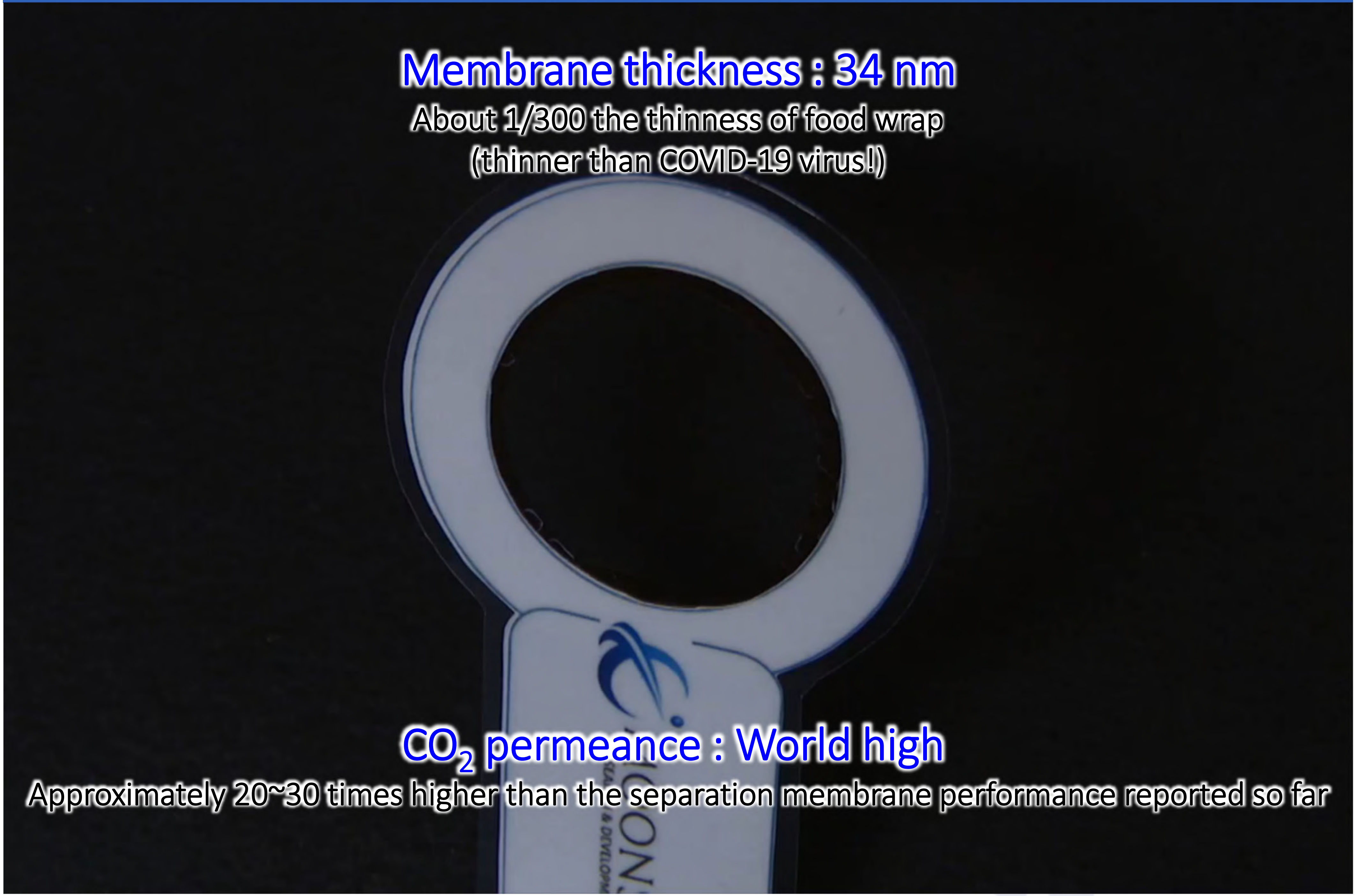
Development of Global CO_2 Recycling Technology towards "Beyond-Zero" Emission

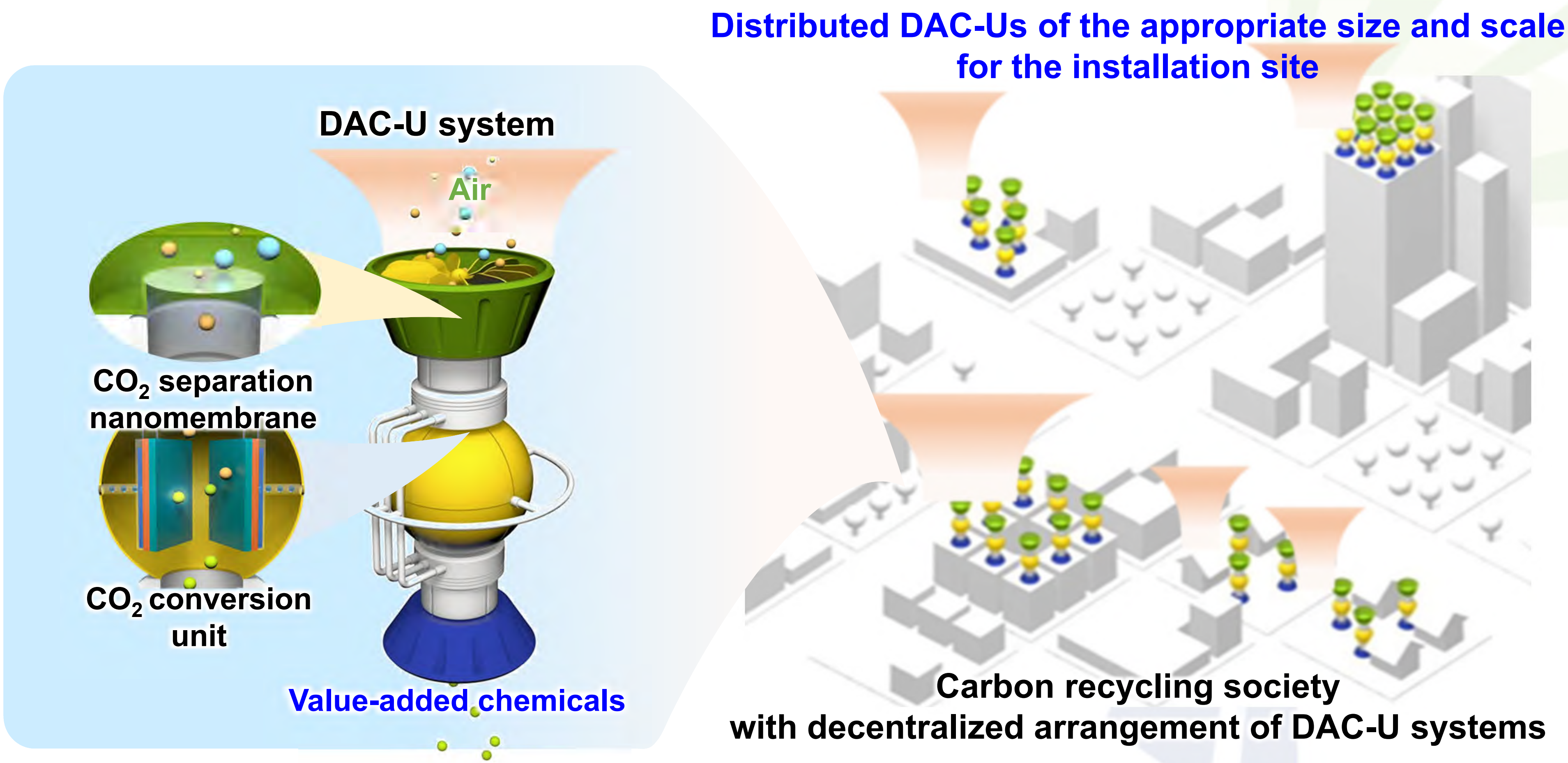
PM : Shigenori FUJIKAWA
International Institute for Carbon-Neutral Energy Research, Kyushu University, Professor
PJ partner institutes :
Kumamoto Univ., Hokkaido Univ., Univ. Tokyo, Kagoshima Univ., Osaka Inst. Tech., Univ. Illinois at Urbana Champaign, Nanomembrane Tech. Inc.

CO_2 separation nanomembrane with the world's highest CO_2 permeability from Kyushu University [2]



New carbon recycling society: resources from the air

The innovative separation nanomembranes with overwhelmingly high CO_2 permeability realizes CO2 capture directly from the atmosphere, which has been thought to be impossible until now. This membrane separation unit is integrated with an electrochemical or thermochemical CO_2 conversion unit to create the Direct Air Capture and Utilization (DAC-U) system, a continuous process from atmospheric CO_2 capture to carbon fuel production. The size-scalable DAC-U system will be distributed and deployed to contribute to the construction of a carbon-circulating society based on local production for local consumption.



"Moonshot for beyond Zero Emission Society"

[4]

MOZES
Moonshot for beyond Zero-Emission Society

CO_2

CO_2 capture nanomembrane

highly CO_2 permeable nanomembrane

1000 times concentration

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM

CO_2 conversion

Permeate gas : concentrated CO_2 + N_2, O_2, Ar

CO_2 conversion under oxygen

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM

Green fuel production from CO_2 mixture gas

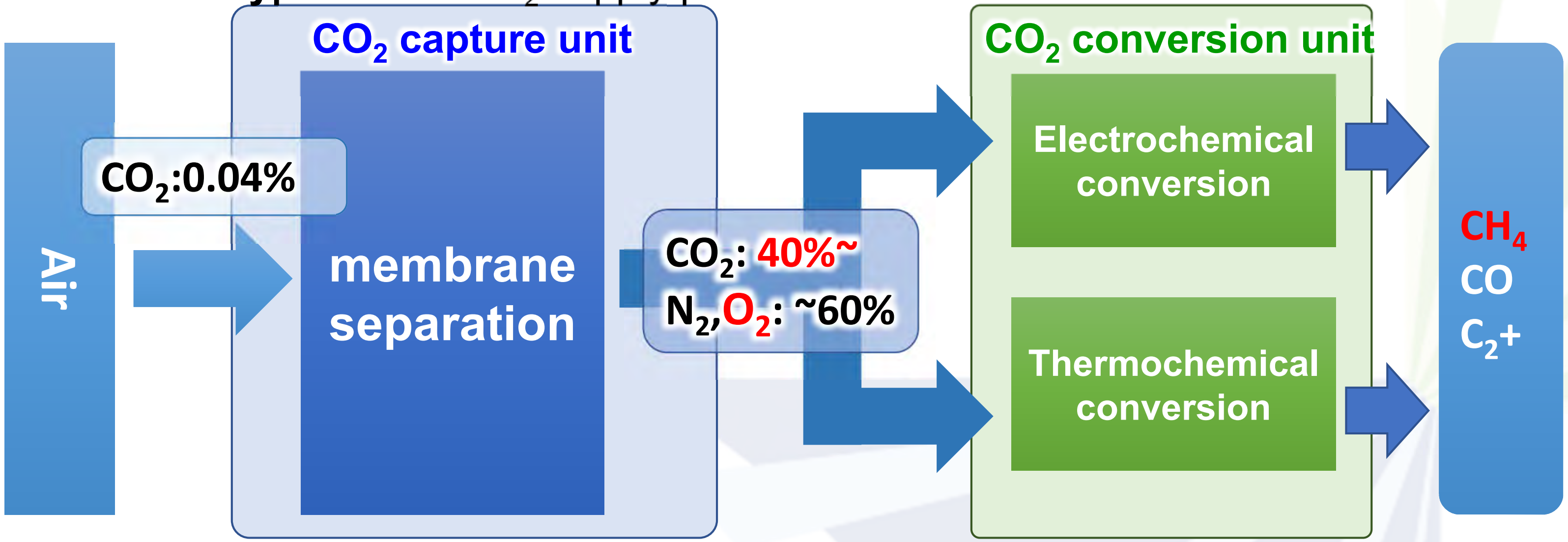
CO, CH_4, Ethanol, C_xH_y

Target pilots for this project

Target developments

- **CO_2 capture unit from the atmosphere by membrane separation**
- **CO_2 conversion unit by electro- and thermo-chemistry**
  Electrochemical type: Use the point with no H_2 supply
  Thermo-chemical type: Used at H_2 supply points

Final target pilot
Small system with each unit integrated



Primary issues at the beginning of the project

- **Is it possible to fabricate large-area nanomembranes for CO_2 separation?**
- **What kind of chemical products can be produced?**
- **Can CO_2 be converted from O_2 mixed gas as feed gas?**

KPI for 2022

Select basic membrane materials that exhibit high CO_2 selectivity.
Demonstrate **conversion from CO_2 mixed gas to CO, CH_4, and C_2H_4**

Organization

Special Advisor to Project Manager
Toyoki Kunitake
Atsushi Takahara

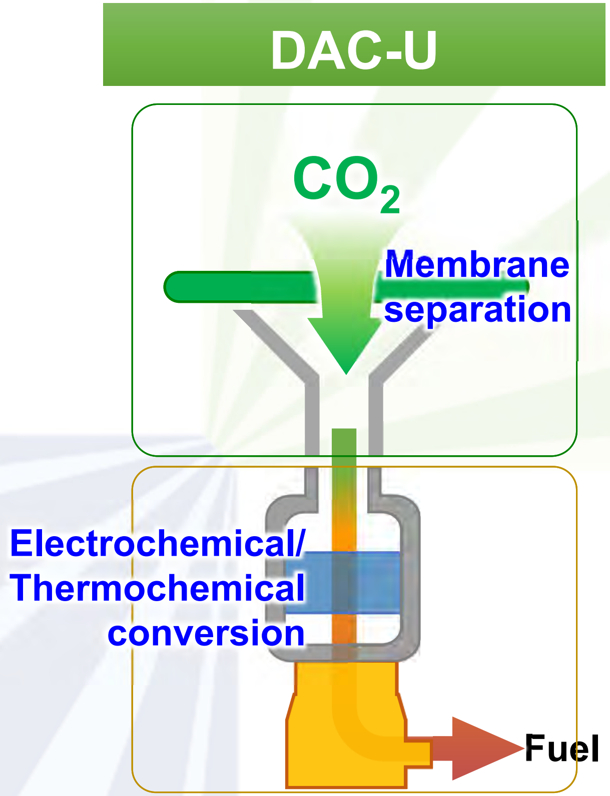
Project Manager
Shigenori Fujikawa

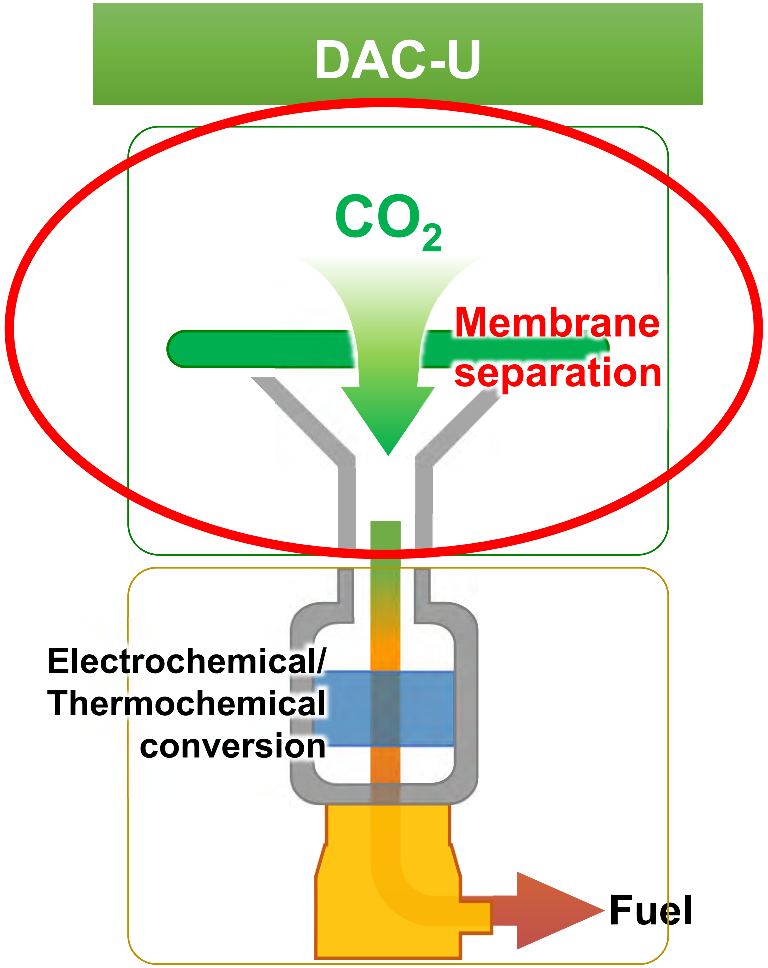
- **CO_2 capture research unit** — UL : Masashi Kunitake
- **CO_2 conversion research unit** — UL : Miho Yamauchi
- **Structure analysis unit** — UL : Ken Kojio
- **Energy and social analysis unit** — UL : Andrew Chapman

Special Assistant to Project Manager
Research: Kimihiro Matsukawa
IP: Hiroshi Tsubouchi

- **IP Management Committee**
- **Project Support Office**

Program Director,
Research Institute of
Innovative Technology for the Earth (RITE)
Kenji Yamaji



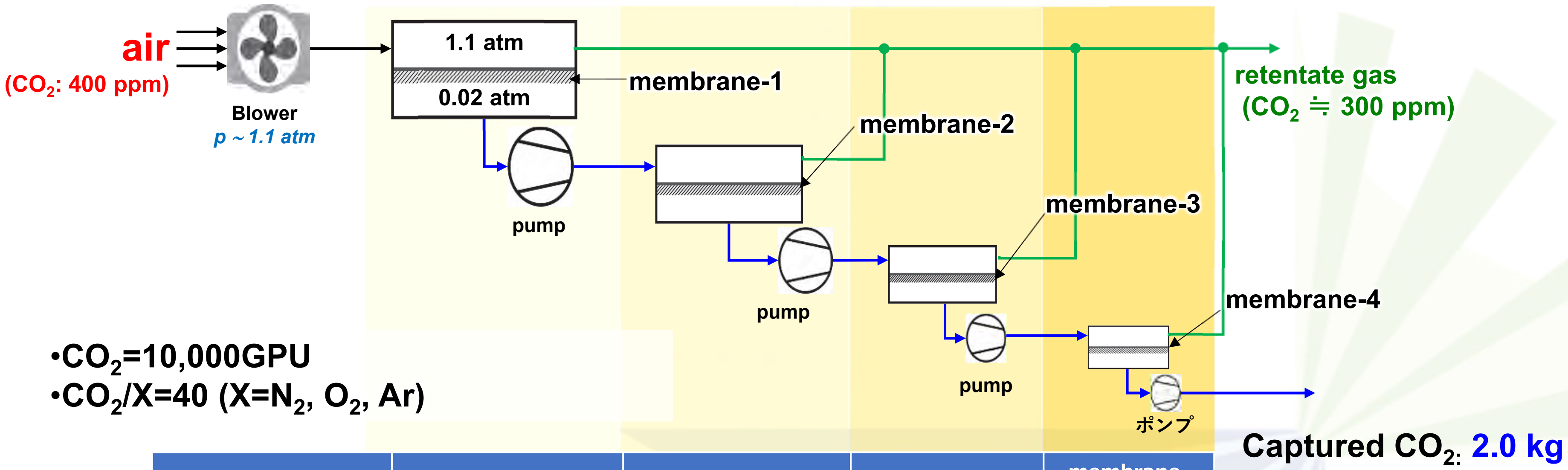


Realization of highly scalable and distributable CO_2 capture technology

Shigenori FUJIKAWA (Kyushu Univ.)
Masashi Kunitake (Kumamoto Univ., Unit leader)
Tomoyasu HIRAI (Osaka Inst. Tech.)
Yoshiro KANEKO (Kagoshima Univ.)
Shin-Ichiro NORO (Hokkaido Univ.)
Toyoki KUNITAKE (NanoMembrane Tech. Inc.)

CO_2 Capture Research Unit ~Membrane Performance Targets~.

•Final amount of captured CO_2量: 2.0 kg/day
•Final CO_2 concentration: >40 %



•CO_2=10,000GPU
•CO_2/X=40 (X=N_2, O_2, Ar)

	membrane-1	membrane-2	membrane-3	membrane-4
Area(m^2)	7.32	0.988	0.195	0.047
CO_2 conc. (%)	0.8	5.6	23.2	56.3

Targets of membrane performance

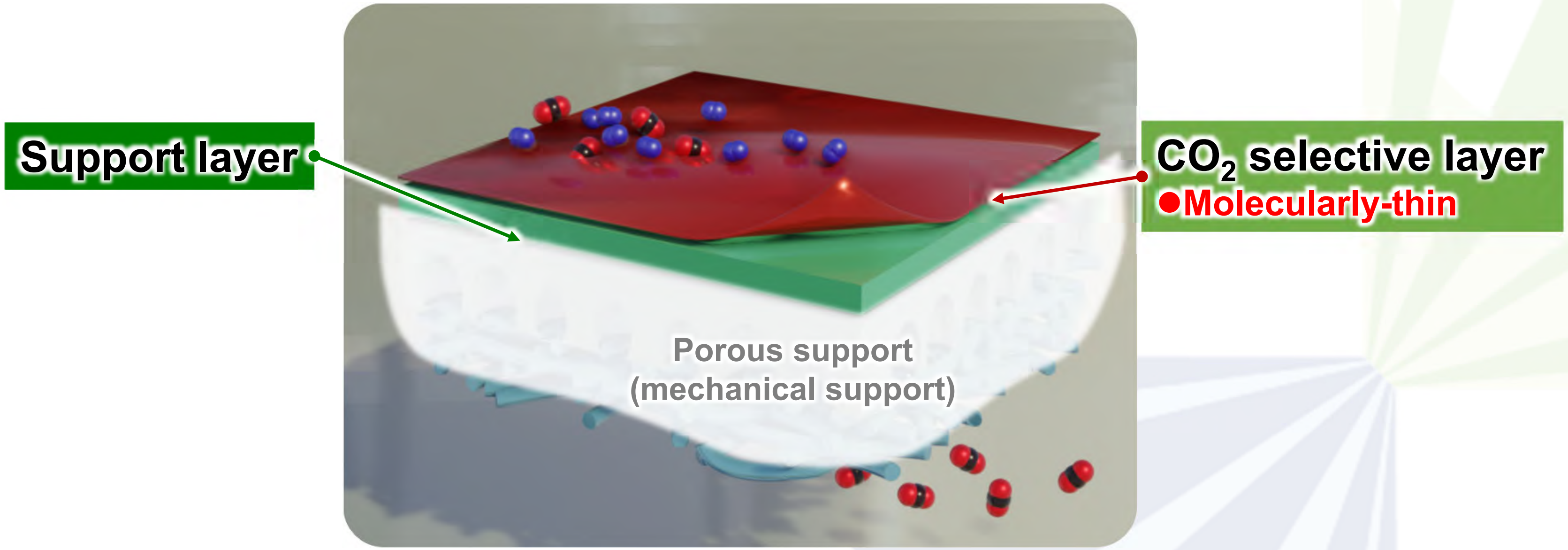
•CO_2 permeance：>10,000 GPU
•CO_2/O_2, CO_2/N_2 selectivity：>30
•Membrane area（4step：<10 m^2

CO_2 capture research unit

Approach of membrane preparation

Membrane structure：Thin film composite of CO_2 selective and support layers

- **Support layer: Free-standing and highly gas permeable**
- **Selective layer：variety of CO_2 selective materials**



Development step

①Support layer

- Development of silicone material with high CO_2 permeabilities

②Selective layer

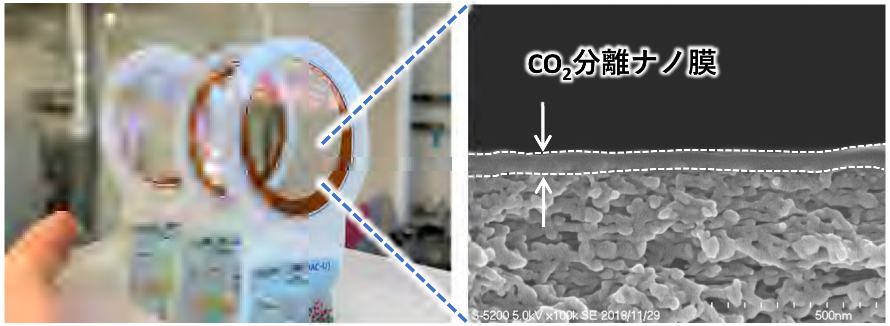
- Systematic exploring CO_2-philic materials

→molecularly thin layer on a support layer

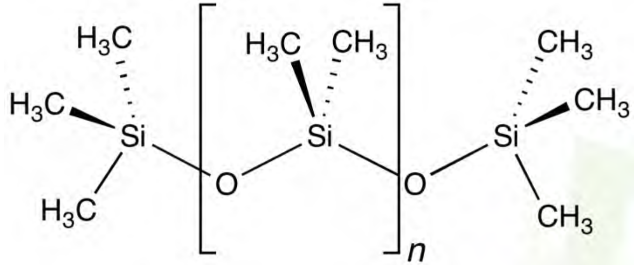
③ Controlled bonding of the selective layer to the supporting layer

④Large area production of separation nanomembranes

Development of silicone supported nanomembrane with high CO_2 permeability

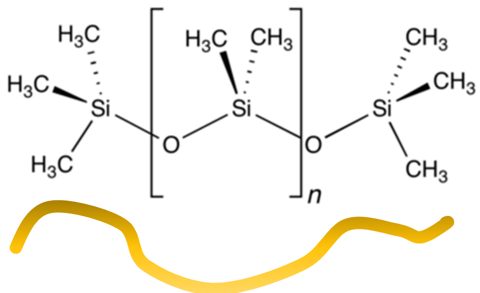


Fujikawa, et.al., Chem. Lett. **2019**, *48, 11, 1351-1354*



Polydimethylsiloxane (PDMS)（silocone）

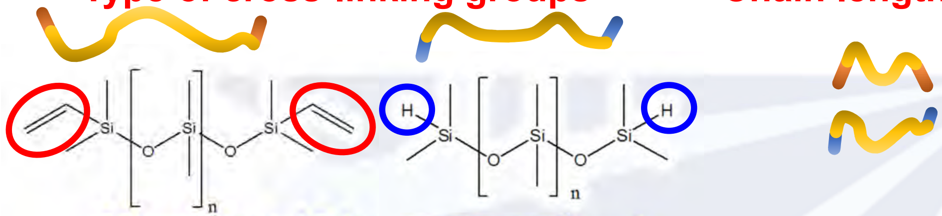
Basic molecular structure



Cross-liking

Terminally bifunctional PDMS

- Type of cross-linking groups
- Chain length

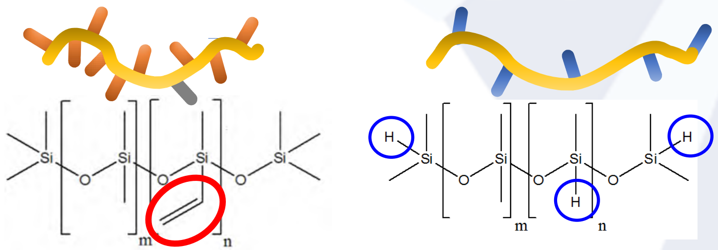


More than 10 types of synthesis completed

✕

Side-chain reactive PDMS

- Density of reactive group



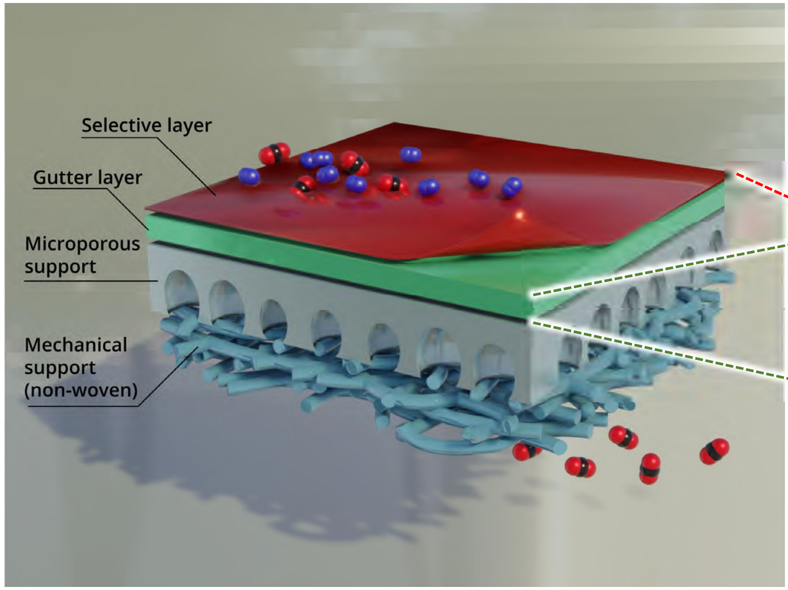
More than 20 types of synthesis completed

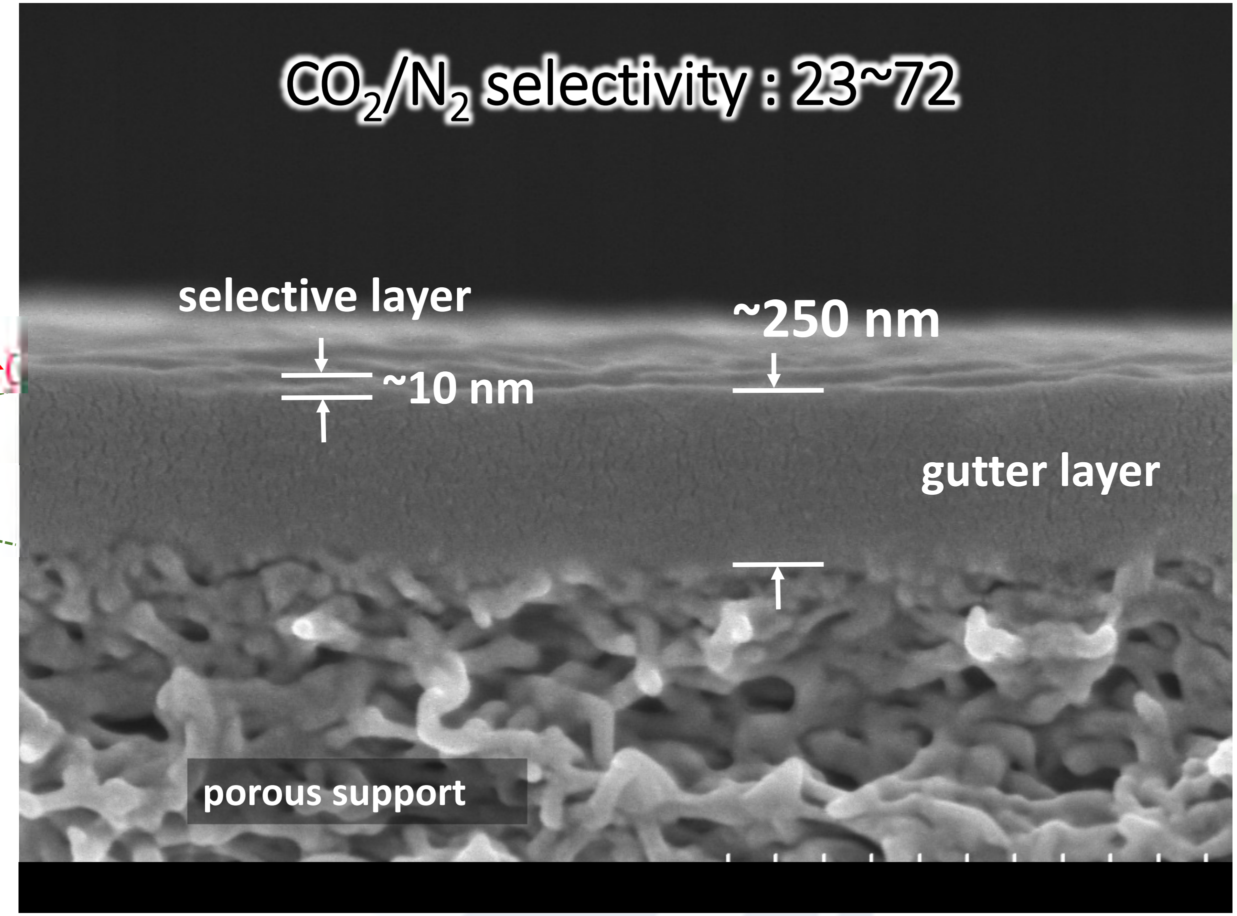
Candidate Structures

- Low cross-linking
- High molecular weight

Improved CO_2 selectivity of separation nanomembranes

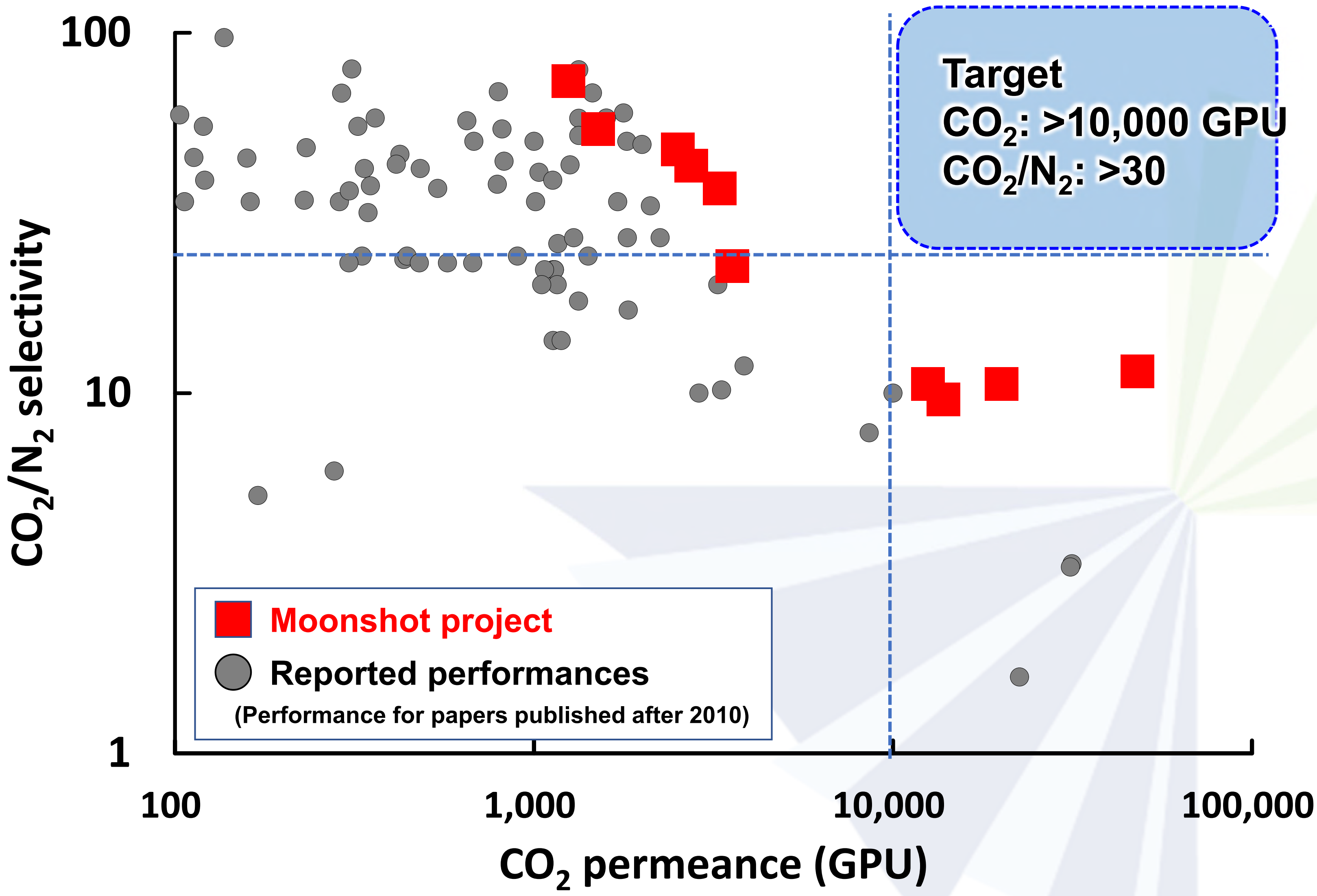
[11]





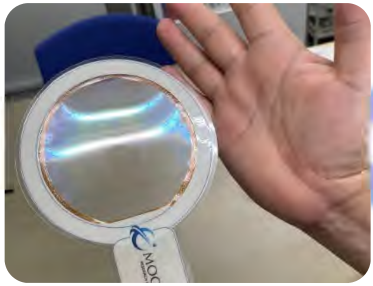
Selyanchyn O., Selyanchyn R., Fujikawa S. *ACS Appl. Mater. Interfaces,* 2020

Performance of developed membranes (international comparison)



World-leading membrane performance

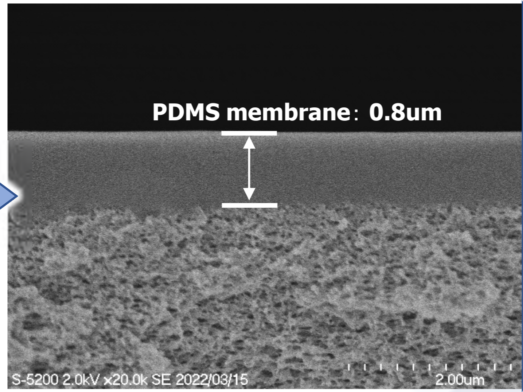
Large area of separation nanomembrane

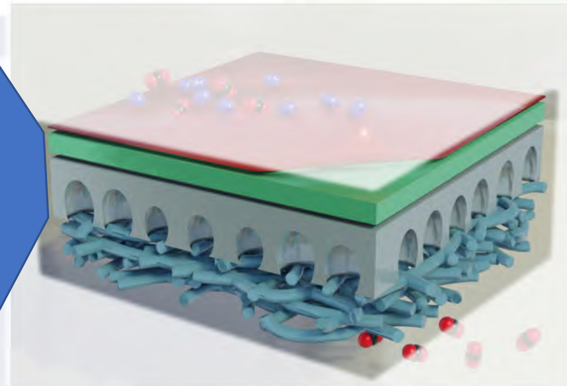


~ 10 cm^2

>10m

Roll-to-roll production of nanomembrane

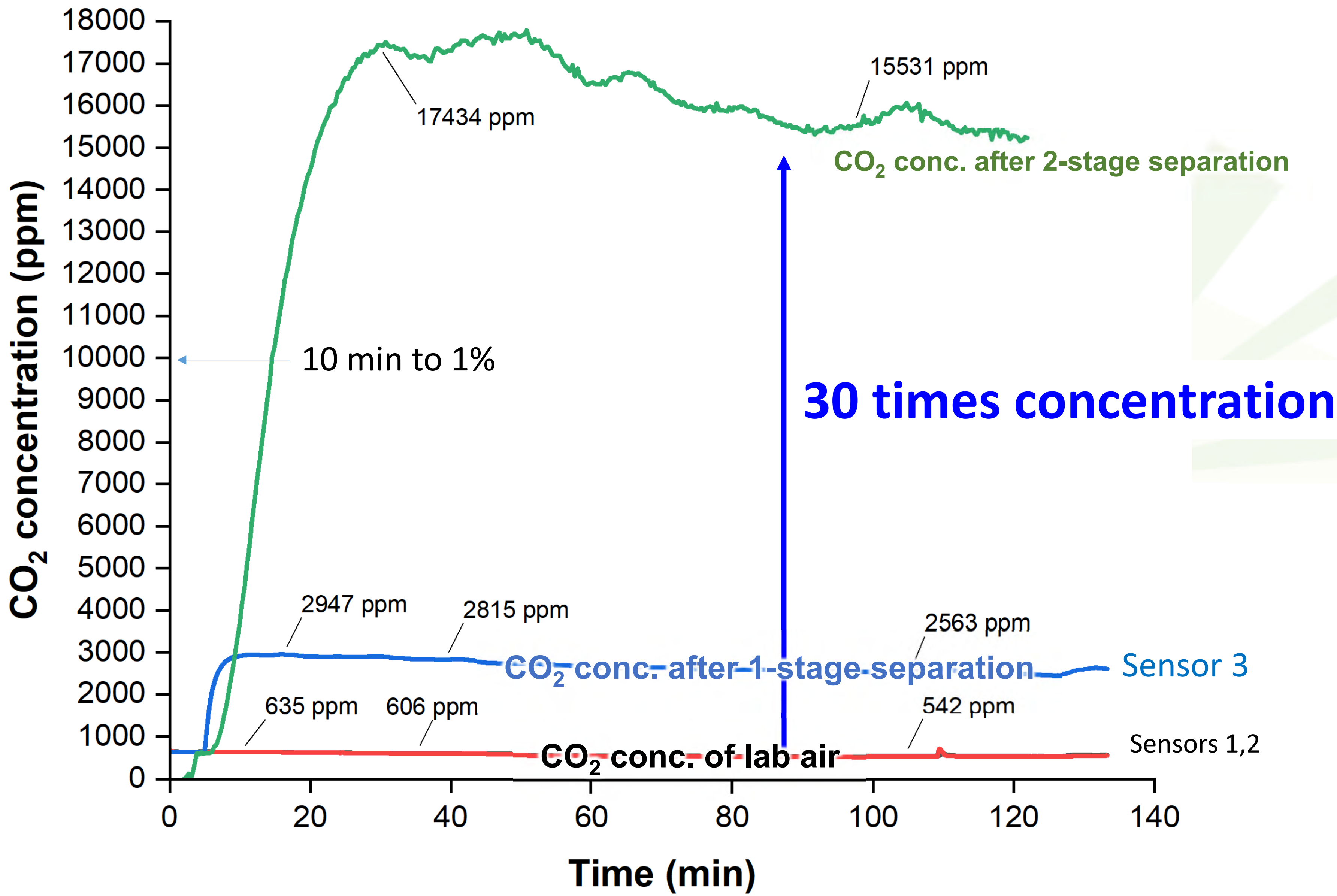




CO_2: ca. 3600 GPU
N_2: ca. 450 GPU
O_2: ca. 780 GPU

Reasonable separation performance
→further membrane thinning

Separation performance of 2-stage membrane separation module

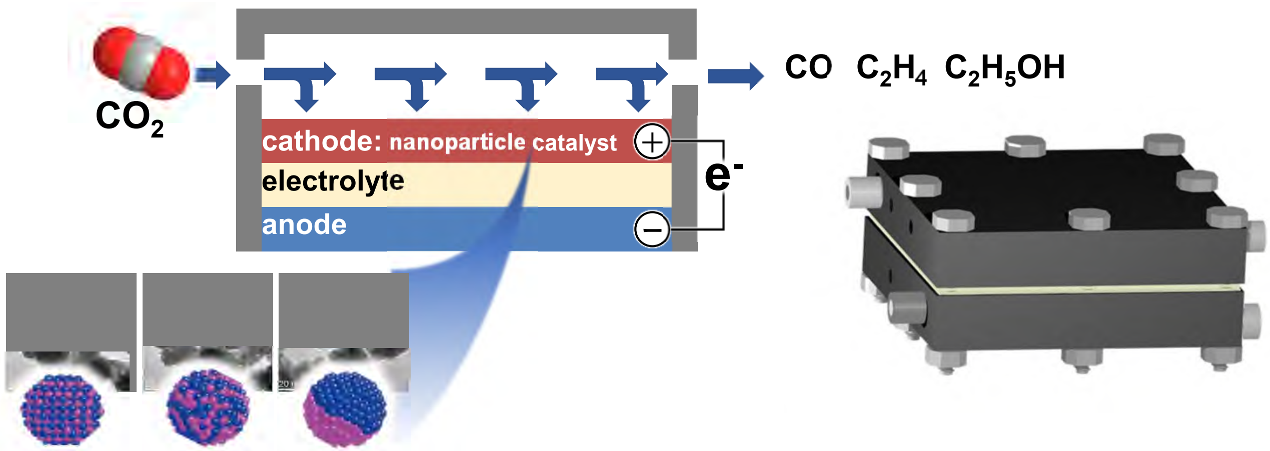


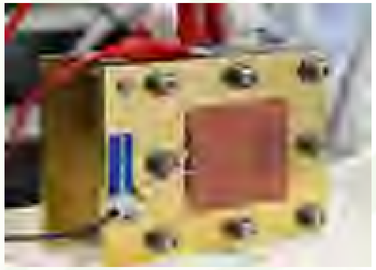
Demonstration of CO_2 enrichment at module level

Development of CO_2 conversion unit using electrochemical and thermochemical reactions

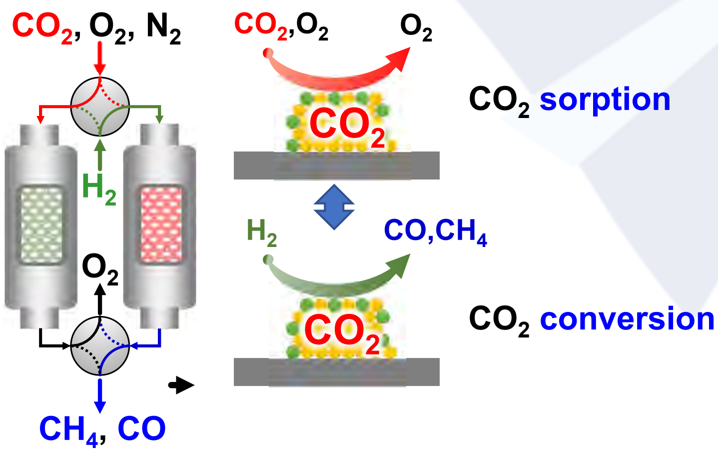
Production of carbon resources from CO_2 mixed gas separated by separation nanomembranes

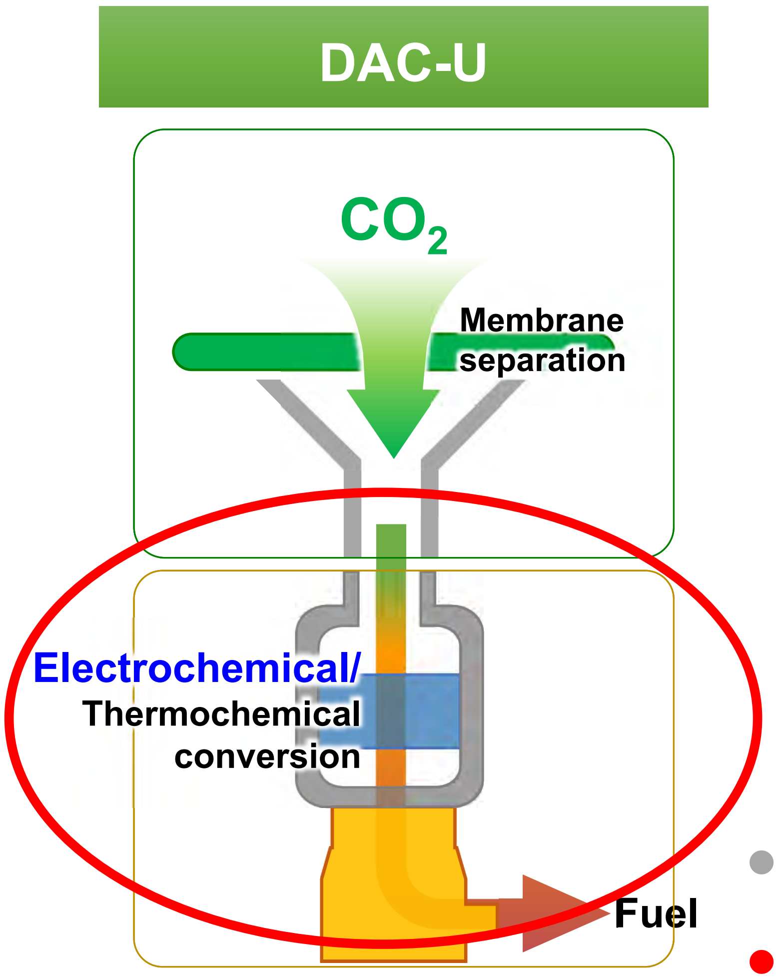
1. Production of basic chemicals and fuels by electrochemical conversion



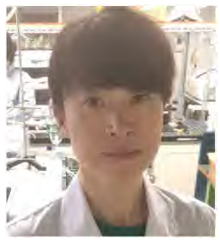


2. Production of C1 compounds by thermochemical conversion





Development of an electrochemical unit to produce carbon compounds from CO_2 mixed gas



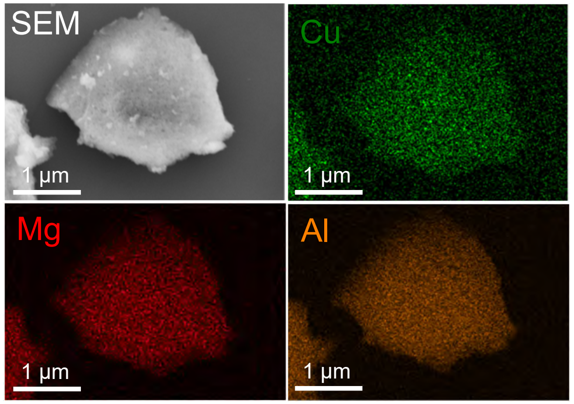
Miho YAMAUCHI （Kyushu Univ/）
Paul KENIS （Univ. Illinois at Urbana Champaign）

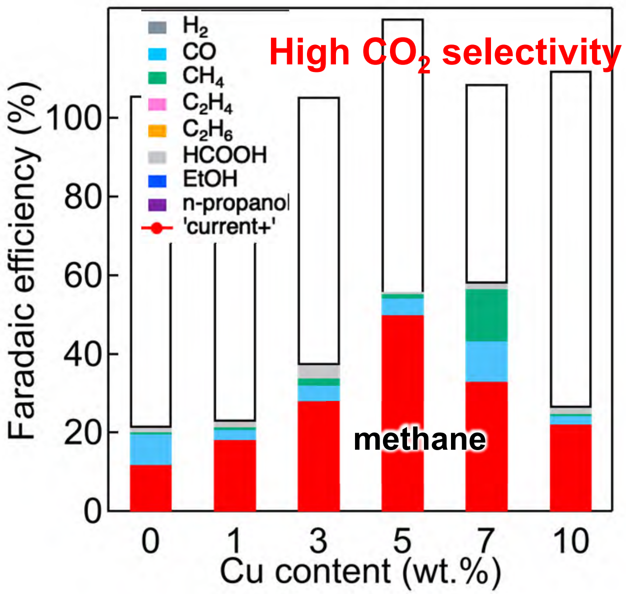
- Is it possible to fabricate large-area nanomembranes for CO_2 separation?
- What kind of chemical products can be produced?
- Can CO_2 be converted from O_2 mixed gas as feed gas?

Development of electrocatalysts for the production of carbon compounds from CO_2 (100%)

[17]

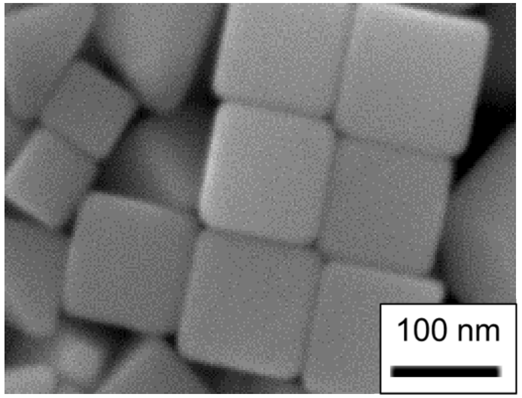
Atomically-dispersed Cu composite catalyst

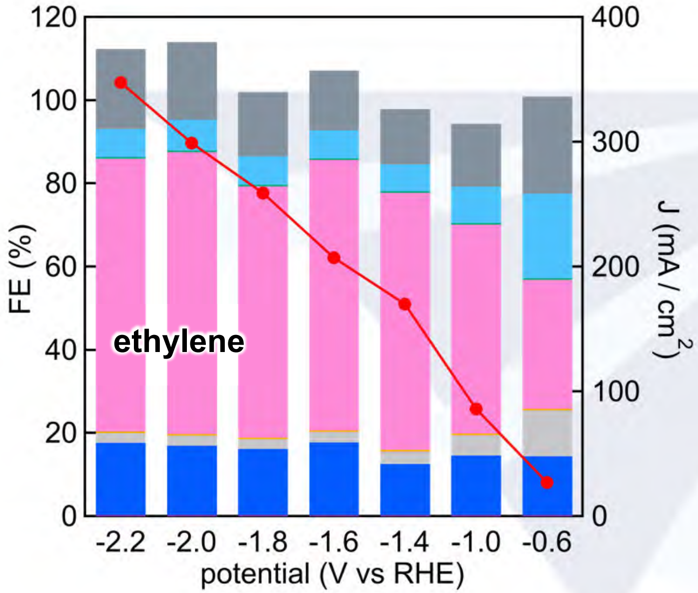




methane

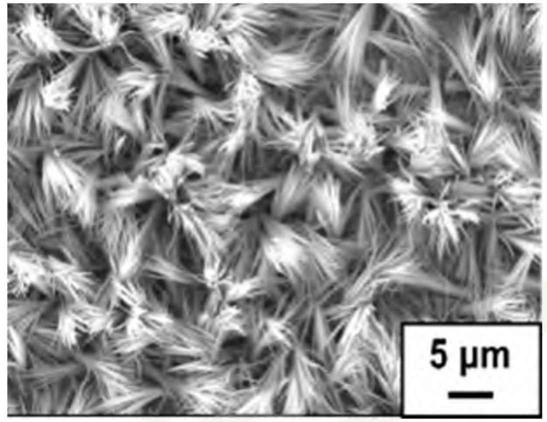
Nano cubic Cu catalyst

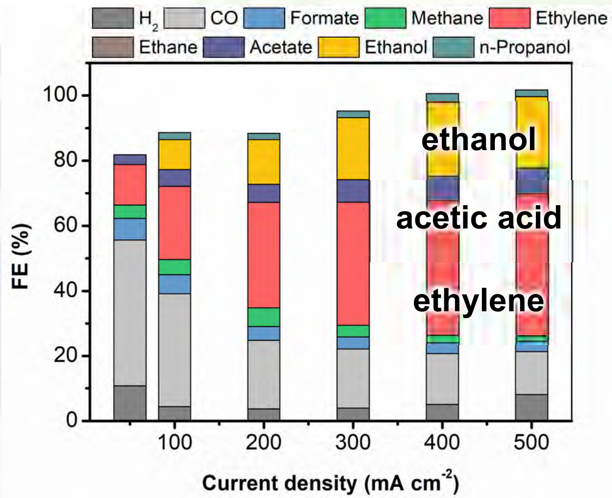




ethylene

Needle-shaped Cu catalyst





ethanol

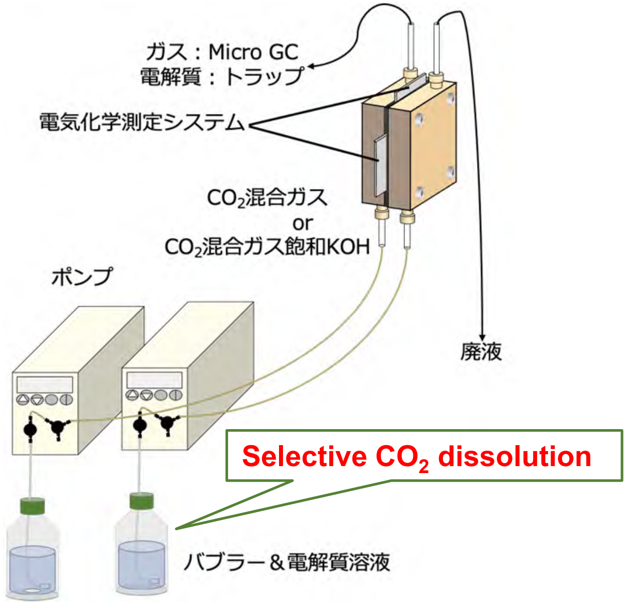
- **What kind of chemical products can be produced?**

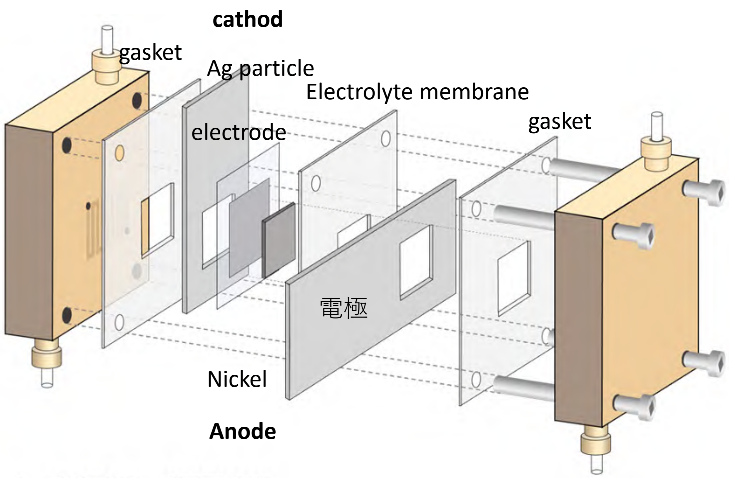
→C1 and C2 compounds can be produced electrochemically

CO production from CO_2/O_2 mixture gas
~ electrolyte dissolution method + new MEA cell ~

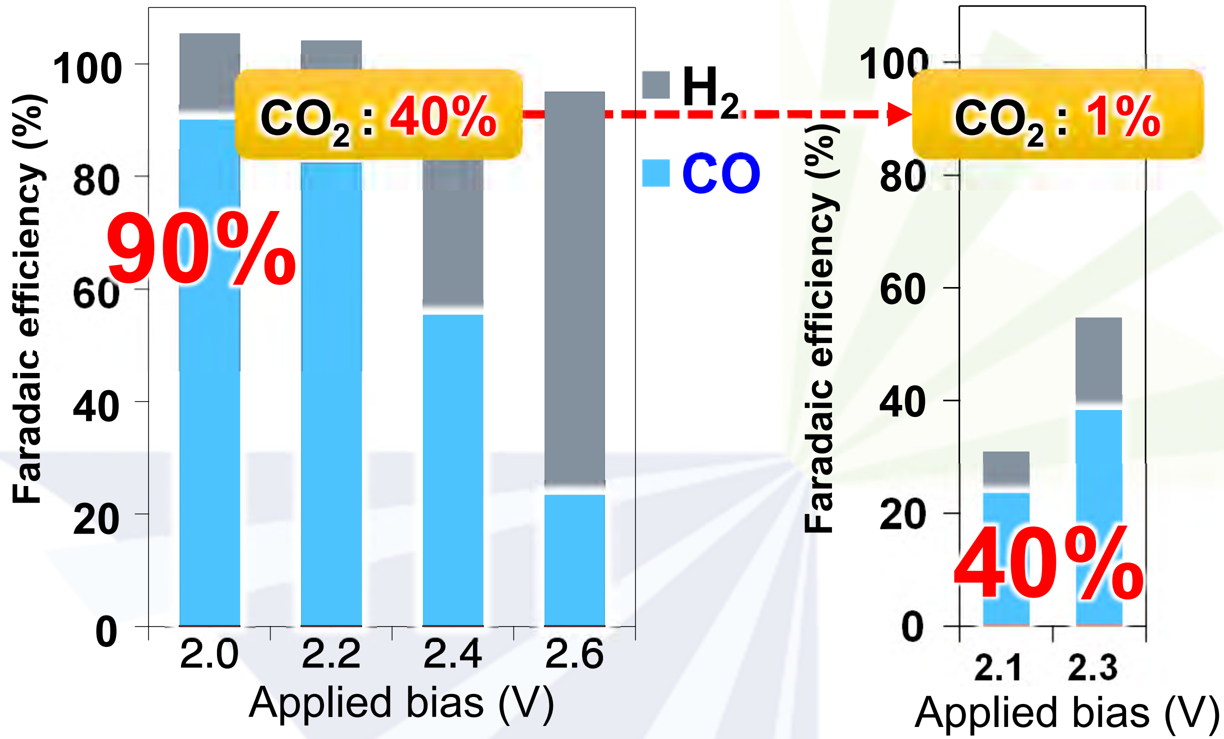
"Can CO_2 be converted using CO_2/O_2 mixture gas?"

source：CO_2(40 or 1%) + N_2(48%) + O_2(12%)
catalyst：Ag （→CO production）





Pat. 2022-47744



World first!

Syngas production from low concentrations of CO

原理実証

2024 target

Ultrahigh energy conversion efficiency η：53%

$$\eta(energy\ conversion\ efficiency) = \frac{theoretical\ potential}{applied\ potential} \times FE$$

Only CO and H_2 can be produced

A,W

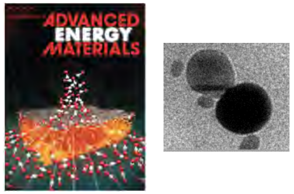
Design and systemization of electrochemical reaction cells

Paul Kenis (Professor)

University of Illinois at Urbana Champaign(UIUC)

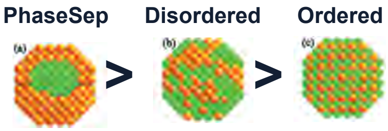
Electrochemical CO_2 conversion system using various catalysts

Ag NPs



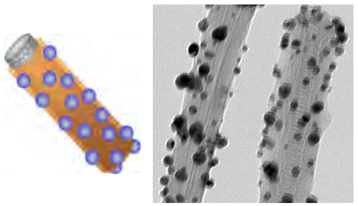
Adv. Energy Mater., **2013**

Bimetallic Cu-Pd NPs



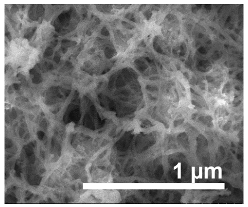
J. Am Chem. Soc., **2017**

Au on poly CNTs



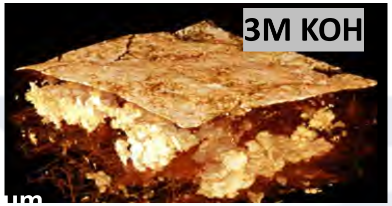
ChemPhysChem, **2017**

CuAg-wire

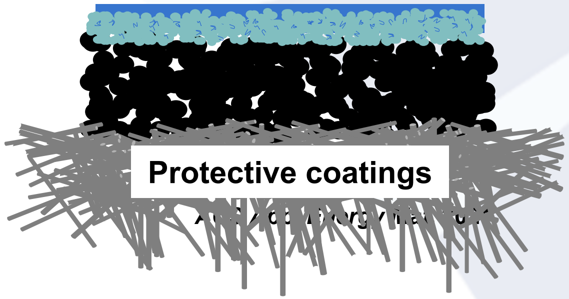


J. Am Chem. Soc., **2018**

Improved electrode durability



***ACS App. Mater. Interface.* 2021**



Design of unique high-performance electrolytic cells

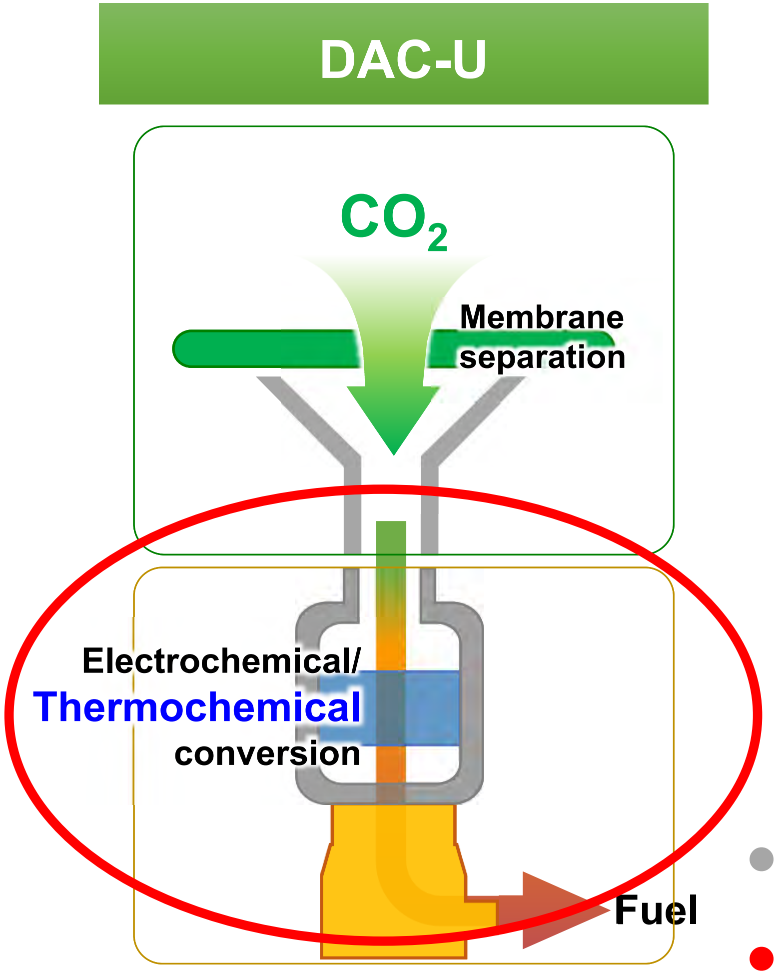
Flow Cell

Moonshot!

MEA Stack

Design and process development of an electrolytic cell capable of performing with the catalysts developed by Moonshot Project

Development of a thermal conversion unit to produce carbon compounds from CO_2 mixture gas from DAC

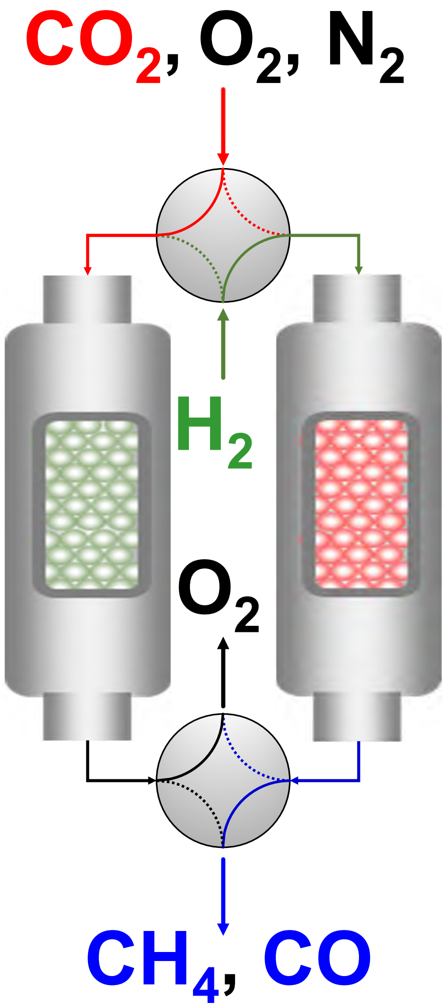


Prof. Ken-ichi SHIMIZU (Hokkaido Univ.）

Conversion of CO_2 mixed gas from DAC to CH_4 and CO

- Is it possible to fabricate large-area nanomembranes for CO_2 separation?
- **What kind of chemical products can be produced?**
- **Can CO_2 be converted from O_2 mixed gas as feed gas?**

Thermochemical production of CO, CH_4 from CO_2 mixed gas



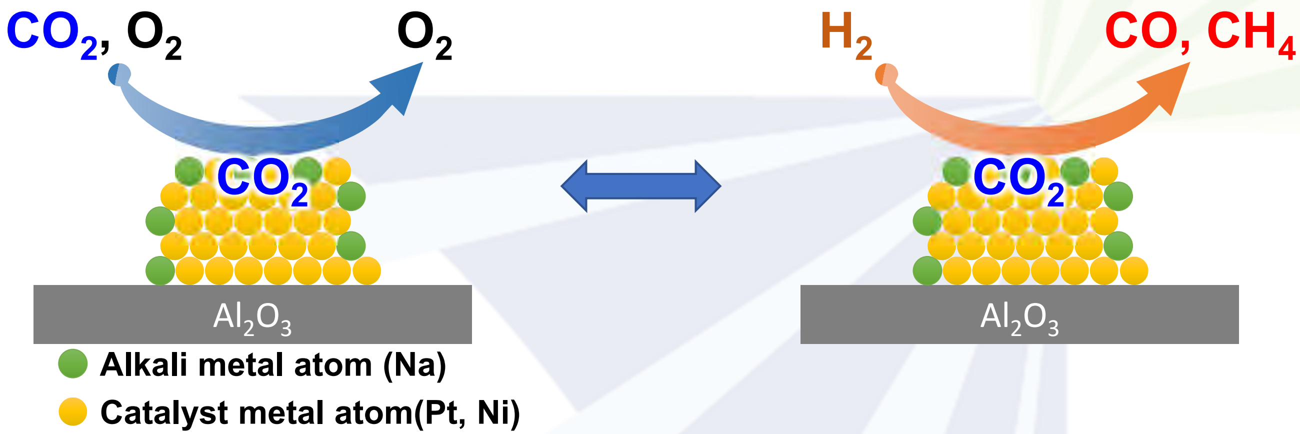
High technological challenge

Producing CO,CH_4 from CO_2/O_2 mixed gas
→ there is almost no example in the world

H_2 does not react with O_2, but reacts with CO_2

O_2 removal and CO_2 hydrogenation

- **O_2 removal**
  (+CO_2 absorption on catalysts)
- **hydrogenation**



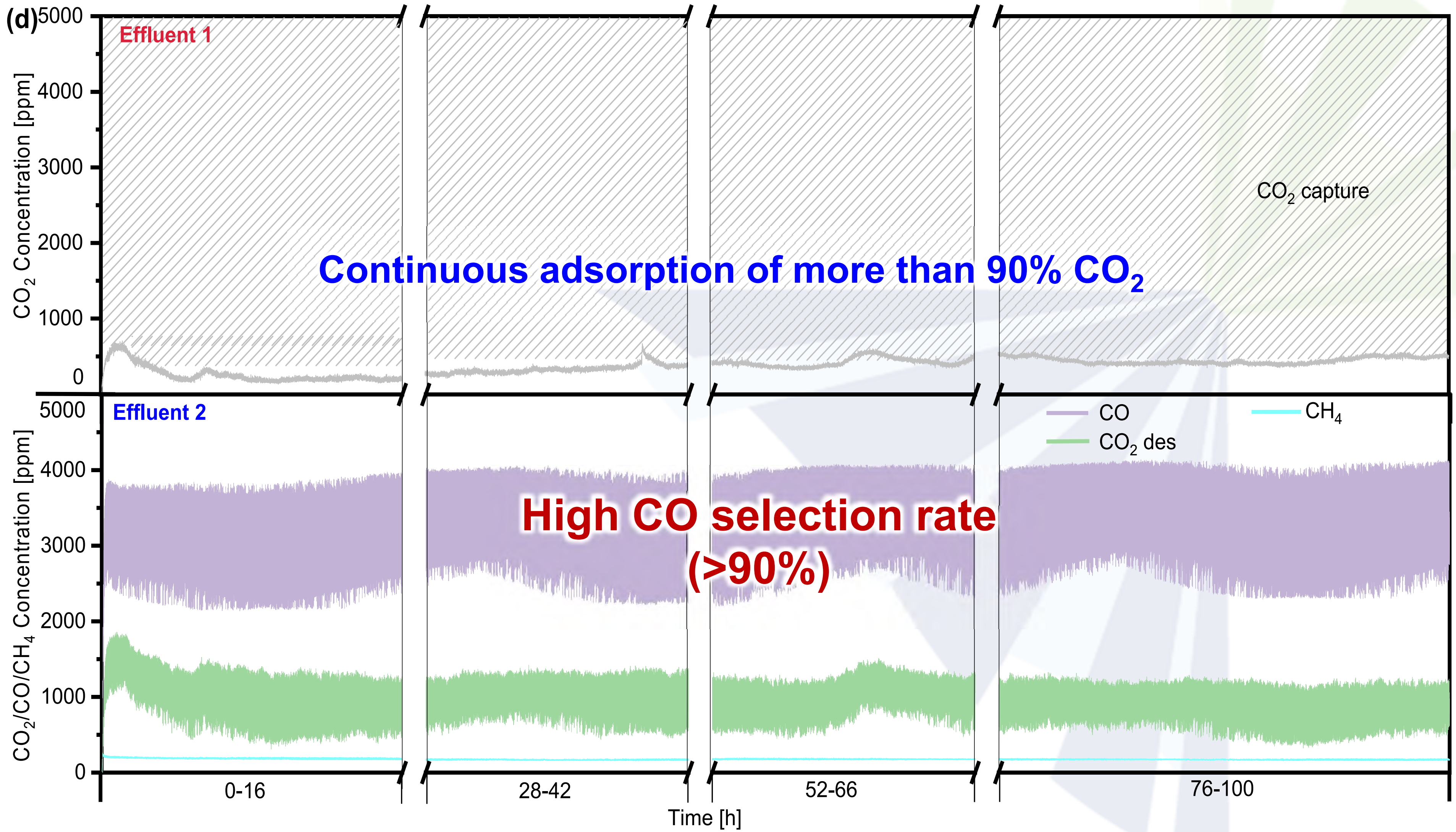
"Can't we use the atmosphere directly?“

CO_2 absorption rate → high concentration CO_2 is more efficient
Introduction of high concentration CO_2
→Increased CO_2 adsorption per unit time
→ Shorter changeover time
→ Higher overall efficiency

⇨ CO_2 enrichment by membrane separation is important

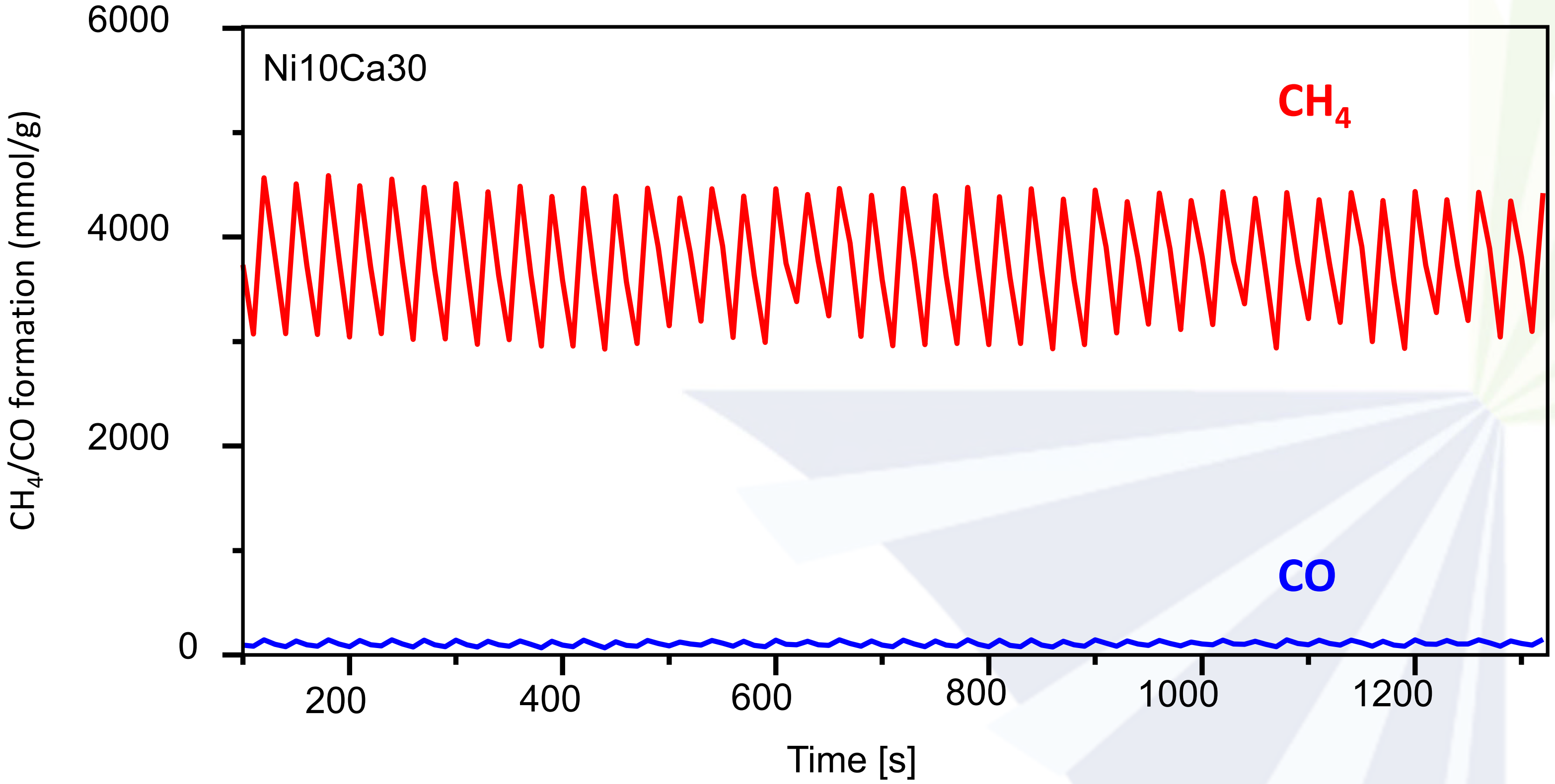
Thermochemical production of CO from CO_2 mixed gas

Catalyst **Pt/Na/Al_2O_3**
Catalyst amount: 300 mg, Reaction temp.: 350°C
Gas flux:100 mL/min
Source gas：**0.5%CO_2/10%O_2/N_2**
Reducing gas：H_2/100%



Thermochemical production of CH_4 from CO_2 mixed gas [23]

Catalyst **Ni/Na/Al_2O_3**
Catalyst amount: 300 mg, Reaction temp.: 250-500 °C
Gas flux:100 mL/min
Source gas：**0.5%CO_2/10%O_2/N_2**
Reducing gas：H_2/100%



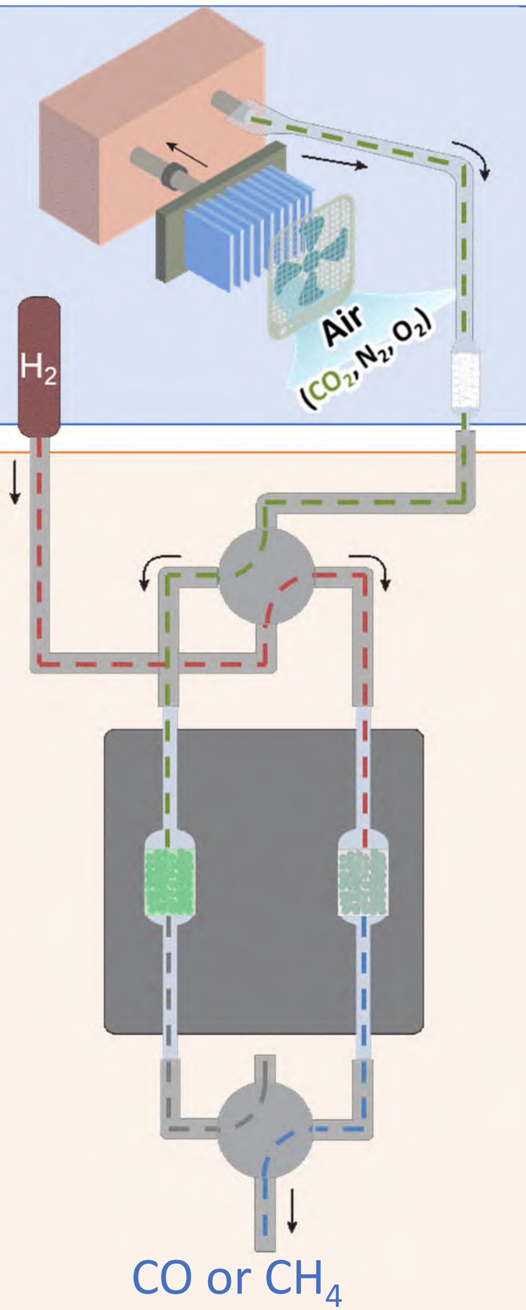
- **Continuous adsorption of 80% of introduced CO_2**
- **Converts about 80% of absorbed CO_2 to CH_4**
- **Highly selective CH_4 production**

Catalyst performance (international comparison)

	USA (Farrauto)	Spain (Gonzalez-Velasco)	AIST (Kuramoto)	Our achievements
Cycle number	**50**	**16**	**1**	**3000**
CH_4 production rate (mmol/g/h)	**0.4**	**1.3**	**0.8**	**1.1**
Temp.(℃)	350	400	450	350
Reactor type	**Single reactor type (Alternating flow)**	**Single reactor type (Alternating flow)**	**Single reactor type (Alternating flow)**	**Dual reactor type (continuous flow)**
Literature	*Fuel* **2022**, 320, 23842	*J. CO_2 Util.* **2018**, 27, 390	*ACS Sustain. Chem. Eng.* **2021**, 9, 3452	

World-leading performance

Construction of an integrated system by connecting DAC and thermo-chemical CO_2 conversion unit [25]



Direct Air Capture (DAC) by CO_2 capture nanomembranes

Enrichment of CO_2 from the air (400 ppm → 2000 ppm)

Continuous CO_2 adsorption & Reduction

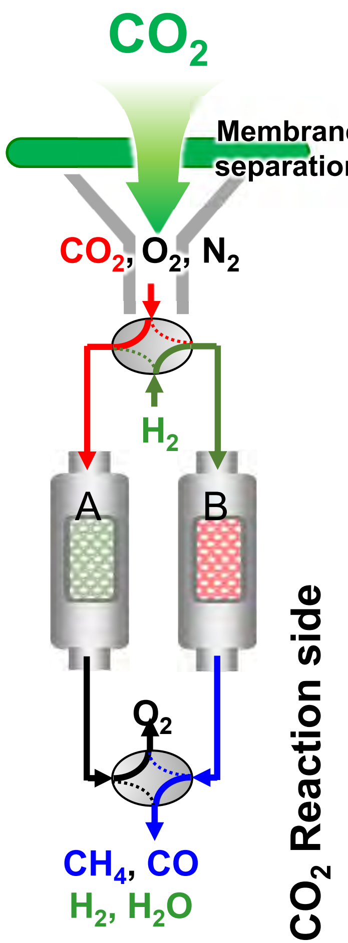
Advantages

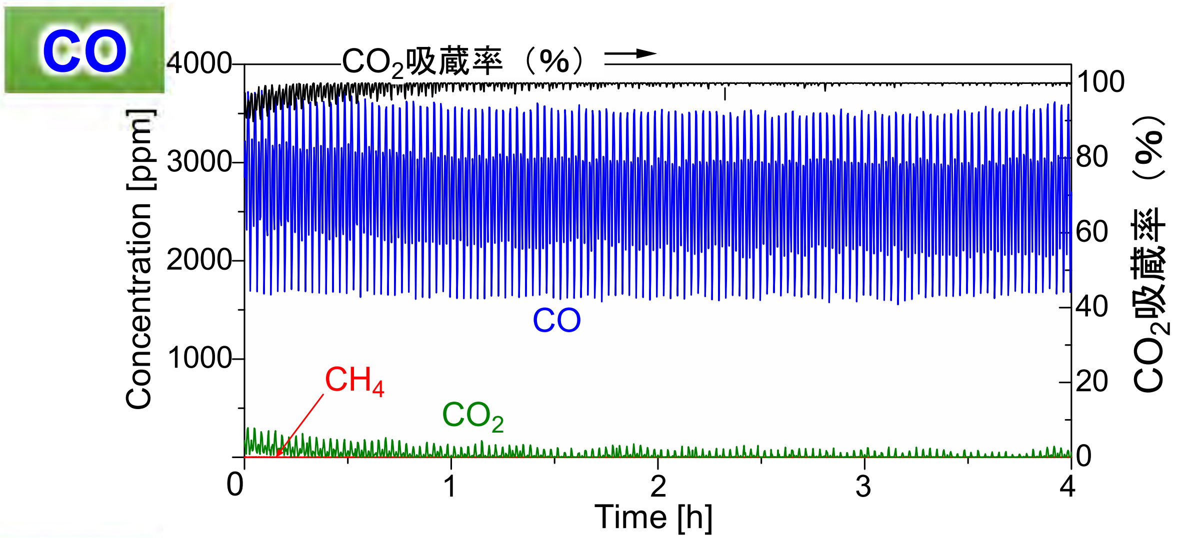
✓Conversion of concentrated $CO_2/O_2/N_2$ mixtures to CH_4 and CO "directly" and in one step

Challenges

✓Requires highly selective, low-temperature catalysts

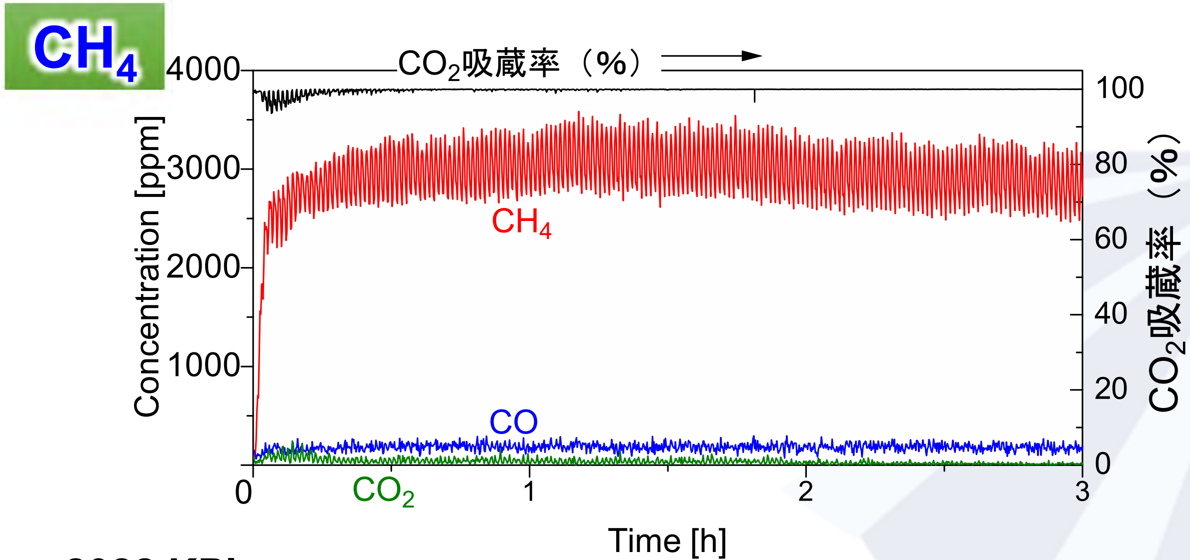
Continuous production of CO, CH_4 by DAC-U system





selectivity>98%
Conversion rate >90%

Reaction condition
Catalyst amount：500 mg
Temp.：450°C
Source gas：100 mL/min
H_2 flux：100 mL/min
Valve change：every 30 sec



selectivity>90%
Conversion rate>90%

Reaction condition
Catalyst amount：300 mg
Temp.：300°C
Source gas：500 mL/min
H_2 flux：100 mL/min
Valve change：every 1 min

2022 KPI

Achieved "Demonstration of CO and CH_4 conversion from CO_2 mixed gas

(Patent pending, paper in preparation)

Future task

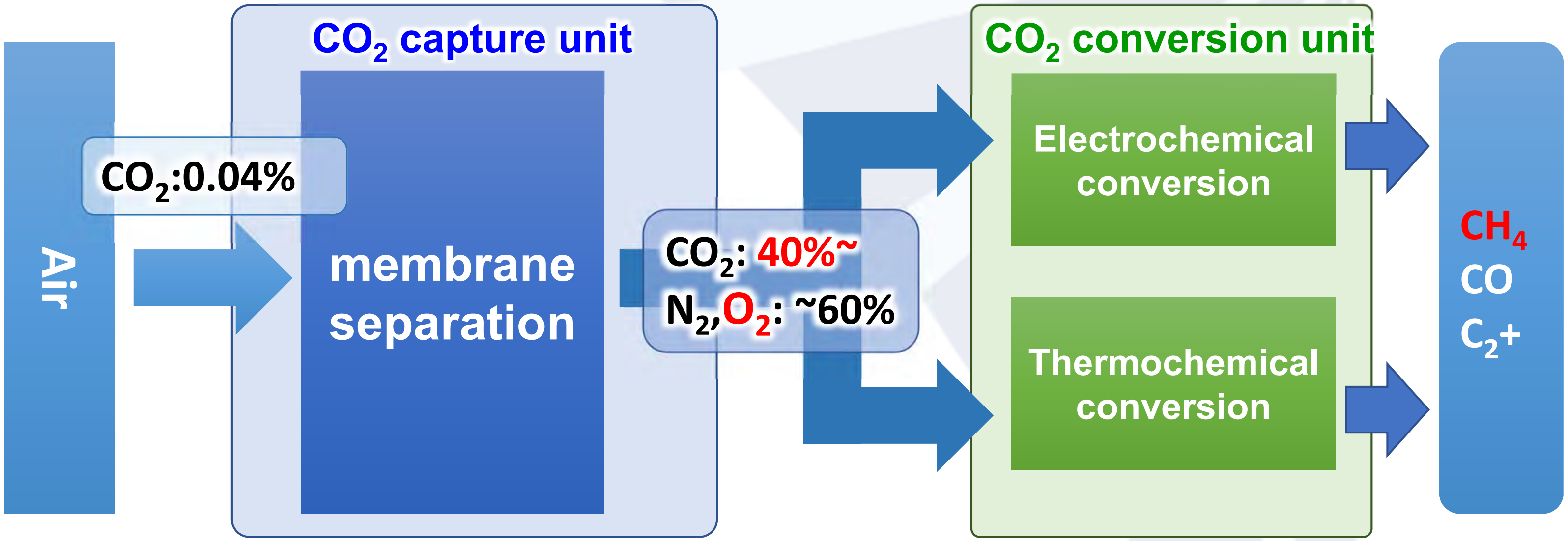
- **Optimization of H_2 introduction conditions**
- **Recycling unreacted H_2**

Primary issues at the beginning of the project

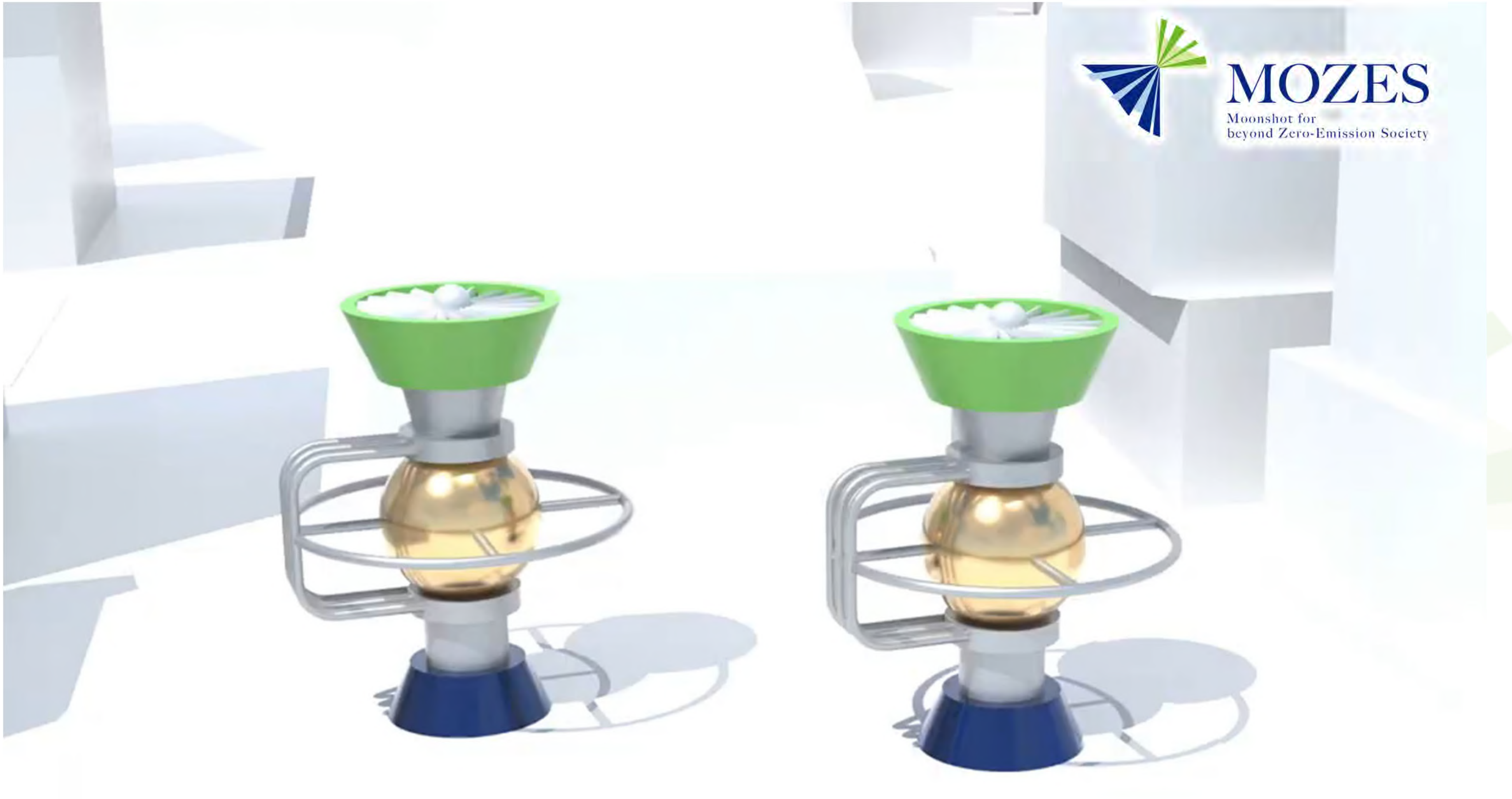
- Is it possible to fabricate large-area nanomembranes for CO_2 separation?
  → **Possible**
- What kind of chemical products can be produced?
  → **CO_2 conversion is possible even with O_2-mixed feedstock gas**
- Can CO_2 be converted from O_2 mixed gas as feed gas?
  → **CO, CH_4, C2 can be produced**

KPI for 2022

Select basic membrane materials that exhibit high CO_2 selectivity.
Demonstrate **conversion from CO_2 mixed gas to CO, CH_4, and C_2H_4**



Distributed deployment of DAC-U systems [31]



Carbon resource recycling society
based on local production for local consumption

MOONSHOT
RESEARCH & DEVELOPMENT PROGRAM