 9/2001) was derived from FSPEEK that had low sulfonation. Thus water absorption rate and ion conductivity were rather low, while high molecule membrane 13752-63 (delivered on 4/12/2001, 12x12cm in size) was derived from FSPEEK of which sulfonation was known to be optimum (sulfonation 80%). On the other hand, development of synthesis of PEEK based on fluorinated sulfonic acid by applying amino-functional silica instead of PBI was started.

It was found that the high molecule membrane 13752-63 had 52% of water absorption rate (weight% after boiling for 1 hour), 0.073 S/cm of conductivity based on dried membrane thickness under the room temperature and 0.4 S/cm of conductivity based on dried membrane thickness of 3.2μ under 150℃. This particular membrane is the only membrane processed by a coater. The characteristics of the membrane processed by the coater was found to be different from those processed by manual casting even though chemical properties were the same. It is considered that mechanical properties of the membrane processed in the the coater facility was improved protecting the separation of high molecule composite (FSPEEK and PBI) resulted from extremely quick drying process of the membrane.A membrane in the size of 12x90cm was produced in the coater facility as shown below(Fig8.2.3-1).

Fig.8.2.3-1 FSPEEK and PBI A membrane

8.2.4 Evaluation of high temperature resistant molecule electrolytic membrane

Evaluation of conductivity rate and water electrolytic performance of the newly developed temperature resistant high molecule electrolytic membrane have been conducted. This year, they conducted evaluation of ion conductivity and electrolysis performance of the membrane in the pure water with varied temperature condition from 100℃ to 150℃. For the membrane with 3.3 mil thickness, relatively satisfactory performance was obtained at the temperature below100℃, but the performance dropped at the temperature higher than 100℃. As to ion conductivity, they were 0.006S/cm at 80℃, 0.07S/cm at 100℃, 0.03S/cm at 120℃ and 0.02S/cm at 150℃. As to electrolytic performance at 1A/cm^2 of the current density, they were 1.7V at 80℃, 1.64V at 100℃ and 1.82V at 120℃.

Voltage efficiencies were approximately 87%, 90% and 81% (on ΔH basis) respectively. At the temperature 100℃, the current density was raised to 3A/cm^2 . The result was 1.95V for electrolytic performance and 75% for voltage efficiency.

It is required to evaluate the membrane at higher temperature and higher current zone and to develop membrane equipped with improved mechanical properties, durability and reliability. The currently available membranes are still in the stage of development, thus the mechanical strength of the membrane and its assembly is far from the required level. Unexpected voltage increase and damage of membrane happened during evaluation process. Thus, be minded there are still no data available being measured under stable and sustainable conditions.

8.2.5 Research of Documents related to Water Electrolysis

Water electrolysis is one of the important industrial processes that has been industrially practiced to produce hydrogen that is required in the chemical processing particularly in the ammonia synthesis plant. In these days, hydrogen production by steam reformed process on the fossil fuels such as oil and natural gas seems more dominant in the economical viewpoint, however the importance to produce hydrogen through water electrolysis that is the only established industrial method to produce the clean secondary energy has never be faded away. Thorough review and study of the research documents in this aspect are extremely important. Subsequent to the policy in the last year, research of the documents related to water electrolysis published in the technical magazines or similar publications was continued in this year limiting the period for one year from 7/2000 to 6/2001. A list of the documents was prepared with description of outline of each report. The purpose of the list is to enable foreseeing general trend of the researches in this field. Thus the details of the individual content should be obtained from the original publication.