

Development of CO₂ hydrogenation-water electrolysis tandem reactor

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The authors have developed a new ECLSS technology for future manned space missions, demonstrated in a tandem device to generate oxygen, water, and methane. The device consists of a water electrolyzer integrated with a Sabatier reactor. The water electrolyzer is thermally coupled to a CO₂ hydrogenation reactor that directly transfers thermal energy generated by the catalytic CO₂ methanation. This paper reports the experimental proof of concept followed by subscale testing. The testing achieved 1 L/min H₂ production with corresponding CO₂ methanation provided by a scale-model tandem reactor.

Nomenclature

CO ₂	=	carbon dioxide
H ₂	=	hydrogen
JAXA	=	The Japan Aerospace Exploration Agency
ECLSS	=	Environmental Control and Life Support Systems
Ru	=	ruthenium
TiO ₂	=	titania
ZrO ₂	=	zirconia
Al ₂ O ₃	=	alumina
ΔS	=	entropy change
$T\Delta S$	=	energy change based on the Entropy change at a temperature T [K]
ΔH	=	enthalpy change

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- ΔG = the change of Gibbs free energy
- PEEC = polymer electrolyte electrolysis cell
- I-V = relationship between current (I) and voltage (V) for water electrolysis

I. Introduction

This paper discusses a novel process development that combines the generation of hydrogen (H_2) from water electrolysis and methanation of carbon dioxide (CO_2) with the Sabatier reaction. Not only has hydrogen been regarded as a promising medium to decarbonize our energy supply on the Earth,¹ but it can also be applied to close the loop of air revitalization systems for future manned space missions.

The process is called methane formation for ground technology, or Power to Gas.² For space applications, the Environmental Control and Life Support System (ECLSS) technology generates water from CO_2 by the Sabatier reaction. To investigate a dual-use technology that can be used for both Earthbound and space applications (Fig. 1), the authors have integrated water electrolysis and the Sabatier process into one device, as shown in Fig. 2. The tandem device is expected to reduce the amount of energy consumed and the size and weight of the system.

The system concept was previously supported by numerical analysis.³ The analysis revealed the importance of maintaining the Sabatier reaction around $220^\circ C$. This temperature allows a high conversion efficiency in the combination of this study's Sabatier reactor and water electrolyzer. In addition, we developed a low-temperature catalyst for CO_2 methanation and a water electrolysis cell with an integrated electrode structure. This report describes the stepwise development of this tandem device in a subscale model, which successfully demonstrated 1 L/min H_2 generation and corresponding CO_2 methanation.

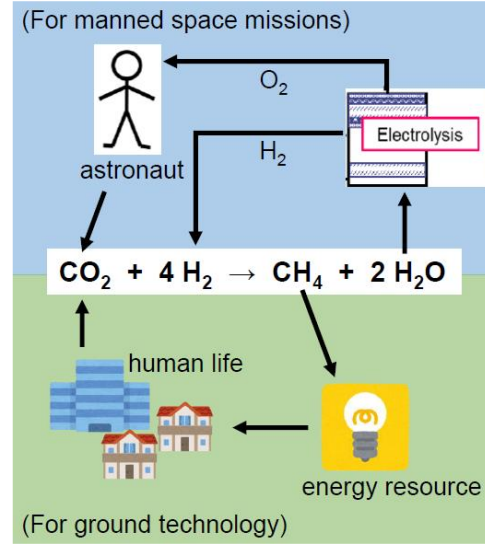


Figure 1. Schematic drawing of CO_2 hydrogenation as a dual-use technology on the ground and in space.

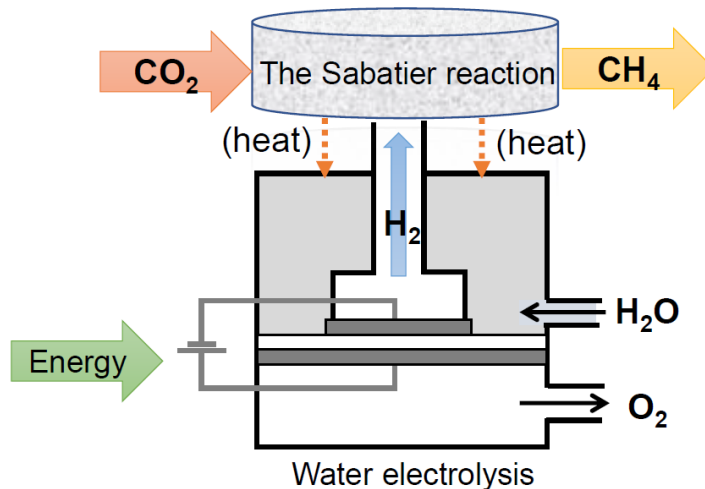


Figure 2. The concept design of the tandem reactor in which the water electrolyzer is combined with the Sabatier reactor.

II. Development of Ruthenium Catalyst for the Sabatier Reaction

JAXA and the University of Toyama have collaborated to investigate Sabatier-reaction catalysts for practical use in Environmental Control and Life Support Systems (ECLSS).⁴ We reviewed their results, showing suitable conditions for catalyst manufacture, because high CO₂ conversion around 220°C is still challenging, even with the developed catalyst. The study found that the size of catalytic ruthenium (Ru) particles on the surface of titania (TiO₂) affects the reaction rate and ignition temperature.

High CO₂ conversion at the targeted temperatures was achieved with the simultaneous sputtering of Ru with other metal oxides to control the growth of the Ru particle size.⁵ When Ru was sputtered with zirconia (ZrO₂), the CO₂ conversion was higher than with previous Ru/TiO₂ catalysts. This co-sputtering technique resulted in a decreased reaction temperature and maintained the deposition of nano-scale Ru particles during reaction at higher temperatures.⁶

Immobilization of the Ru-ZrO₂/TiO₂ catalyst (Fig. 3) was another topic of our research. An immobilized catalyst with a three-dimensional framework of silicon carbide⁷ proved unable to accommodate the catalyst onto the endplate of a water electrolyzer due to size limitations. As an alternative, a Ru-ZrO₂/TiO₂ catalyst was immobilized onto porous alumina (Al₂O₃) plates without binders or high heat.⁸ The catalyst particles were fixed uniformly and securely on the plates and retained their high CO₂ methanation performance. Since an Al₂O₃ plate could be easily molded into various sizes, this new method can prepare catalyst layers of various sizes for large Sabatier reactors.

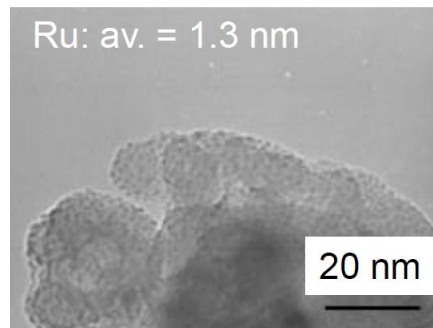
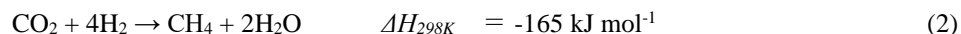
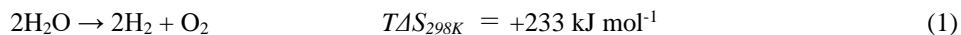


Figure 3. A typical TEM image of Ru-ZrO₂/TiO₂ catalyst.

III. Development of Water Electrolyzer

Water electrolysis partially determines the energy utilization efficiency and H₂ supply of the entire device. As shown by Eq. (1), water electrolysis requires an energy change based on a change of entropy at temperature T [K] ($T\Delta S$). The change in Gibbs free energy (ΔG) for water electrolysis in the standard state requires 1.23 V. However, the reaction always begins at 1.48 V, the thermally neutral voltage. The overpotential for thermally neutral electrolysis comes from $T\Delta S$ to generate hydrogen and oxygen, but it can be aided by thermal energy. If the heat generated by the exothermic Sabatier reaction (Eq. (2)) can be utilized for water electrolysis, the required electrical energy can be reduced, and the energy efficiency of the system is enhanced.



The water temperature for electrolysis in ground applications determines the device's efficiency. With sufficient heat to compensate for the entropy change by thermally coupling water electrolysis with the Sabatier reaction, higher efficiencies of energy utilization can be realized. An even more efficient design that allows stronger thermal coupling between the electrolyzer and reactor must be considered.

During water electrolysis, liquid water usually circulates around the electrodes. In this case, heat must be transferred from the Sabatier reactor to the electrolytic cell using a heat exchanger that imposes an energy loss. However, to simplify and reduce the weight of the system, using a Sabatier reactor to heat the electrolytic cell directly without a heat exchanger is the key. Thus, the authors combined an electrolyzer and a reactor into a single unit, as shown in Fig. 2.

Pressurized water without circulation is supplied to the water electrolysis area shown in Fig. 4. The water passes through the diffusion layer approaching a proton-conductive membrane then migrates to the electrodes where the catalyst is located.

In this case, the surface of the electrode must be covered with a hydrophobic material. The water, which electrochemically decomposes into hydrogen and oxygen, cannot penetrate a hydrophobic electrode. If there is a difference in pressure between the water and the generated gases, the gases can be separated from the electrode instantaneously. Based on the schematic shown in Fig. 4, we developed a water electrolysis cell with integrated flow channels.^{9,10} If the electrolyzer is operated at a high temperature, $T\Delta S$ can be supplemented by the generated heat. Figure 5 shows the I-V curve representing the best test results for the polymer electrolyte electrolysis cell (PEEC) from the endothermic reaction obtained at 115°C. To operate the PEEC above 100°C, a polymer electrolyte membrane with a thermal tolerance was applied. The dotted line in Fig. 5 results from the water electrolysis process with water circulating around the electrode at 80°C. For comparison, the solid line results from water electrolysis at 115°C using pressurized water without circulation, starting from 1.23 V. This result indicates that the reaction just started, based on the conversion for ΔG and implies that the endothermic reaction was achieved with the correct compensation of $T\Delta S$.

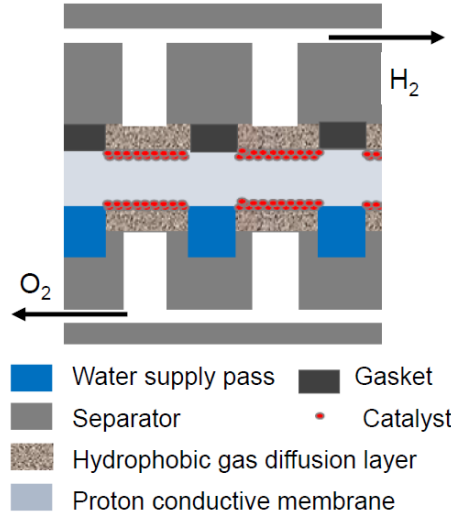


Figure 4. The design concept for the water electrolysis cell using integrated flow channels.

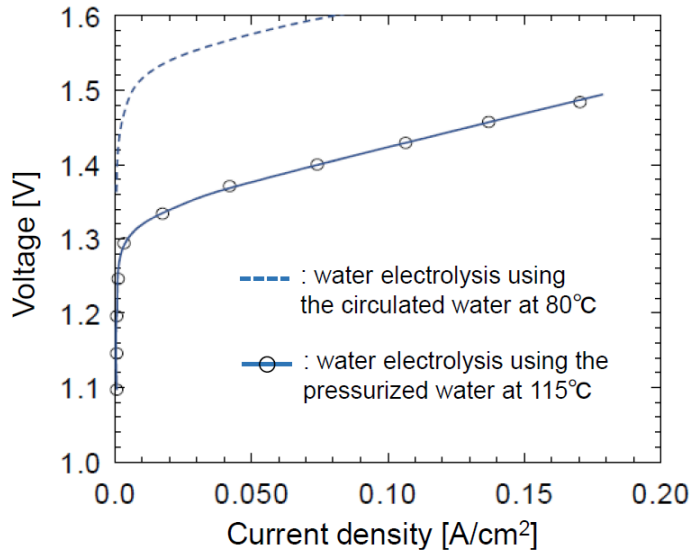


Figure 5. The I-V curves obtained from endothermic water electrolysis at 115°C.

IV. The Demonstration of Tandem Device of the Sabatier Reaction and Water Electrolysis

Using the essential technologies described above, a conceptual model of the water electrolysis-Sabatier reaction tandem device was prototyped, as shown in Figure 6a). In the device, the Sabatier catalyst (Fig 6b)) was accommodated into the right side of the endplate of the electrolyzer (Fig. 6c)).

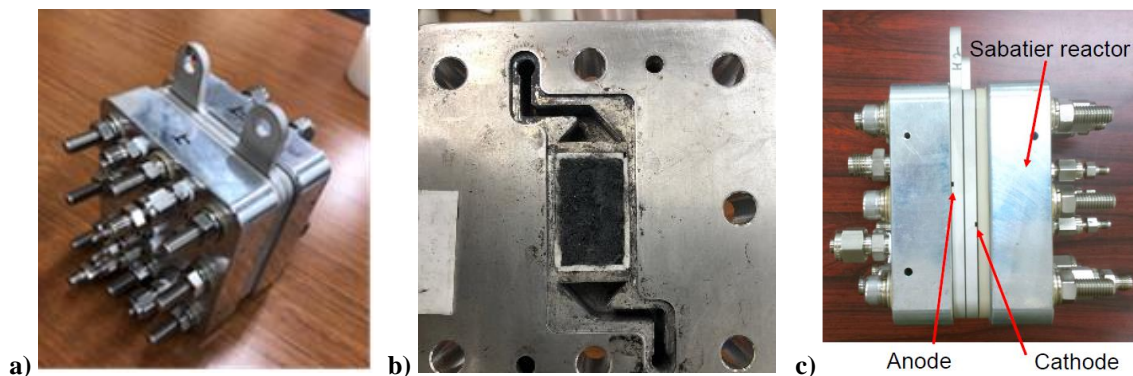


Figure 6. The conceptual model of the water electrolysis-Sabatier reaction tandem device: a) external view, b) the Sabatier reactor in the endplate, and c) side view.

The conceptual model demonstrated the Sabatier reaction with the Ru-ZrO₂/TiO₂ powder catalyst diluted with ca. 2 g of glass wool. The device was heated with sheathed heaters inserted into the endplate on the Sabatier reactor side. The temperature of the electrolysis water was maintained above 100°C. The 40 mL/min of H₂ generated by the electrolyzer was mixed directly with 10 mL/min CO₂ provided from a cylinder and transferred to the Sabatier reactor. The amount of the provided H₂ was monitored with the measured current. 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) and argon as a carrier gas at 220 kPa. The peaks observed on the GC chart were identified and calculated using external standard calibration curves. Assuming that the volume of fed CO₂ was equal to the sum of the volumes of CH₄ and CO₂ in the effluents during the steady-state reaction, the formed CH₄ and unreacted CO₂ peaks were identified on the chart according to the equation $(\% \text{ of produced CH}_4) / [(\% \text{ of unreacted CO}_2) + (\% \text{ of produced CH}_4)] \times 100$.

Figure 7 shows the CO₂ conversion versus the reaction temperature, corresponding to the maximum temperature in the data measured at the top, middle, and bottom of the catalyst bed, respectively. In reacting with H₂ from the cylinder, the CO₂ conversion increased gradually with increasing temperature and eventually reached 95.8% at 212°C. The reaction with H₂ from the electrolyzer showed similar reactivity, suggesting the technical feasibility of our combining the electrolyzer and Sabatier reactor directly.

Parameters obtained from the experiment were used to model the tandem system with the COMSOL Multiphysics® solver.¹¹ Based on the calculations, a subscale model of the tandem device was designed and tested as described in the following section.

In addition, the simulation showed that thermal independence is established regardless of the size of the device, provided that an appropriate outer thermal insulator is installed.¹¹

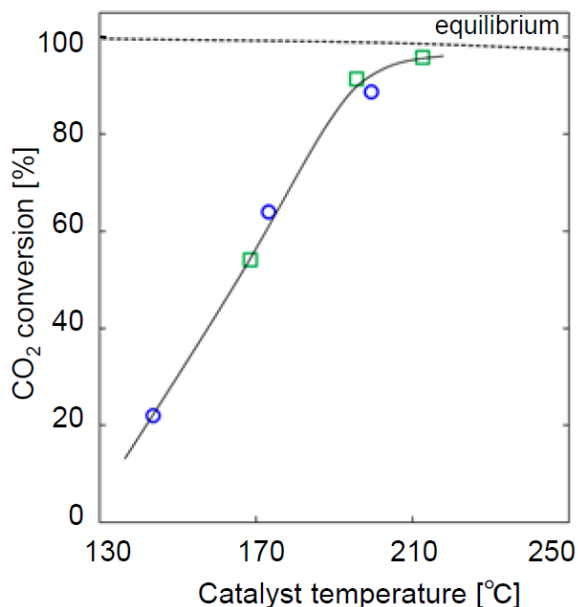


Figure 7. The CO₂ conversion versus reaction temperatures obtained during CO₂ methanation by the Ru-ZrO₂/TiO₂ catalyst in the tandem device with 40 mL/min of H₂ provided from a cylinder (□) and the electrolyzer (○), respectively.

V. Development of Subscale Test Models of the Tandem Device

Practical applications require approximately 4 L/min of H₂ to be generated as well as water to be produced by the CO₂ hydrogenation. Based on the numerical analyses, the subscale tandem device was prototyped with a large electrolysis cell stack, whose endplates and cells were 15 cm square externally. The Sabatier catalyst layer, in which 6 g of Ru-ZrO₂/TiO₂ powder catalyst was immobilized onto Al₂O₃-plates of 10 cm x 10 cm x 2 mm (Fig. 8a))

The subscale integration test was carried out with the mixed gas of 1 L/min of H₂ continuously generated by the electrolysis section and 250 mL/min of CO₂ supplied from the gas cylinder. The operation was conducted according to the method of the conceptual model testing.

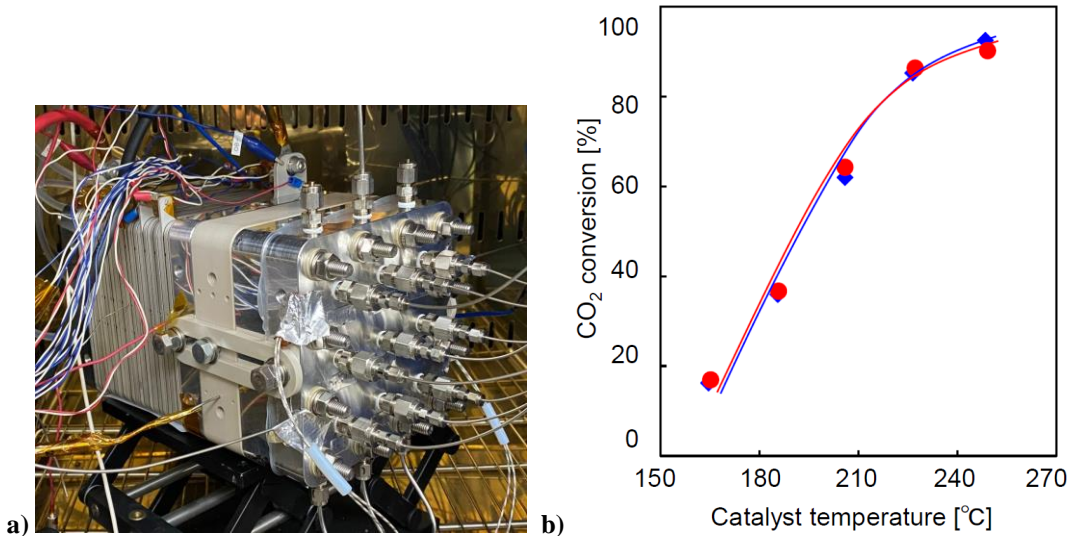


Figure 8. a) The overall view of the subscale tandem device and b) CO₂ conversion versus reaction temperature obtained during subscale CO₂ methanation with H₂ provided from a gas cylinder (◆) and electrolyzer of the device (●).

Figure 8b) shows the temperature dependence of the obtained CO₂ conversion rate. Compared with the results of the Sabatier reaction using H₂ supplied from a gas cylinder described as red circles (●), the conversion rates obtained in the integrated test (◆) showed excellent agreement. The GC chart obtained from the integrated test showed only peaks identified as H₂, CH₄, and CO₂. No by-products, such as carbon monoxide, were detected, as shown in Fig. 9. Thus, we experimentally demonstrated that the target methanation reaction is established with H₂ generated by water electrolysis even on a subscale.

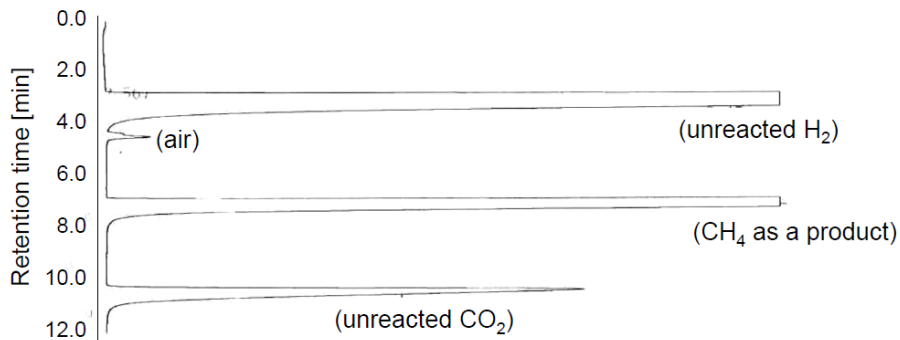


Figure 9. The GC chart of the Sabatier reaction at 206°C with the subscale tandem device (250 mL/min CO₂ + 1 L/min H₂ from the electrolyzer).

VI. Conclusion

We obtained the following results from this study.

1. We successfully developed a Sabatier catalyst that provided conversion of over 90% at 220°C. This catalyst also showed tolerance against sintering after experiments at high temperatures.
2. The water electrolyzer utilized pressurized water without circulation to realize endothermic water electrolysis. The electrolyzer has a hydrophobic electrode area that also demonstrated an acceptable separation of gases from liquid water without mixing hydrogen and oxygen.
3. The Sabatier catalyst was supported inside the endplate of the water electrolyzer, which demonstrated the sequential operation of water electrolysis with Sabatier reaction inside the tandem device.
4. The experimental parameters of the tandem device were introduced to COMSOL Multiphysics®. The calculations demonstrated the scalability of the device to larger models that would demonstrate independent thermal operability based on the balance between the exothermic Sabatier reaction and endothermic water electrolysis.
5. The developed subscale tandem device successfully demonstrated water electrolysis generating 1 L/min H₂ and the corresponding Sabatier reaction, which achieved 92% conversion of 250 mL/min CO₂ at 250°C.

Next, a scaled-up tandem model of CO₂ methanation and water electrolysis for a four-member crew is planned. The device will be demonstrated under stoichiometric conditions and a practical operation in which the amount of H₂ is determined by the produced O₂. In parallel, long-term testing will be done to verify the robustness of both the Sabatier catalyst and the electrolyzer.

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