Improvement of the Full-Scale Model of Carbon Dioxide Reduction-Oxygen Production Tandem Reactor

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A "carbon dioxide reduction-water electrolysis tandem reactor" has been developed as a new concept of ECLSS technology. The reactor utilizes the heat generated by carbon dioxide reduction (Sabatier reaction) to operate water electrolysis. A full-scale model was previously prototyped, which achieved a hydrogen generation of ca. 3.6 L/min and the corresponding Sabatier reaction. In this study, we report modifications to the Sabatier reaction and water electrolysis in the previously developed full-scale model tandem reactor to improve the reactor's pressure conditions and durability.

Nomenclature

ARS	=	Air revitalization system
ECLSS	=	Environmental Control and Life Support System
ISS	=	International Space Station
CO_2	=	Carbon dioxide
O_2	=	Oxygen
CH_4	=	Methane
PEM	=	Proton Exchange Membrane
SLM	=	Standard liter(s) per minute
H_2	=	Hydrogen
Ru-ZrO_2/TiO_2	=	Titania-supported co-sputtered ruthenium-zirconia
Al_2O_3	=	Alumina

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MFC = Mass flow controller
GC = Gas chromatograph
TRL = Technology readiness level

I. Introduction

THE air revitalization system (ARS) is one of the main functions of the Environmental Control and Life Support System (ECLSS) for manned space missions. The closed ARS (Figure 1) based on the current technologies onboard the International Space Station (ISS) consists of trace contaminant control, carbon dioxide (CO_2) removal, CO_2 hydrogenation providing water, and oxygen (O_2) generation. Those subsystems have been developed independently though they accommodate gases, water, or both. For this situation, we conceived conjugation of exothermic CO_2 hydrogenation by the Sabatier reaction, in which water and methane (CH_4) are obtained as main products, and O_2 generation using proton exchange membrane (PEM) water electrolysis. Integrating O_2 production and CO_2 reduction into a single tandem device will potentially reduce system mass and energy consumption for future projects such as the Gateway project and lunar exploration requiring smaller, lighter, more energy efficient, more durable, and more reliable systems than those currently installed on the ISS.[1]

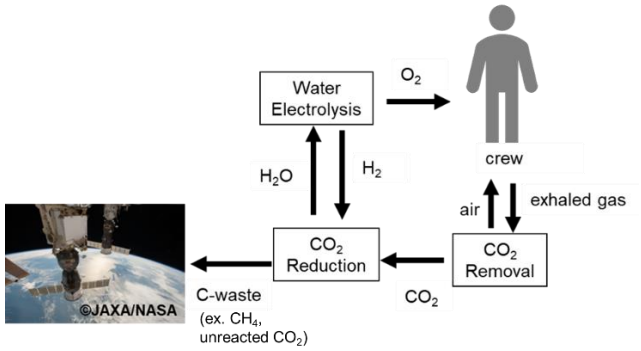

Figure 1. Schematic diagram of a closed ARS.

The CO_2 reduction-O_2 production tandem device has been developed stepwise from an academic primitive model to a practical scale (Figure 2). Previously, we reported that the developed prototype of the tandem reactor successfully generated ca. 3.6 standard liters per minute (SLM) hydrogen (H_2), equivalent to producing O_2 for four astronauts (hereinafter referred to as this reaction scale and "full scale") followed by methanation with the generated H_2 and a considerable amount of CO_2.[2] It was the first concept feasibility demonstration of the tandem device at a practical level. At the same time, the testing revealed many technical issues on both sides of the water electrolysis cell stack and the Sabatier reactor section. To increase the technology readiness level (TRL) of this reactor concept and lead to its future practical application, the tandem device has been improved. Herein, we report our attempts to solve the pressure issues on the Sabatier reaction section and to obtain higher performance of the water electrolysis cell stack.

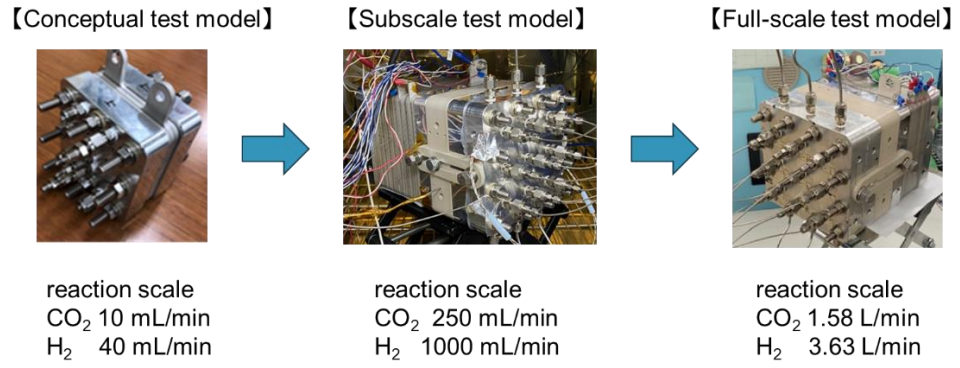

Figure 2. Schematic diagram of stepwise development of the CO_2 reduction-O_2 production tandem device. The conceptual and subscale models were reported in 2022,[3] and the full-scale model was shown in 2023.[2]

II. Results and Discussions

A. Modification of the Sabatier reactor

In the previous integrated testing of the tandem full-scale reactor, the pressure inside the Sabatier reactor section was approximately 100 kPaG as reported at ICES2023.[2] The pressurized Sabatier reactor demands higher pressure H_2 from the electrolysis cell stack. The cell stack requires the provided water pressure to be higher than the generated gasses. Thus, the internal pressure of the Sabatier reactor influences the operating pressure of the total system. Theoretically, higher pressure is preferable for the Sabatier reaction from the viewpoint of reaction rate. Also, pressurized water electrolysis reduces the amount of water vapor accompanying the generated gases. However, from the viewpoint of actual system operation, it is preferable that the reactor is not pressurized automatically but can be set to a desired pressure by control. Additionally, the pressure resistance of the water electrolysis part was not guaranteed at this time. Therefore, we lowered the pressure in the Sabatier reaction section and improved the pressure controllability of the tandem reactor.

In the verification tests of the factors that increased the pressure in the Sabatier reactor, it was strongly suggested that the dense property of the immobilized catalyst layer and the volume of the reactor played dominant roles in the reactor pressure, respectively. Thus, the catalyst layer was modified although the external dimensions remained unchanged from the original prototype as shown in Figure 3. The catalyst volume was increased from 60 cm^3 to 100 cm^3. In addition, the density of the immobilized titania-supported co-sputtered ruthenium-zirconia ($Ru\text{-}ZrO_2/TiO_2$) catalyst onto a porous alumina (Al_2O_3) plate of 10 cm x 10 cm x 0.2 cm was decreased by about 6% on average. The final catalyst properties for the reactor were fixed at a volume of 100 cm^3, five catalyst plates, and an immobilized $Ru\text{-}ZrO_2/TiO_2$ powder catalyst amounting to 17 g.

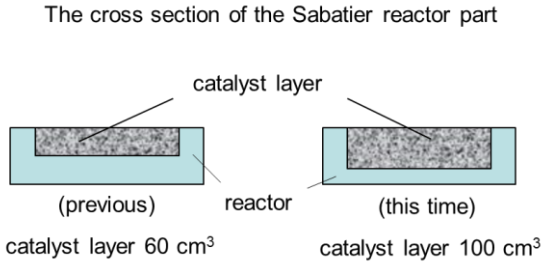

Figure 3. Schematic diagram of the Sabatier reactor section.

The effects of reactor modification were apparent. When a full-scale mixed gas of 1.58 SLM CO_2 and 3.6 SLM H_2 flowed under control by mass flow controllers (MFCs), the upstream pressure of the Sabatier reactor remained less than 10 kPaG (Figure 4a)).

The modified reactor was evaluated at the viewpoint of the catalytic activity of CO_2 hydrogenation: In those experiments, the reactor was heated with sheath heaters inserted from the side of the reactor with PID control. When the catalyst temperatures measured at nine points as shown in Figure 4b) became almost constant respectively, the reaction was regarded to have reached a steady state, and then the effluent gas was sampled. The CO_2 conversion (%, the theoretical maximum conversion is 57%) 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 coking takes place in hydrogen starvation conditions under equilibrium. We did not, however, observe such coking on our catalyst under the experimental conditions, even though the operation time was about 20 hours. Furthermore, a pressure increase was not observed during the tests. Thus, it was assumed that the material balance should be established for carbon species before and after the reaction, i.e., the volume of fed CO_2 was consistent with the sum of the volumes of CH_4 and CO_2 in the effluents and carbon formation did not occur during the steady-state reaction, the formed CH_4 and unreacted CO_2 peaks were identified on the chart according to the equation (% of produced CH_4)/ [(% of unreacted CO_2) + (% of produced CH_4)] × 100.

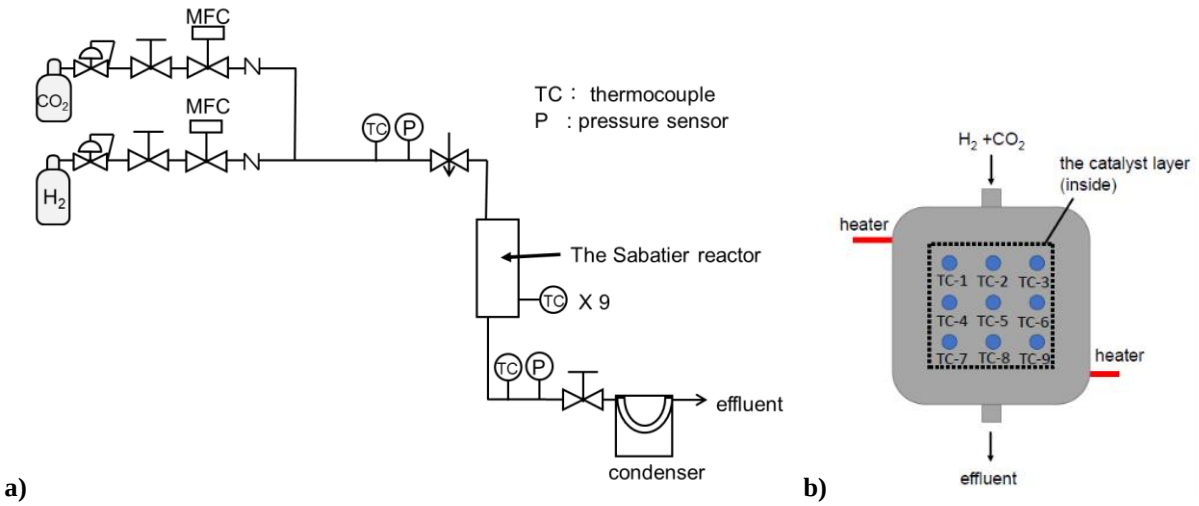

Figure 4. Schematic diagrams of a) the Sabatier reactor section evaluation test and b) temperature measuring points in the Sabatier reactor.

The Sabatier reaction was carried out with the modified catalyst, where 8.4% of CO_2 was converted at 162°C as shown in Figure 5●. The CO_2 conversion increased with the catalyst's temperature and reached 55% at 262°C. In the full-scale test, the provided 3.6 SLM H_2, which is about 2.3 equivalents of CO_2, is not stoichiometrically enough to reduce all the provided CO_2 with the Sabatier reaction. Thus, from the viewpoint of H_2 consumption, the 55% CO_2 conversion means more than 95% of the provided H_2 was consumed. Compared to the previous test (Figure 5▲), the higher CO_2 conversion was achieved at a lower shifted temperature. This would be attributed to an increase in the amount of catalyst in the layer and/or a decrease in the internal pressure of the reaction section, resulting in reaction temperature suppression.

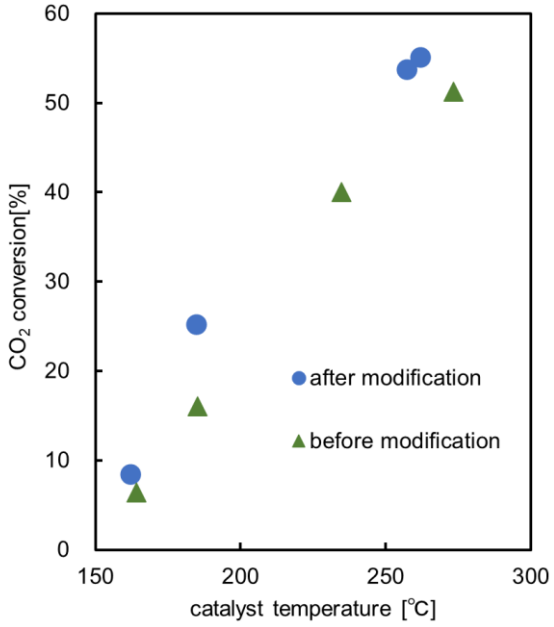

Figure 5. Temperature dependence of CO_2 conversion rate before and after re-prototyping the Sabatier reactor section. The data before the modification was reported in 2023.[2]

B. Modification of the oxygen generation part

The full-scale oxygen generation by the previous prototype reactor was the first example of a water electrolysis cell stack using pressurized water. During the test, the cell stack successfully provided the expected amount of H_2 and O_2 gases. However, degradation of the electrode was observed. Reviewing the inner structure of the cell with a 1/4 simulation model revealed a water pressure distribution on the electrode surface as shown in Figure 6a). The water pressure decreases from red to blue via yellow. Less water pressure indicates less water supply resulting in water depletion which causes increasing cell voltage and severe damage to the cell. Since our water electrolyzer uses pressurized still water for electrolysis, it needs water supplied with pressure higher than the generated gas to prevent gas backflow to the water passes.

The reason for the water drying is suspected to be the outermost electrode part only having one water-providing part on the inside. In contrast, the inner electrode part had a water-providing part on each side (Figure 6a)). Thus, the internal structure of the electrolysis cell was redesigned with a water-providing part on both edges of an electrode as shown in Figure 6b). At the same time, the cell preparation method was reviewed for the reproducibility of the cell.

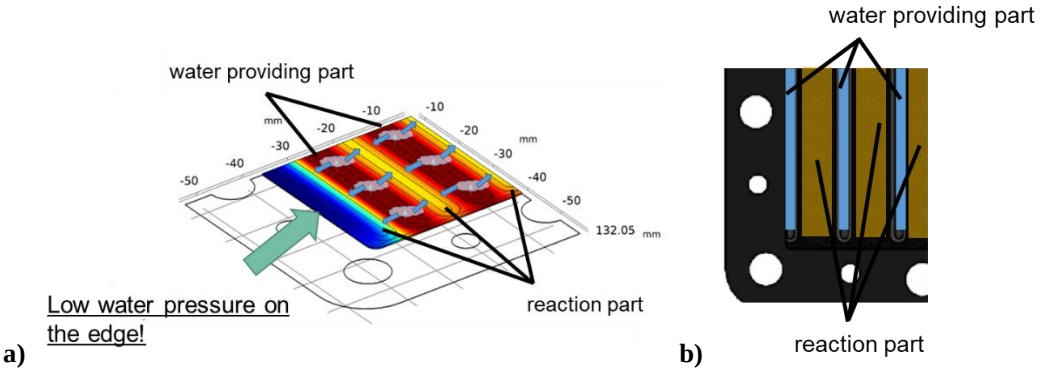

Figure 6. a) Modeling of water pressure distribution on the electrode surface (one-fourth) and b) diagram of the redesigned electrode (one-fourth).

The effects of the property changes of the electrode were confirmed through preliminary tests using small electrolysis cells. By using a small cell with the electrode design in Figure 6b), a current twice as large as in the case using the previous cell designed as Figure 6a) could be applied at the same water electrolysis voltage.

Based on the result, we prepared a modified full-scale cell stack. Figure 7 shows the appearance of the cell stack. This time, we increased the number of cell stacks to 15 from the previous 10 to lower the electrolytic voltage of each cell. Nevertheless, the total thickness of the cell stack was slightly reduced by reviewing the thickness of the separators and end plates.

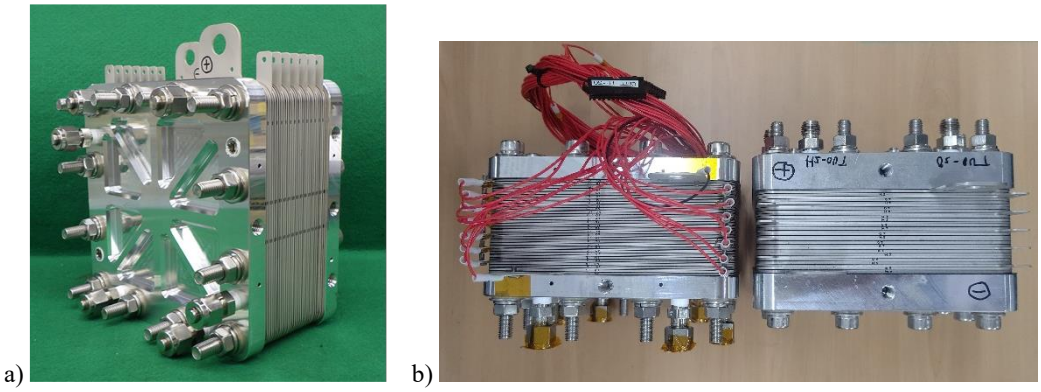

Figure 7. Modified oxygen generation cell stack: a) Exterior view; b) Comparison of the 15-cell stack model prototyped this time (left) and the previous 10-cell stack (right).

C. Integrated testing

The improved Sabatier reactor and oxygen generation parts were integrated and evaluated in a full-scale integration test as a modified tandem reactor (Figure 8).

The test was conducted following the test procedure reported in 2023.[2] Figure 9 shows a schematic diagram of the test system. In the integrated test, the Sabatier reactor was heated first without supplying gases. Then the water electrolysis used that heat to electrolyze water. Then CO_2 from a gas cylinder, and H_2 from the water electrolysis were fed to the Sabatier where the exothermic reaction provided the excess heat needed for electrolysis.

Practically, the generated H_2 gas was increased gradually with the applied current increasing until the H_2 side MFC in the open state reached the target value of 3.6 SLM. The fed CO_2 was introduced continuously at a rate of 1.58 SLM by increasing the set flow rate of the MFC in stages so as not to exceed the amount of H_2 produced. Following the test of Section A, the Sabatier reaction in the integrated test was determined to have reached a steady state when the measured catalyst temperatures became almost constant, and then the effluent gas was sampled. The CO_2 conversion rate was calculated from the GC analysis results of the sample gas.

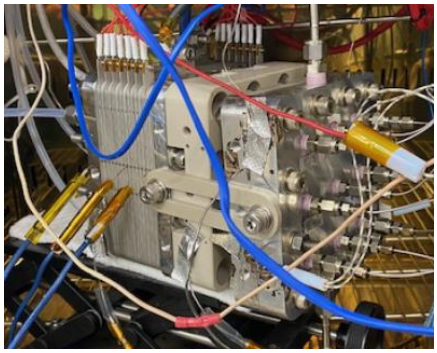

Figure 8. Picture of the modified full-scale tandem reactor.

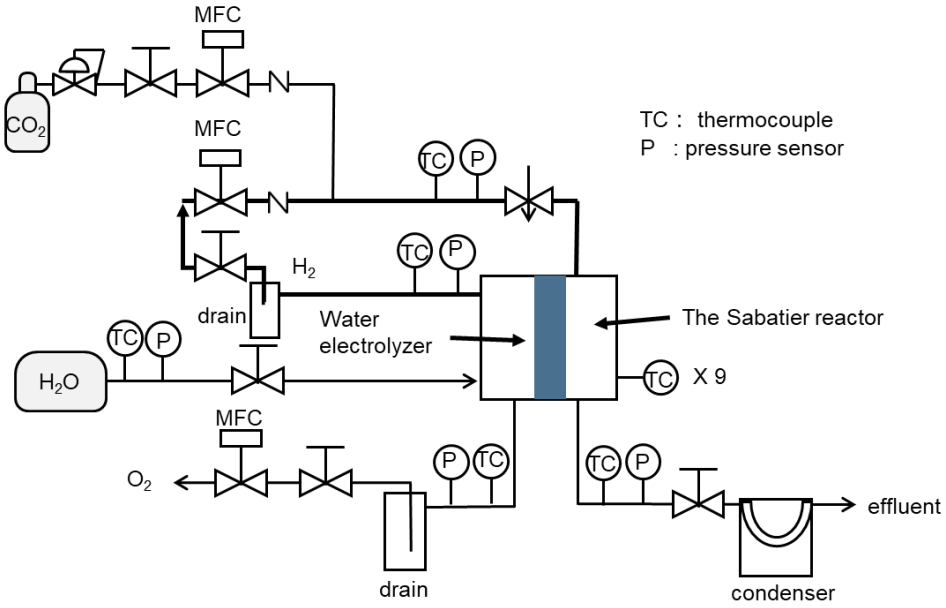

Figure 9. Schematic diagram of the integrated test system.

For the integrated reactor, the CO_2 conversion (Figure 10■) was 8.7% at 167°C and increased gradually with the reaction temperature to 54.8% at 257°C in the Sabatier reactor section. When comparing with the plots for the Sabatier stand-alone test (Figure 10●), the catalyst temperature and resulting CO_2 conversion showed good agreement. It supports that the generated H_2 from the electrolysis part was good enough for using the Sabatier reaction without any additional purification for this experimental period. It might be noted that future development testing will include long-duration tests with representative CO_2 and ISS water feed. On the other hand, the water electrolysis section operated stably with a stack current of 35 A and a stack voltage of 22 V to provide 3.6 SLM H_2 constantly as shown in Figure 11. At the same time, each cell's voltage was also kept at about 1.5 V and did not show quick degradation which was observed in the previous experiment (Figure 11).[2] The calculated power consumption by water electrolysis was 770 W, which was more energy efficient than the previous cell stack (822 W).

Table 1 summarizes the main properties of the improved tandem reactor and those of the previous reactor. In terms of pressure circumstance, the lower pressure in the Sabatier reactor demanded less than 100 kPaG of water pressure for the provided water and about 20 kPaG of H_2 gas pressure, respectively. Both pressures were less than half of those in the previous testing, and thus, the pressure controllability of the system was significantly improved. In the oxygen generation part, both the stability of each cell voltage and the reduction of power consumption were successfully achieved with the modified cell stack. The design change of the electrode contributes to performance as expected from the results of the preliminary small cell evaluation.

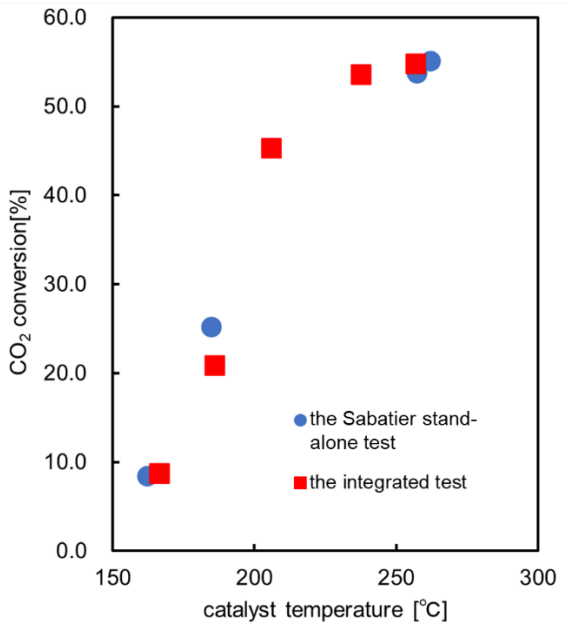

Figure 10. Comparison of the temperature dependence of CO_2 conversion observed in the integrated test (■) and the Sabatier stand-alone test conducted in Section A (●).

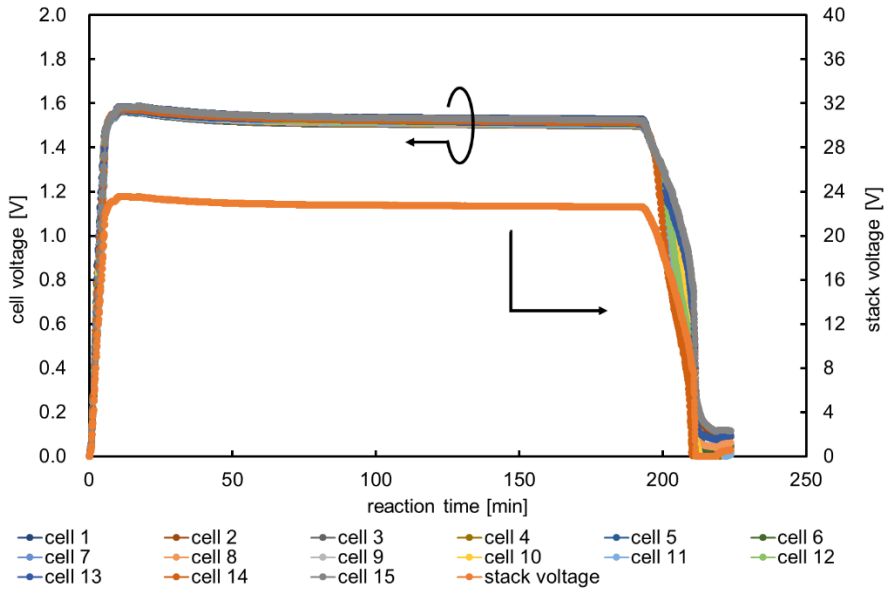

Figure 11. Measurement of cell voltages and the stack voltage of the modified electrolyzer during the full-scale integrated testing.

Table 1. Properties comparison of full-scale tandem reactors.

	Original (2023 ver.)	Improved (current)
Overall		
Cross-section size [cm square]	15	15
The Sabatier reactor section		
Catalyst volume [cm^3]	60	100
Weight of Ru-ZrO_2/TiO_2 [g]	11	17
CO_2 conversion [%] (max. 57%)	50	55
Catalyst temperature [℃]	273	262
Reactor pressure [kPa]	100	8
The oxygen generation section		
Number of the cell stack	10	15
Stack voltage [V]	16	22
Stack current [A]	52	35
Generated H_2 [SLM]	3.6	3.6
Power consumption by the cell stack [W]	822	770
Pressure of generated H_2 [kPaG]	120	20
Pressure of the provided water [kPaG]	150-200	100

III. Conclusion

We have developed a tandem reactor in which the Sabatier reactor is thermally conjugated and mechanically integrated with water electrolysis as an air regeneration technology required for future human-crewed space missions. We have modified the full-scale tandem reactor to solve issues revealed in previous experiments. As a result, improvement was achieved in the pressure controllability of the tandem reactor and the performance of the oxygen production section. Particularly in the oxygen production section, we succeeded in suppressing the sudden rise in cell voltage and reducing the power consumption of electrolysis to 770W. Using this improved reactor, we are pursuing the design and development of a breadboard model of a CO_2 reduction-O_2 generation system.

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