

Development of CO₂ Reduction-Water Electrolysis Tandem Device as a Full-Scale Model

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This study describes an advanced tandem reactor for environmental control and life support systems (ECLSS). The reactor consists of a low-temperature (220°C) Sabatier reactor producing water and methane (CH₄) from carbon dioxide (CO₂) and hydrogen (H₂) and a thermally coupled water electrolysis cell with a proton exchange membrane (PEM). The Sabatier component generates heat energy used to operate a tandem water electrolyzer and is thermally self-sustaining. A previous, sub-scale reactor generated 1 L/min of H₂ for the Sabatier reaction and achieved 93 % CO₂ conversion. The model electrolyzer used in this study currently generates H₂ at 3.6 L/min, which the Sabatier reactor can use to convert 1.58 L/min of CO₂ to CH₄ as much as possible.

Nomenclature

<i>ARS</i>	=	Air Revitalization System
<i>ISS</i>	=	International Space Station
<i>CO₂</i>	=	Carbon dioxide
<i>H₂</i>	=	Hydrogen
<i>JAXA</i>	=	Japan Aerospace Exploration Agency
<i>Ru</i>	=	Ruthenium
<i>TiO₂</i>	=	Titania
<i>ZrO₂</i>	=	Zirconia
<i>Al₂O₃</i>	=	Alumina

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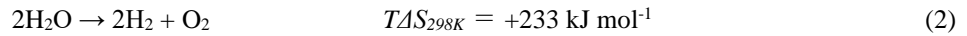
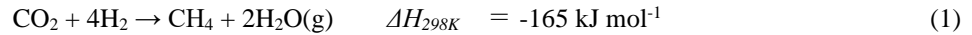
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PEM = Polymer electrolyte/proton exchange membrane
 ΔH = Enthalpy change
 $T\Delta S$ = Energy change based on the entropy change at temperature T [K]
 PEEC = Polymer electrolyte electrolysis cell

I. Introduction

Closed-Air Revitalization Systems (ARSs) are crucial to long-duration human space exploration. The current ARS on the International Space Station (ISS) consists of four subsystems: trace contaminant control, carbon dioxide (CO₂) removal, CO₂ hydrogenation, and oxygen (O₂) generation. ARSs supply necessary O₂ with minimal resupply from the Earth and keep the onboard CO₂ concentration at a safe level. However, new technologies for air revitalization must mature to meet the constraints imposed by future exploration, which will require stricter limitations on mass, volume, and power consumption than current ISS conditions.¹

The Japan Aerospace Exploration Agency (JAXA) has been working on an advanced ARS to reduce supply while improving reliability for years.²⁻⁶ As part of our advanced research for application to future missions, we investigated the thermal conjugation of water electrolysis and the CO₂ methanation process in one device. The tandem device is expected to reduce energy consumption because the heat generated by the exothermic Sabatier reaction (Eq. (1)) can be utilized for water electrolysis (Eq. (2), Fig. 1).⁷



Thermodynamically, the energy required to split liquid H₂O into gaseous H₂ and O₂ is equal to the enthalpy change (ΔH_{elec}) in H₂O, which is the sum of the Gibbs free energy change (ΔG , electrical demand) and entropy change times the temperature ($T\Delta S$, thermal demand). By exchanging the heat generated by the Sabatier reaction to compensate for the water electrolysis thermal demand as $T\Delta S$, the reactor has the potential to improve the overall efficiency. To optimize efficiency in the future, we need to demonstrate the concept of the device based on the experiment. Through these efforts, we will clarify the auxiliaries which will be needed to realize the system.

For the device, the exothermic Sabatier reaction is accelerated by a durable TiO₂-supported Ru-ZrO₂ (Ru-ZrO₂/TiO₂) catalyst prepared by a co-sputtering technique using a polygonal barrel system with a high yield at 200 °C.⁸⁻¹⁰ We previously reported the development of a tandem device using this catalyst that successfully generated H₂ and carried out corresponding CO₂ methanation simultaneously. The reactor development increased the reaction scale from 40 mL/min H₂ generated in a concept model to 1 L/min H₂ in a sub-scale model.¹¹ Further, a three-dimensional numerical model of the prototyped tandem device demonstrated that an appropriate heat balance between the reactor and electrolyzer yields a CO₂ conversion above 90 % and thermal self-sustainability.¹² This paper presents

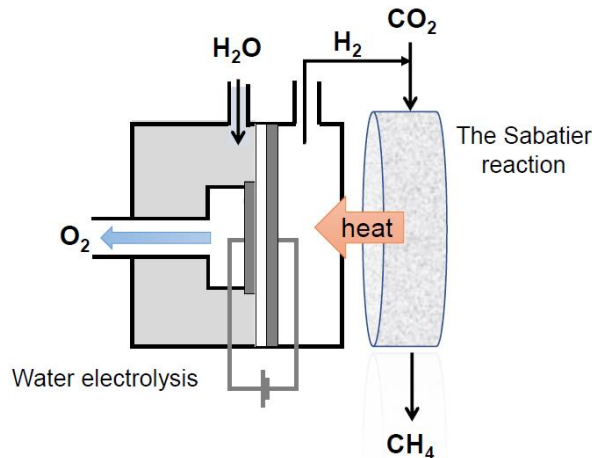


Figure 1. Schematic of the water electrolyzer and thermally coupled Sabatier reactor of the tandem reactor.

our development of a scaled-up tandem device consisting of an electrolyzer that can produce 3.6 L/min H₂ and a Sabatier catalyst component that generates water from the provided H₂ and removed CO₂ at 1.58 L/min. The flow rates of H₂ and CO₂ simulate the demand of the four astronauts expected by the Gateway project. This paper refers to the scaled-up tandem device as the “full-scale model.”

II. Development of a Full-scale Reactor

For increasing the target reaction scale, the 1 L/min-H₂ generation model (the “sub-scale model”) was reviewed in the water electrolysis section and the Sabatier reactor section. Simply using four of the sub-scale models in parallel would increase the mass, volume, and number of components, so we decided to redesign the reactors.

For the water electrolyzer section, we considered three designs: (1) increasing the cell area using a larger reactor, (2) increasing the number of cell stacks from 10 (in the sub-scale model) to ca. 40 cells of the same size, and (3) improving cell performance with a ten-cell stack of the same size as the sub-scale model. Preliminary experiments and numerical analyses showed that enhancing the cell performance would most effectively reach the target flow rate. This decision was supported by numerical analysis suggesting that the effective area of the electrode could be increased by modifying the electrode structure (Fig. 2).¹³ Based on these results, we redesigned areas of the water supply pass and catalyst in the cell and succeeded in expanding the effective area of the cell from the previous 41cm² to 85cm². In addition, the plate used to separate the cells was made thinner to reduce the weight of the cell stack. As a result, we obtained a water electrolysis cell with the same 10-cell stack but only about half the volume of the previous sub-scale model (Fig. 3).

As for the Sabatier reaction section, we increased the amount of the filled Ru-ZrO₂/TiO₂ catalyst in the catalyst layer based on the evaluation of the sub-scale model last year. First, we tried to increase the amount of Ru-ZrO₂/TiO₂ catalyst immobilized on a porous alumina plate of 10 cm x 10 cm x 2 mm, also used in the sub-scale model. However, excessive immobilization of the powder catalyst clogged the porous plate and decreased the effective amount of the catalyst. Thus, the amount of catalyst immobilized on an alumina plate was limited so that the properties of the porous body would not be impaired (Fig. 4a). Instead, the volume of the catalyst layer in the endplate was increased, and the number of alumina plates supporting the catalyst was changed from the two of the sub-scale model to three. The final amount of Ru-ZrO₂/TiO₂ filled in the reactor was ca. 11 g, about double the sub-scale model.

Figure 4b shows the completed full-scale Sabatier reactor and water electrolysis cell of the tandem reactor. By making improvements while maintaining the shape of the end plate, we succeeded in increasing the reaction amount while reducing the device's size.

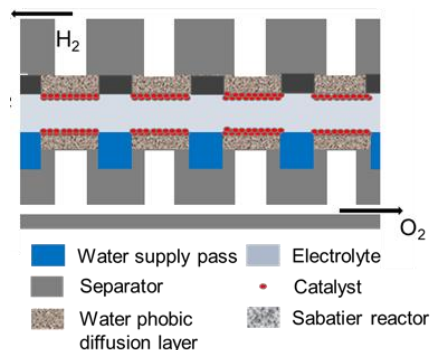


Figure 2. Schematic of the interdigitated electrode in the sub-scale electrolyzer.



Figure 3. Water electrolyzers of the full-scale model (left) and the sub-scale model (right).

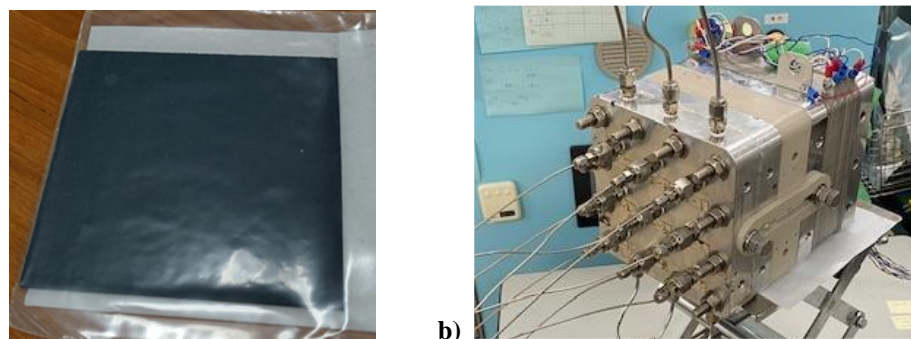


Figure 4. (a) Ru-ZrO₂/TiO₂ catalyst immobilized on a porous alumina plate and (b) the perspective view of the full-scale tandem device.

III. Full-scale Model Testing

The full-scale model was tested according to the previous sub-scale testing.¹¹ Figure 5 is a schematic diagram of the test setup. Pure H₂ was provided from the blue line in the control test and the red line in the main test. The tandem device was heated with sheathed heaters on the sides of the endplate to which the Sabatier catalyst was attached, and the heater maintained the test temperature. The catalyst temperatures were measured by nine thermocouples outside the endplate, as shown in Figure 5b. The reaction reached a steady state when all measured catalyst temperatures were constant. Then, the effluent gas was sampled after condensing and removing the water.

The CO₂ conversion (%) was quantified by analyzing the reaction effluent with a gas chromatograph (GC). The GC was equipped with a thermal conductivity detector (GC-2014, Shimadzu) using the Shincarbon-ST column (Shinwa Chemical Industries) with argon as a carrier gas at 220 kPaG. The peaks observed on the GC chart were identified and calculated using external standard calibration curves. It is known that the coking takes place in the hydrogen starvation conditions under equilibrium, while we had never observed the coking on our catalyst under the experimental conditions. Furthermore, pressure change during the integrated test described later also suggested the absence of coking. Due to these reasons, we assume that the material balance should be established for carbon species before and after the reaction, i.e., the volume of fed CO₂ was consistent with the sum of the volumes of CH₄ and CO₂ in the effluents and carbon formation did not occur during the steady-state reaction, the formed CH₄ and unreacted CO₂ peaks were identified on the chart according to the equation $(\% \text{ of produced CH}_4) / [(\% \text{ of unreacted CO}_2) + (\% \text{ of produced CH}_4)] \times 100$.

The Sabatier reactor section was evaluated by a stoichiometric reaction with a mixed gas of 6.32 L/min of H₂ and 1.58 L/min of CO₂ supplied from gas cylinders. Figure 6a shows the CO₂ conversion versus the reaction temperature, corresponding to the maximum temperature in the data measured at the nine points of the catalyst bed (Fig. 5b), respectively. In reacting with H₂ from the cylinder, the CO₂ conversion increased gradually with increasing

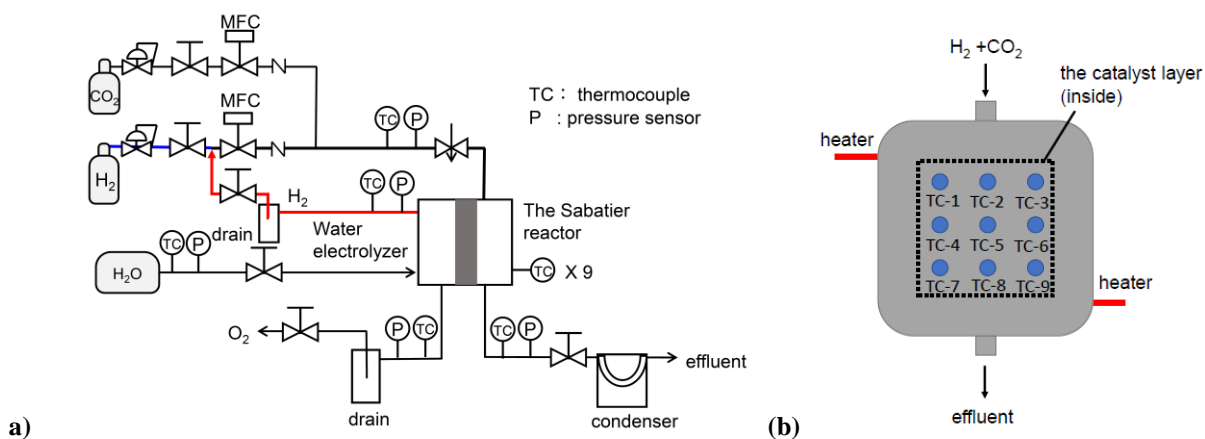


Figure 5. Schematics of (a) the test system and (b) positions of thermocouples for measuring the Sabatier catalyst temperatures.

temperature, eventually reaching 86 % at 288 °C. Although the conversion did not achieve the goal of >90 %, the 86 % was higher on a practical scale than those of previous Sabatier reactions. In addition, the reaction temperature of 288 °C was more than 100 °C lower than for the previous reactions in which the reaction temperatures were above 400 °C. The low measured temperatures were due to the Sabatier reactor, which had a larger contact area with the reactor than a conventional cylindrical reactor. Though the Sabatier reactor must be optimized for full-scale methanation with more than 90 % conversion for future research, the catalyst unit was used for the following integrated test.

The integrated testing was conducted with the two steps of the evaluation. First, 3.6 L/min of H₂ and 1.58 L/min of CO₂ supplied from gas cylinders were introduced into the Sabatier reactor section of the tandem device. The temperature dependence of the CO₂ conversion was evaluated as a control test. Next, the same reactor conducted the Sabatier reaction with a mixed gas consisting of 1.58 L/min of CO₂ from a gas cylinder and 3.6 L/min of H₂ generated from the water electrolysis section for the main test. We set the tandem device to receive the supply of 1.58 L/min of metabolic CO₂ and 3.6 L/min H₂ as a byproduct of oxygen generation without dilution or adjustment of gas flow rates for the stoichiometric reaction as the nominal condition. The obtained CO₂ conversion rates were compared with the corresponding results of the control test to evaluate the technical feasibility of the device as an integrated full-scale model. Figure 6b shows the temperature dependence of each test's obtained CO₂ conversion rate. Since the supplied ca. 3.6 L/min of H₂ was not stoichiometric with the amount of CO₂ feed gas, the maximum CO₂ conversion remained at 57%. Compared with the H₂ supplied from a gas cylinder (●), the conversion rates obtained in the integrated test (■) showed excellent agreement. During the integrated test, the water electrolyzer generated ca. 3.6 L/min of H₂ continuously with 52 A (Fig. 7). This was the first time an electrolyzer of a ten-cell stack using pressurized water with an interdigit structure successfully provided H₂ in a full-scale experimental demonstration.

The full-scale testing clarified some technical issues of the tandem device as well. During the test, for example, the internal pressure of the Sabatier reactor rose to a maximum of about 100 kPaG, as shown in Fig. 8. For providing H₂ continuously to the Sabatier reactor, the water electrolyzer had to maintain the product gas pressures higher than the internal pressure of the Sabatier device. This increased the pressure throughout the device and caused partial degradation of the electrolysis cells. Moreover, variation in cell voltage was observed in some cells even though the

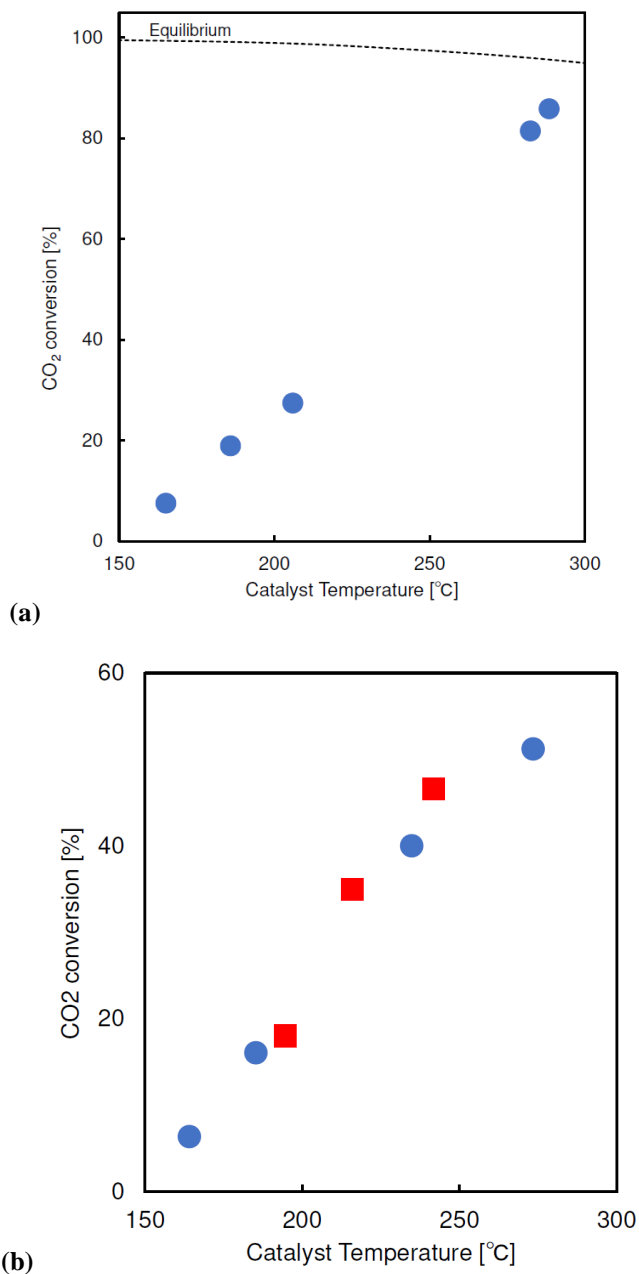


Figure 6. CO₂ conversion versus reaction temperature, (a) full-scale stoichiometric CO₂ methanation with 6.32 L/min H₂ and 1.58 L/min CO₂ and (b) full-scale integrated testing with 3.6 L/min H₂ from a gas cylinder (●) and electrolyzer of the device (■).

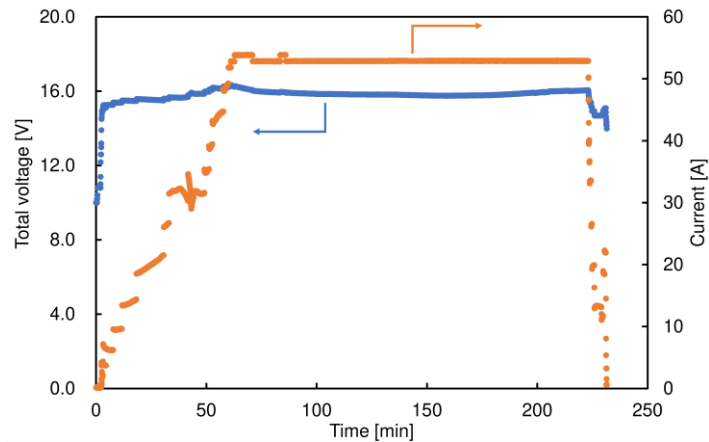


Figure 7. Measured voltage and current of the electrolysis during the full-scale integrated testing. See Fig. 8 for the progress of the testing.

cell stack was supplied with water by pressurization, not by water circulation, as shown in Fig. 9. Though total voltage as the 10-cell stack was almost constant while the electrolyzer generated 3.6 L/min, cells 1, 3, and 5 showed voltages of more than 1.65 V, higher than other cells ca. 50 min after the start of the test. Their voltages gradually decreased to 1.6 V according to the operation duration. The cell voltage of cell 8 increased to 1.8 V, the value we set as the upper limit for continuing the test. This indicates that cell reproducibility needs improvement.

Another perspective on improving the electrolyzer performance is suggested from related research: Nakajima *et al.* investigated the liquid water permeability of a hydrophobic microporous layer, which was used in the porous transport layer of the anode of the electrolyzer with pressurized water.¹⁴ The obtained permeability was used as a parameter for a three-dimensional simulation of the electrolyzer based on the first conceptual reactor design. The simulation model revealed a pressure distribution on the electrode surface and that the water pressure was particularly low near the terminal electrode, as shown in Fig. 10. Low water pressure indicates water depletion at the electrode, which cannot contribute to electrolysis.

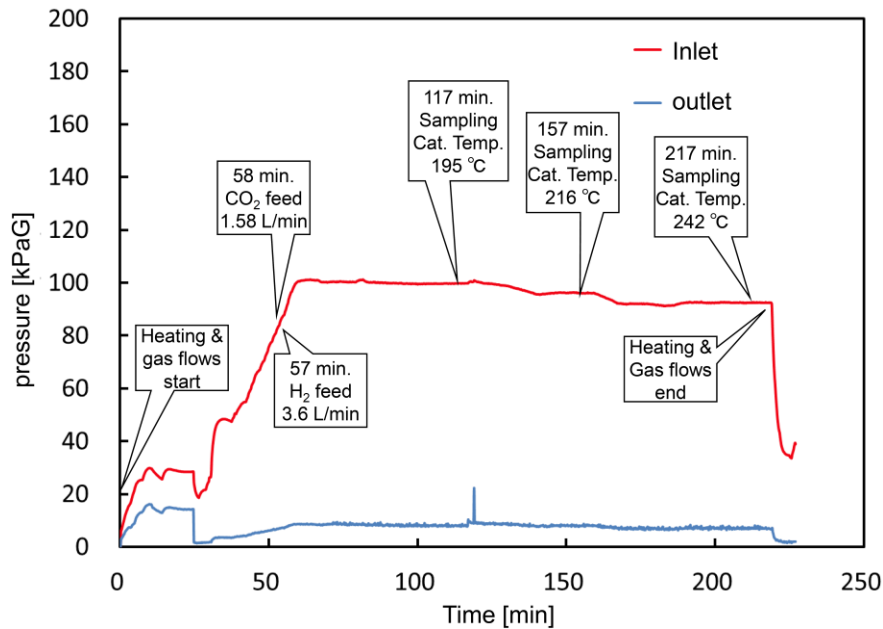


Figure 8. The measured pressure of the Sabatier reactor during the full-scale integrated testing.

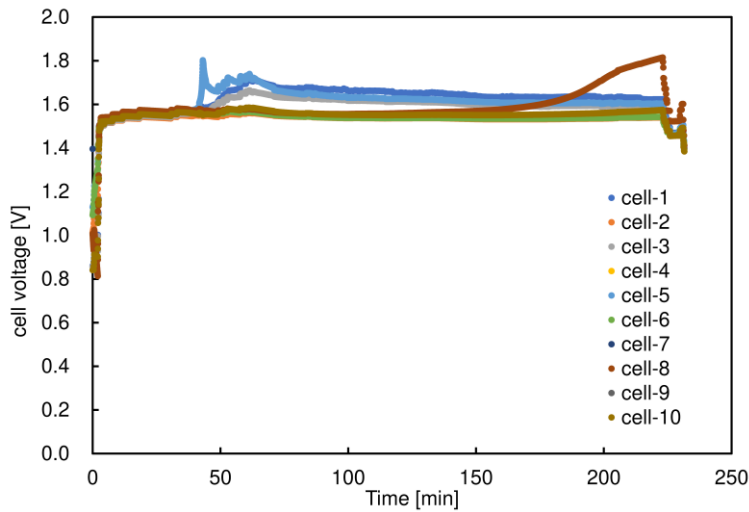


Figure 9. The measured cell voltages of the electrolyzer during the full-scale integrated testing. See Fig. 8 for the progress of the testing.

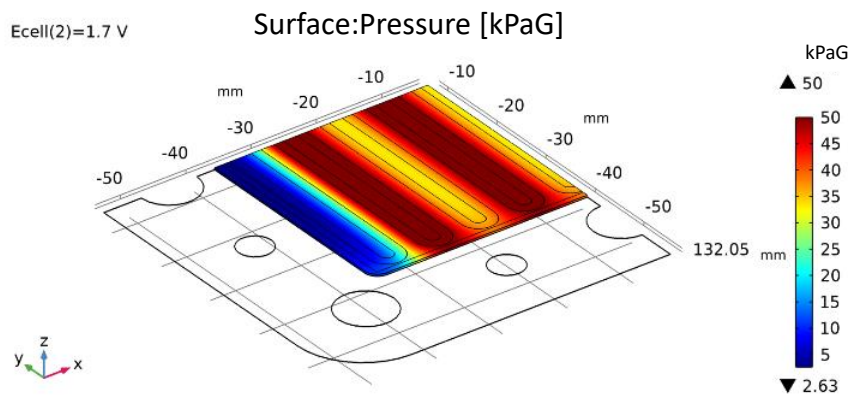


Figure 10. Water pressure distribution on an electrolysis cell (1/4 symmetrical size, 25 °C, 1.7 V, $5.5 \times 10^3 \text{ A/m}^2$).

IV. Conclusion

We prepared the targeted ‘full-scale device’ in which 3.6 L/min-class hydrogen was generated by the ten-cell stack. The hydrogen was introduced to the Sabatier reactor connected directly to the water electrolysis stack and successfully generated methane from CO₂ by using our Ru-ZrO₂/TiO₂ catalyst. Compared with the H₂ supplied from a gas cylinder, the conversion rates obtained in the tandem device showed agreement.

Through the experiment, we recognized that the stability of the water electrolyzer should be improved. Water distribution along the membrane was simulated, which revealed water distribution on the electrode surface.

Based on these results, we will improve the durability of the electrolyzer accompanied by the best optimization of the Sabatier reactor as the tandem device.

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