Carbon-negative and Sustainable CO_2 Conversion to Value-added Chemicals using Microbial Electrosynthesis

신재생전기에너지와 미생물전기합성 기반 CO_2 전환을 통한 탄소네가티브 고부가가치 화학물질 생산

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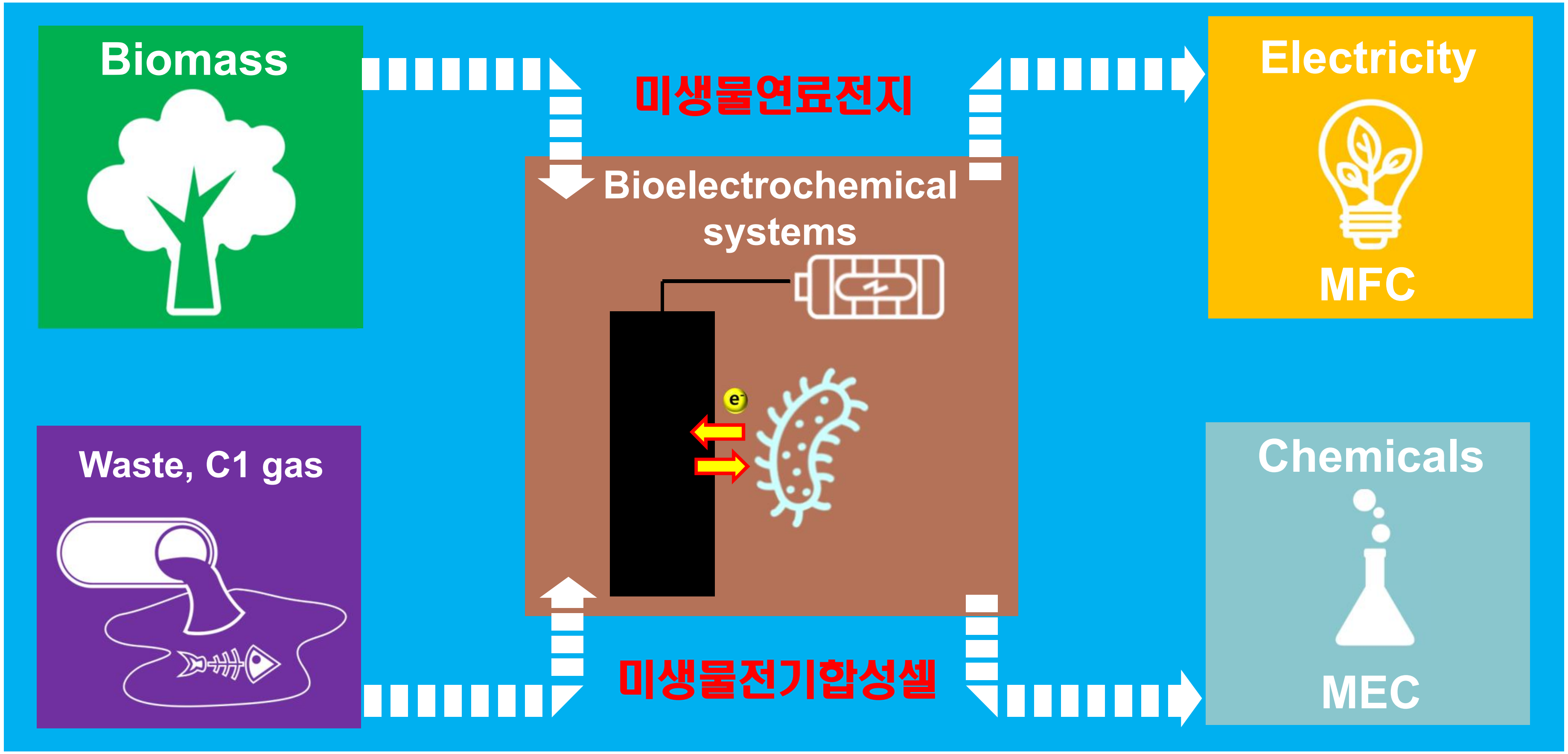
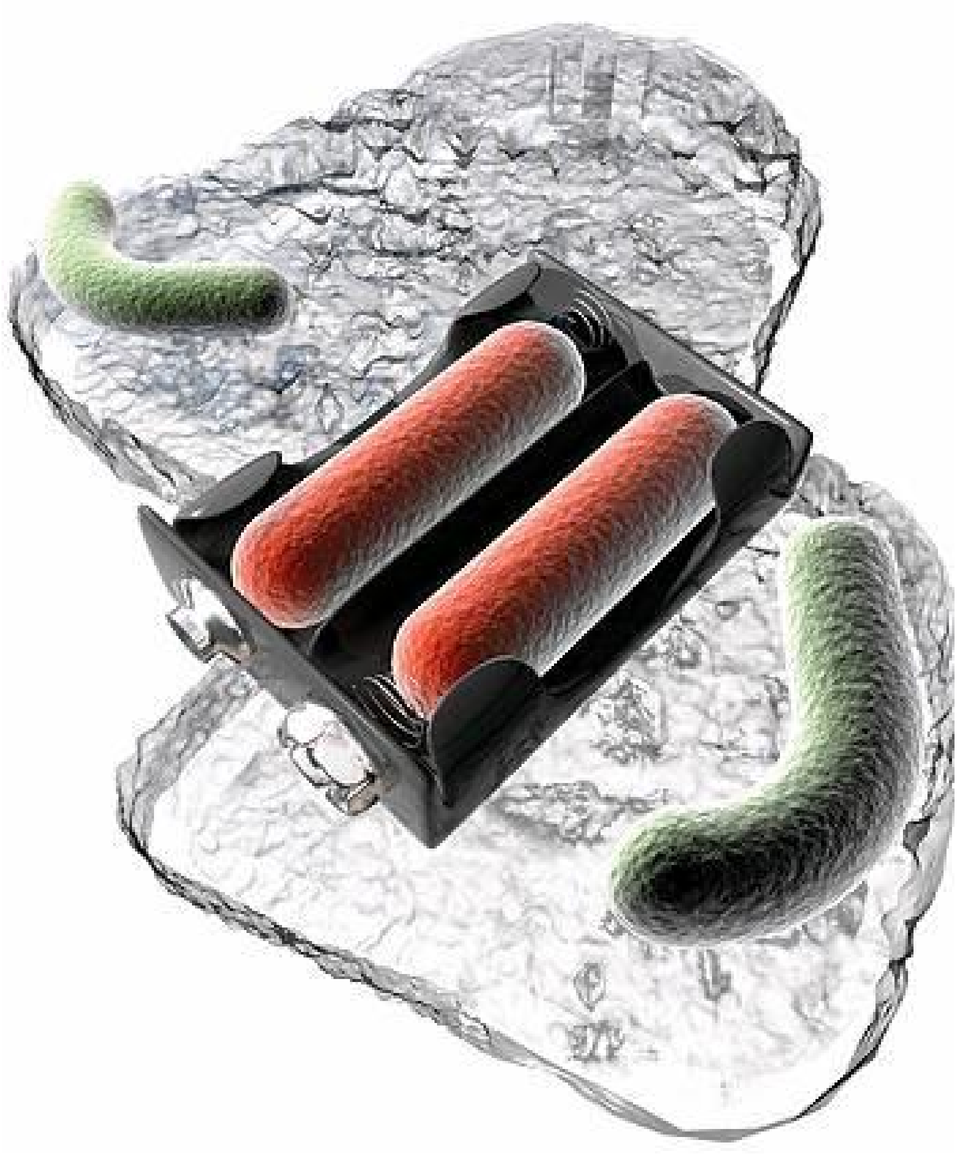
3_ Summary

Bioelectrochemical Sysetem (BES)

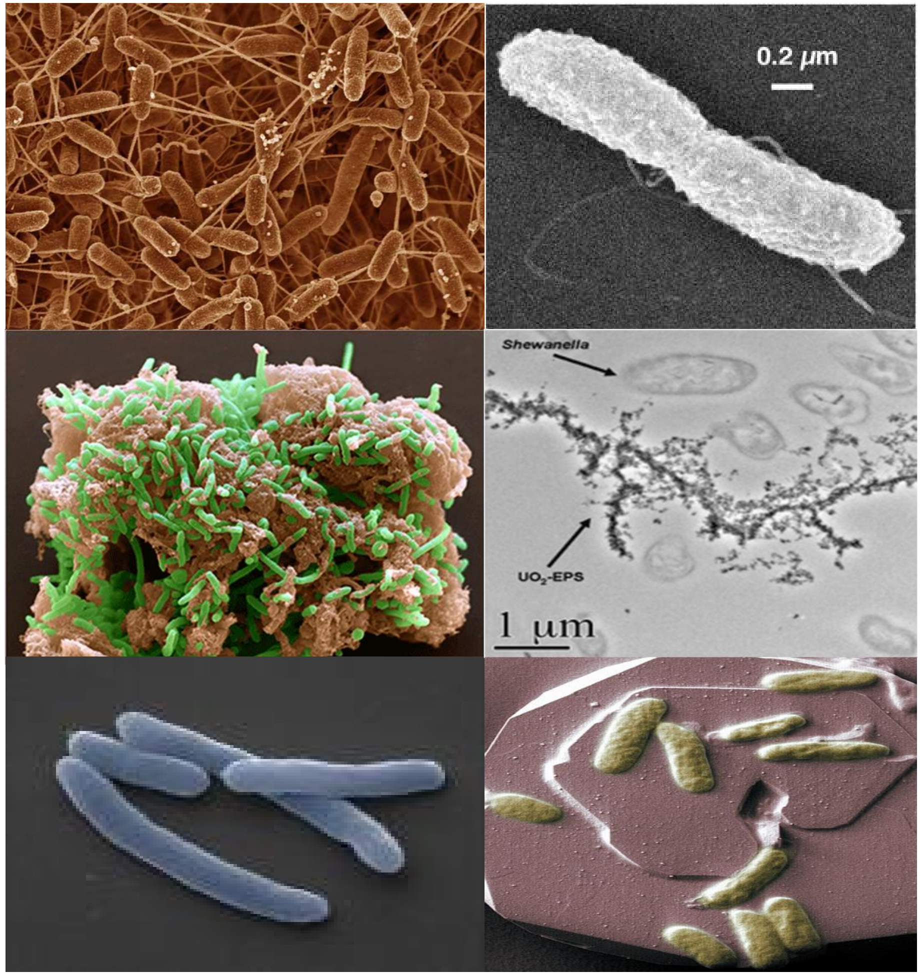
BES converts chemical energy of organic waste, biomass into electricity by **microbial fuel cell (MFC)** or produce hydrogen/chemical products through **microbial electrosynthesis cells (MEC or MES)**



Electrochemically Active Bacteria



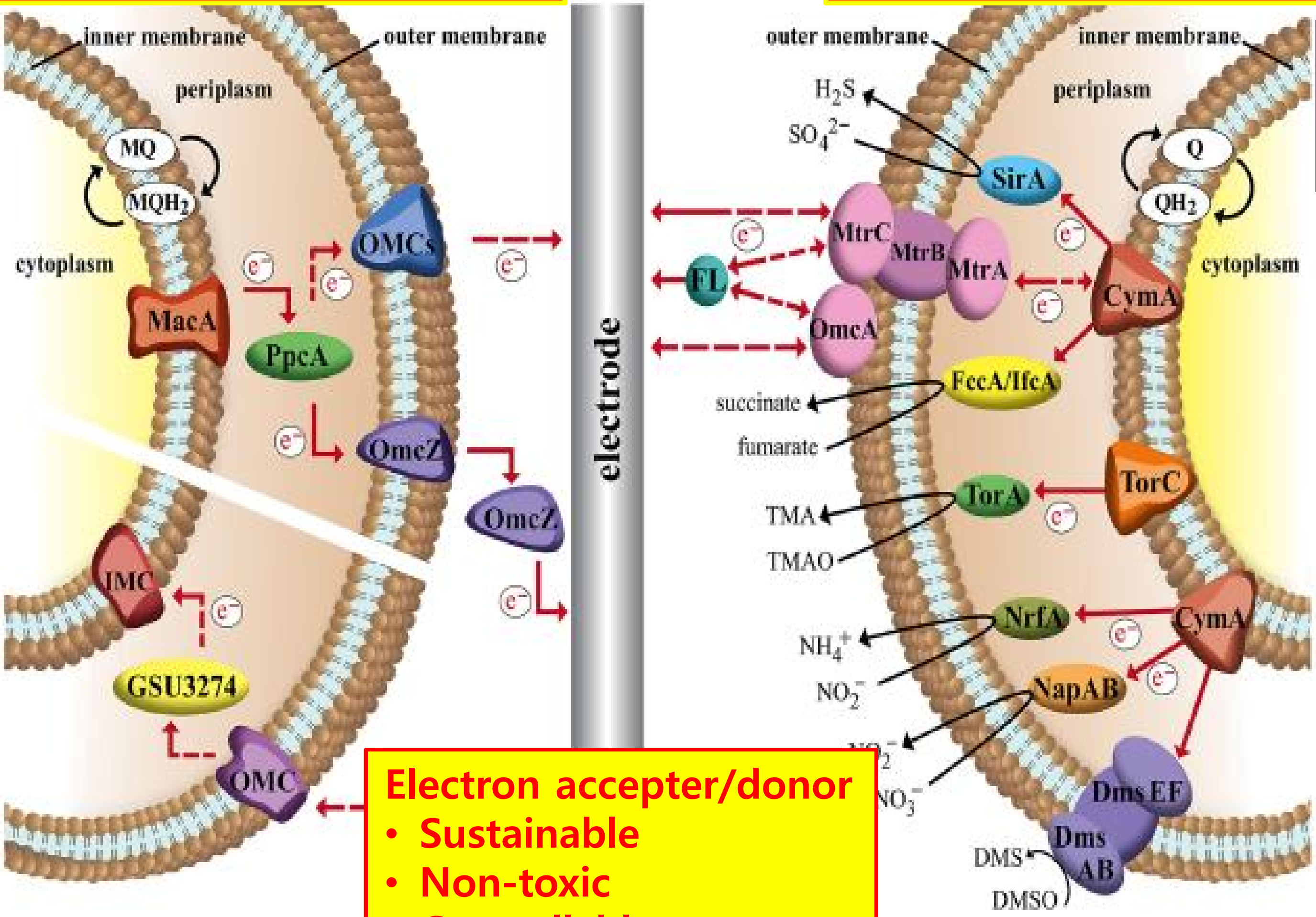
전기화학적 활성 미생물

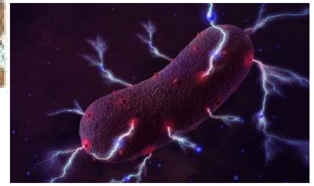


Extracellular Electron Transport

Geobacter sulfurreducens

Shewanella oneidensis

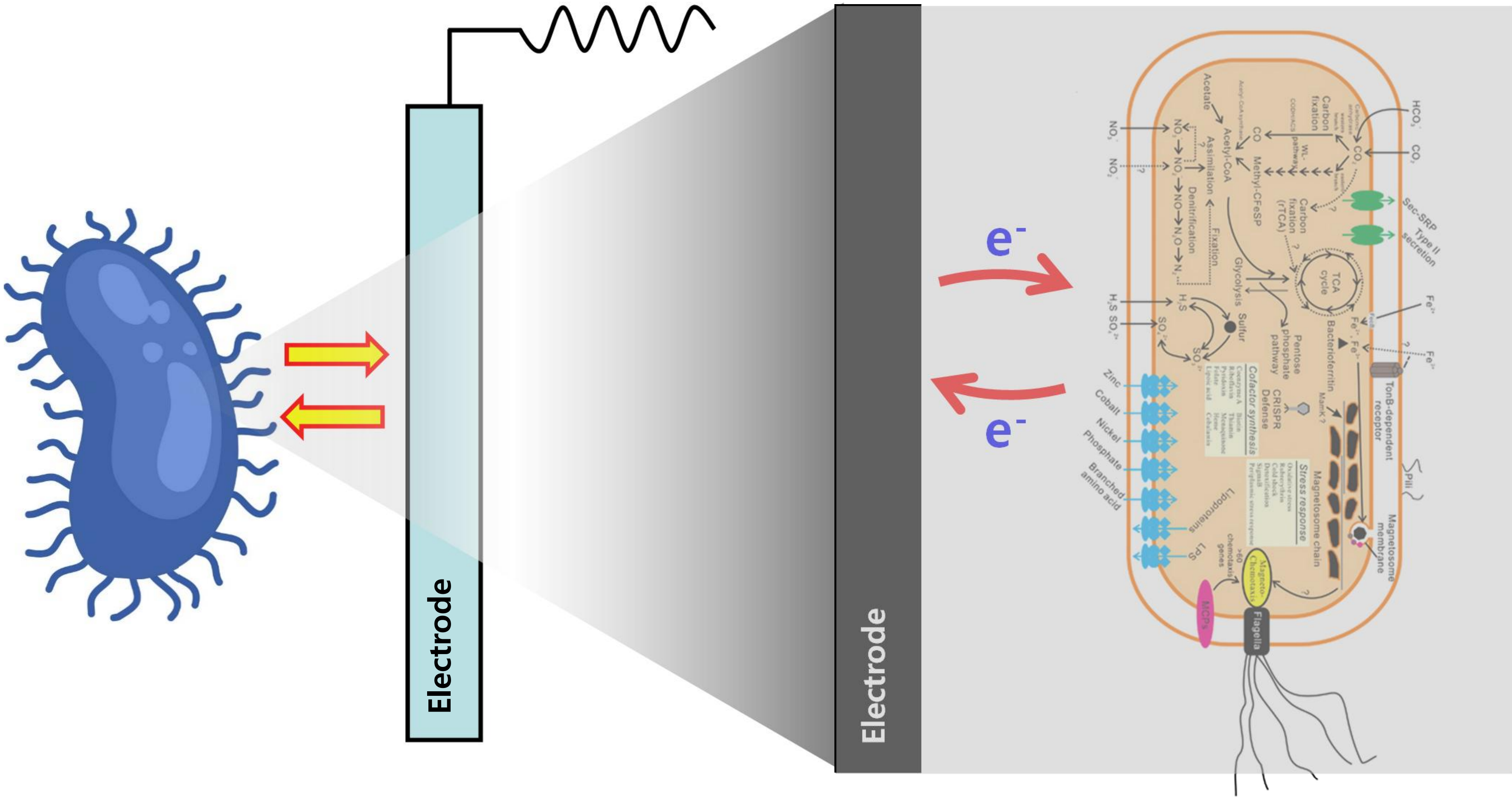




Electron accepter/donor
- Sustainable
- Non-toxic
- Controllable

Kracke et al. Frontiers in Microbiology 2015

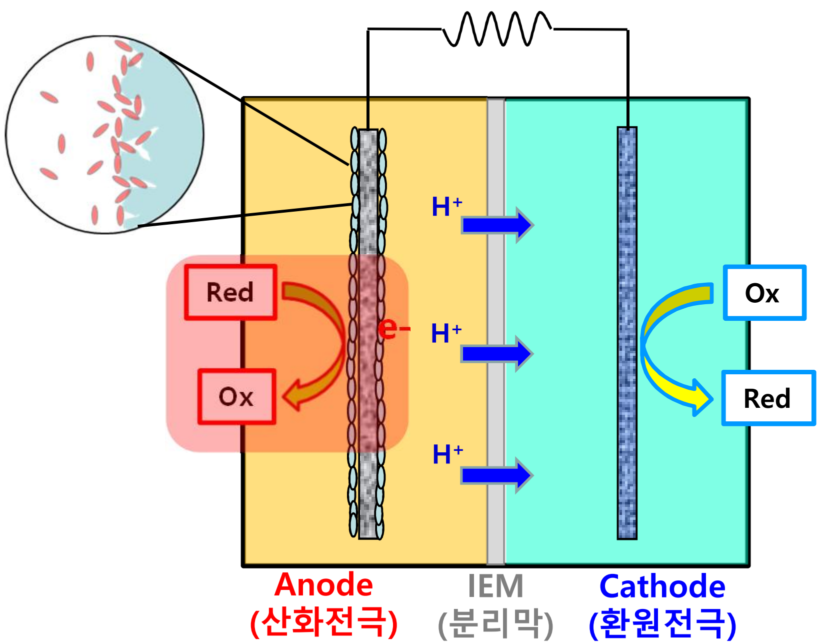
Microbe-Electrode Hybrid System



- Live cell continuously interacts with electrode to exchange respiratory electrons
- Applied potential influences gene expression and metabolic pathway

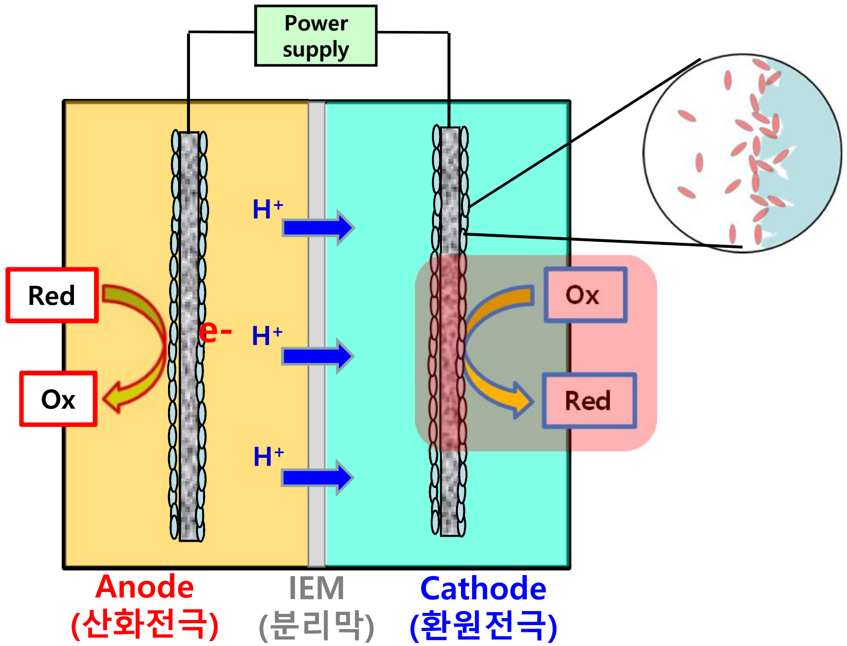
Microbial fuel cell & Microbial electrosynthesis cell

Microbial fuel cell (MFC)



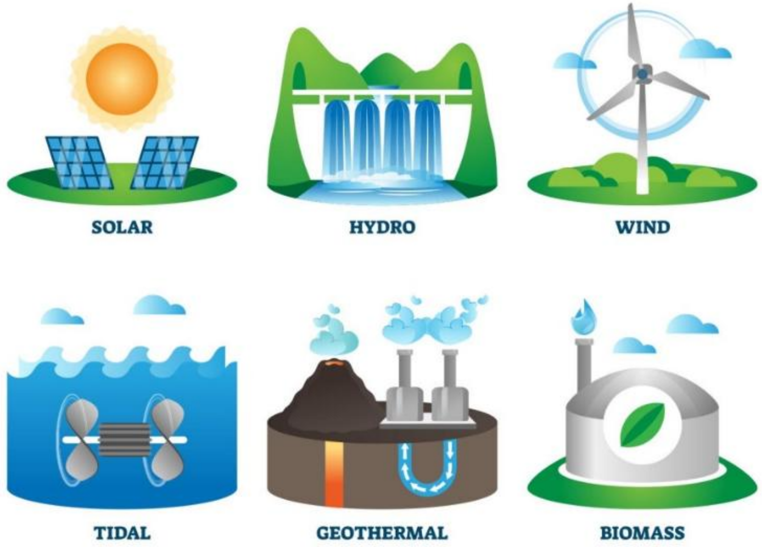
- Spontaneous oxidation/reduction
- Microbial catalyst on anode
- Production of electricity from biodegradable organic materials and waste

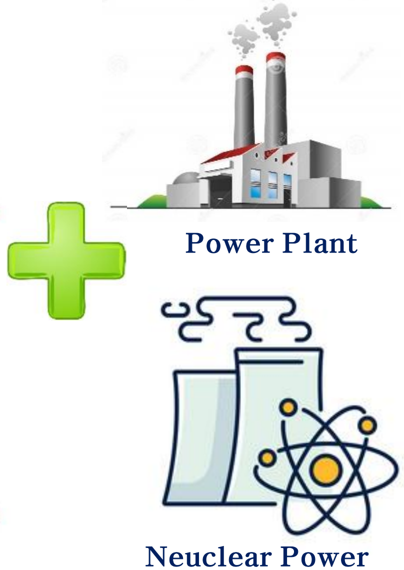
Microbial electrosynthesis cell (MEC)



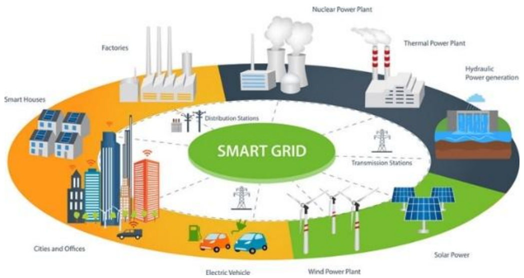
- Non-spontaneous oxidation/reduction
- Microbial catalyst on cathode
- H_2, CH_4, VFA and platform chemical production by electrical energy
- MES can be used for upgrading of CO_2

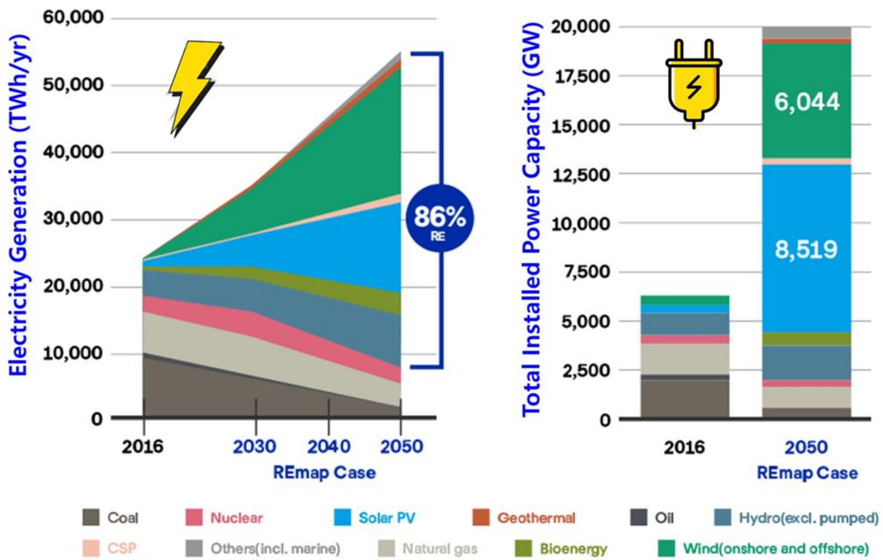
Renewable Energy vs. Electricity





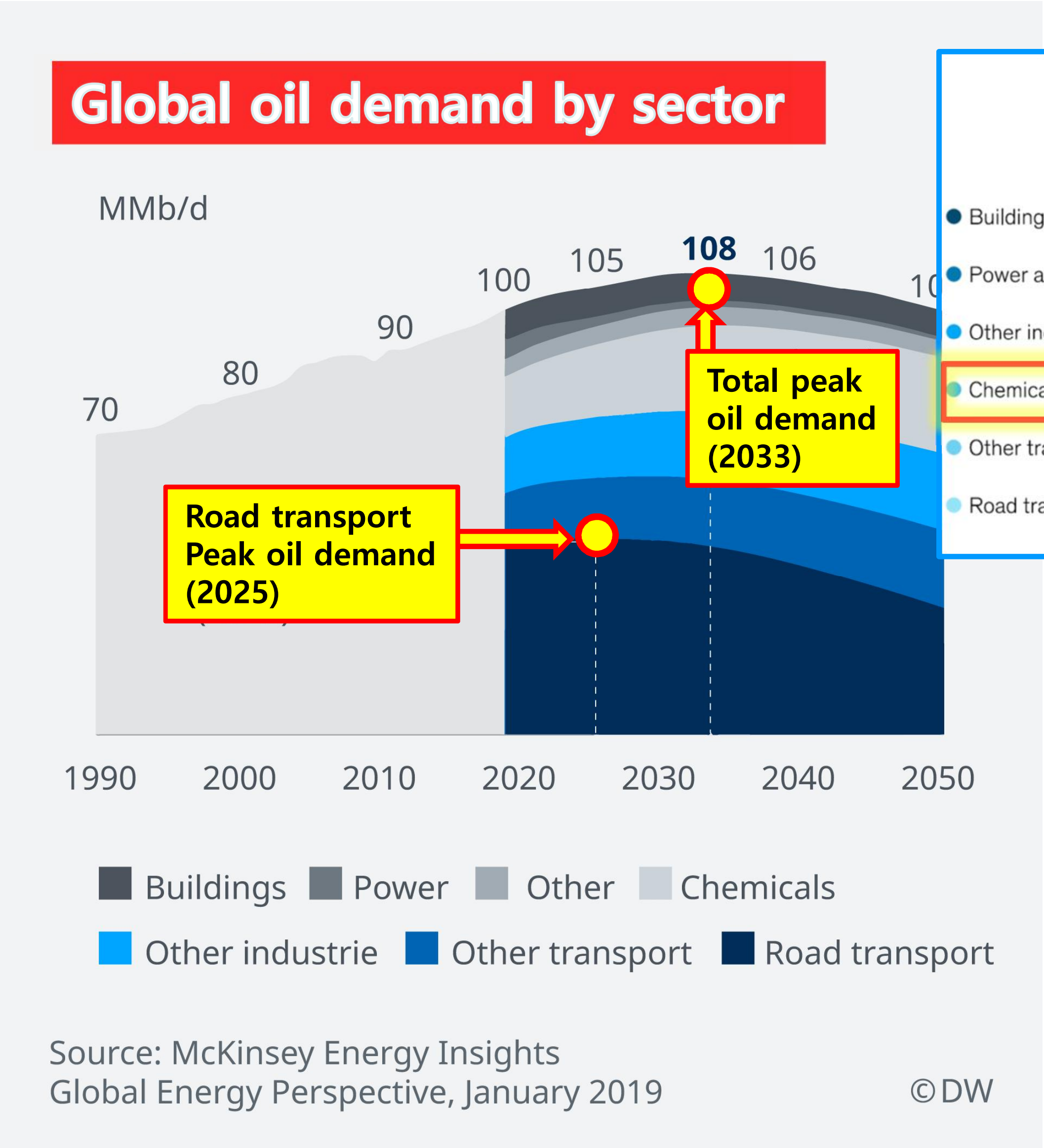
Electricity is key of future energy infra for production/storage /transportation/utilization



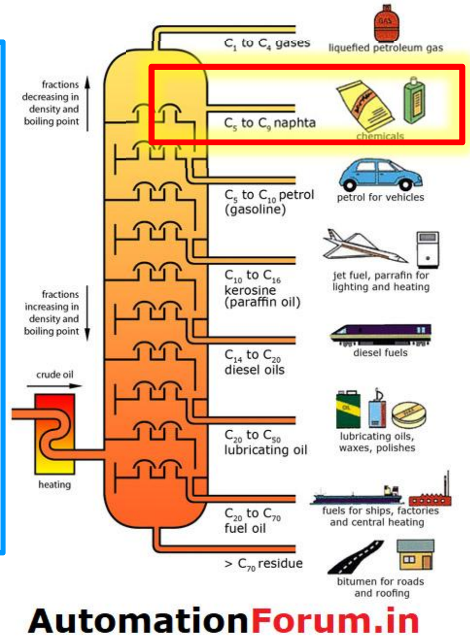


Notes: CSP = concentrating solar power; TWh=terawatt hour.

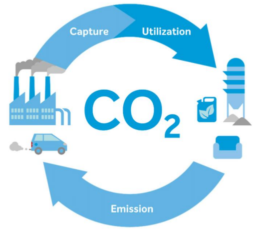
Demand of Fossil Oil for Refinery



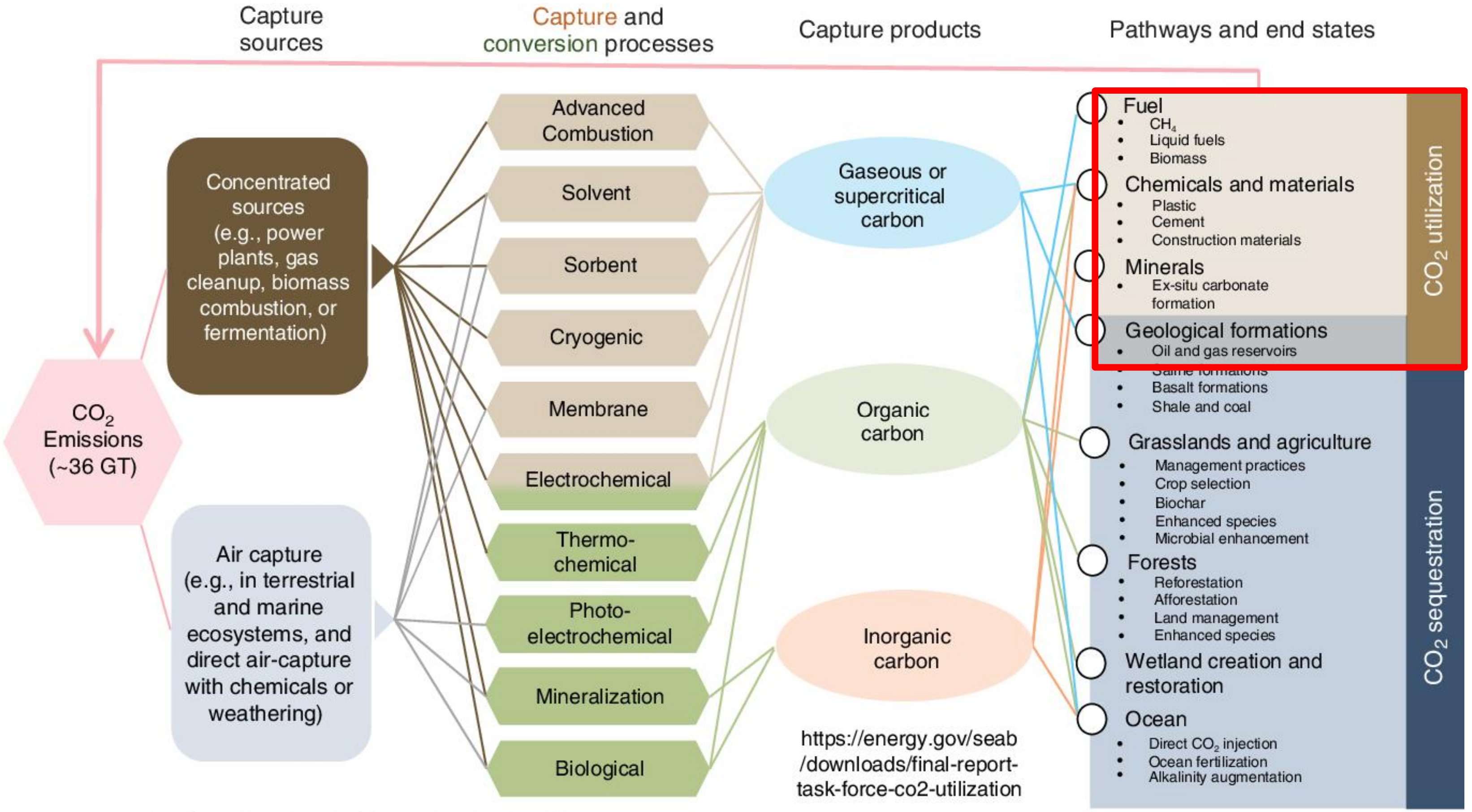
	CAGR[2] 2020–35, %	CAGR 2035–50, %
Buildings	0	0
Power and heat	–8	–5
Other industry[3]	2	0
Chemicals	3	1
Other transport	4	1
Road transport	0	–3



Carbon Capture & Utilization (CCU)



Frontiers in Climate 4:841907

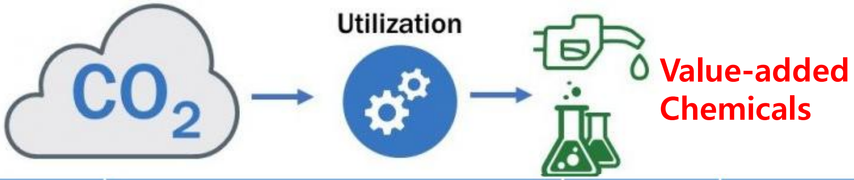


https://energy.gov/seab/downloads/final-report-task-force-co2-utilization

Modified from SEAB Report, 2016. CO_2 Utilization and Negative Emissions

DOI:10.2118/194190-PA

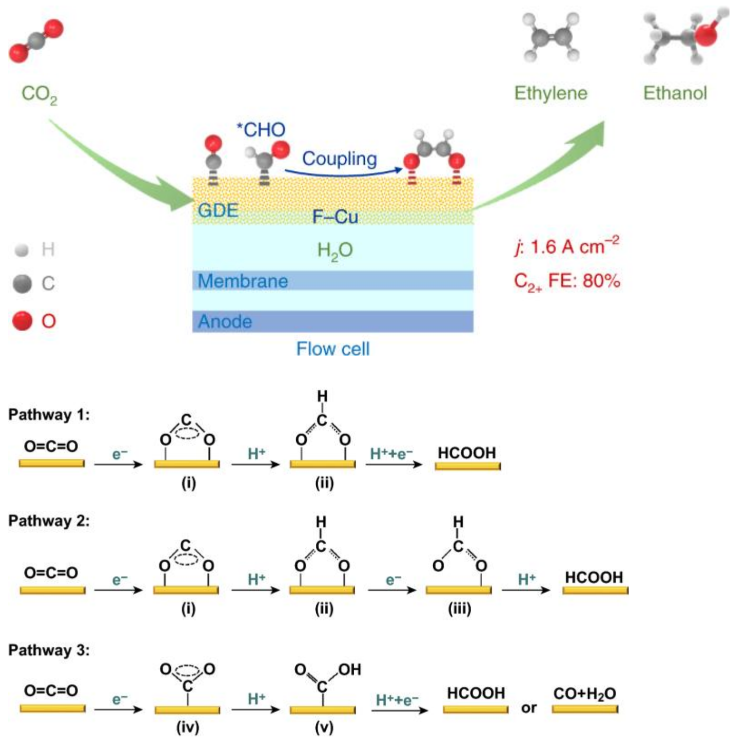
Carbon Neutral Process by CO_2 Valorization



생성물	반응	필요한 전자의 개수	E^o (V vs. SHE)
CO	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	$2e^-$	-0.53
Formate	$2CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$		-0.61
Oxalate	$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$		-0.913
Formaldehyde	$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	$4e^-$	-0.48
Methanol	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	$6e^-$	-0.38
Methan	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	$8e^-$	-0.24
Ethylene	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	$12e^-$	-0.349
Ethanol	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$		-0.329
Ethane	$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	$14e^-$	-0.27
Propanol	$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 3H_2O$	$18e^-$	-0.31

- **CO_2 is very stable and most oxidized form of carbon**
- **Electron/reducing power is required for conversion**

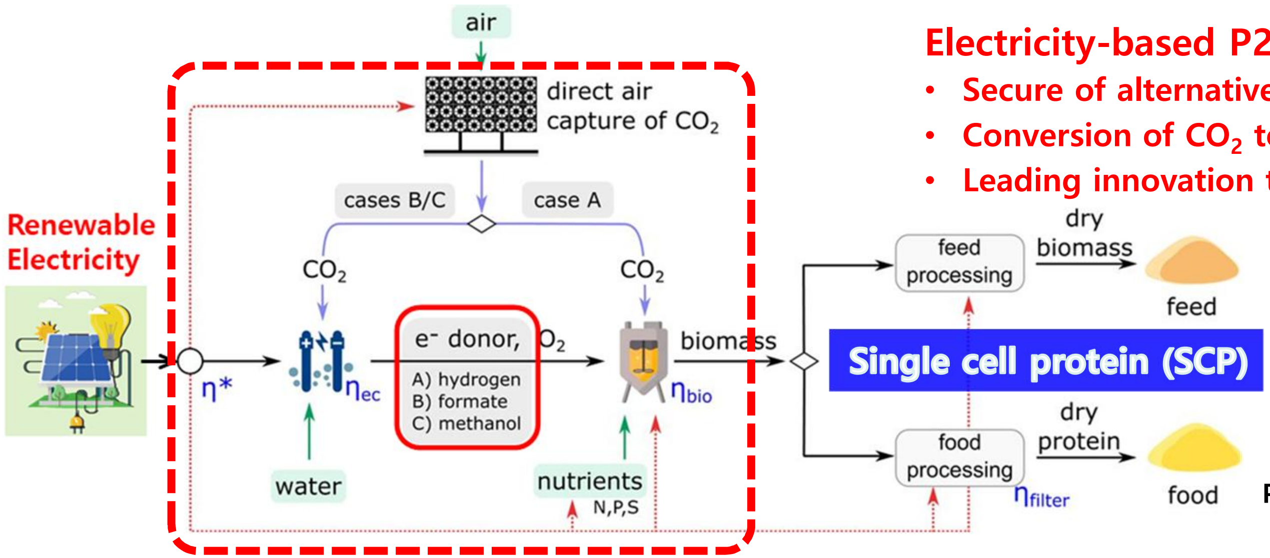
Electrocatalytic CO_2ER reaction pathways



	Advantage	Disadvantage
Chemical Catalyst	Fast reaction rate, Study of reaction mechanism	High temp/pressure, Limited products, Catalyst poison, Limited lifecycle
Biocatalyst	Catalyst reproducible, High value-added products, Room Temp/pressure, Improvement of performance by OMICS	Low reaction rate, Difficult to control the mechanism

Power to Product (P2P) for CO_2 Conversion

Electricity-based single cell protein (SCP) by P2P and CCU

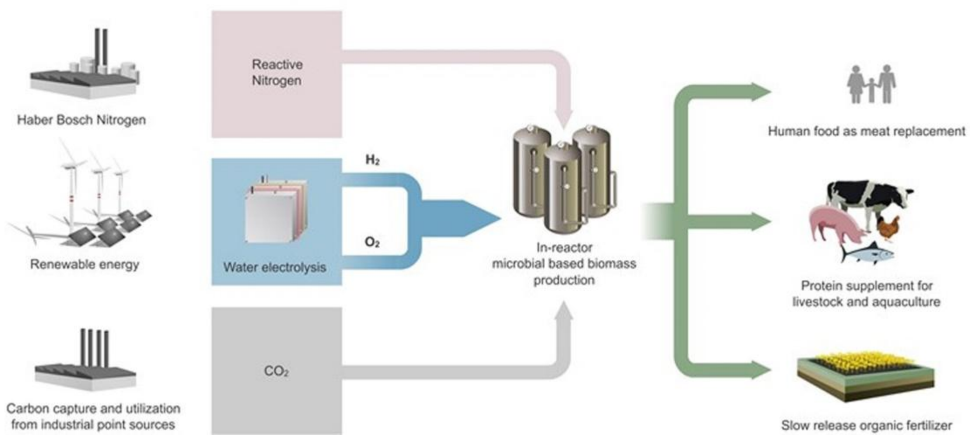


Electricity-based P2P process

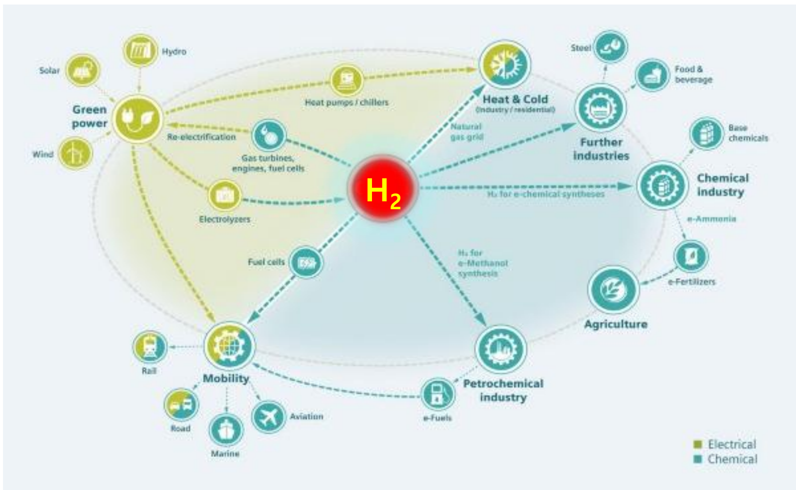
- Secure of alternative chemicals to oil refinery
- Conversion of CO_2 to platform chemicals
- Leading innovation technology of bio-P2P

PNAS 2021 Vol. 118 No. 26 e2015025118

Renewable hydrogen based sustainable protein production

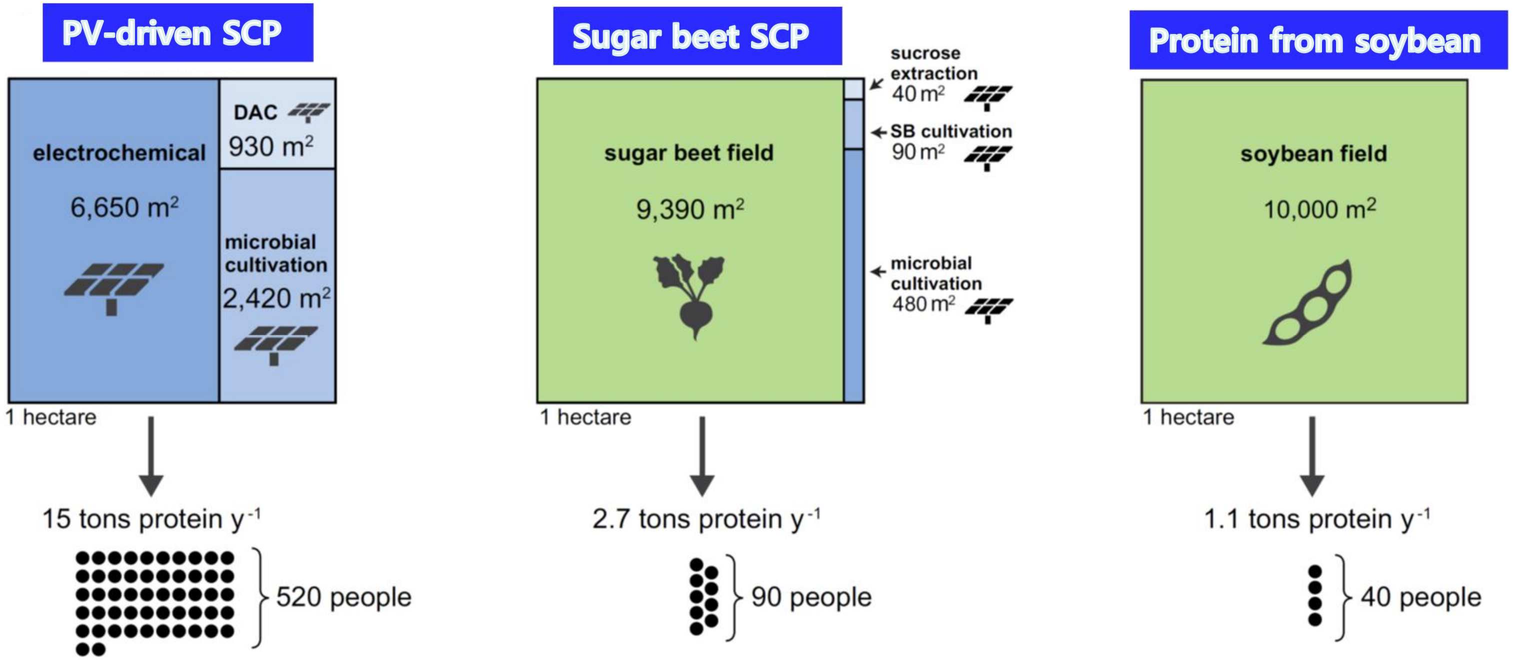


Hydrogen electrolyzer is a major platform for Power to X



Power to Product (P2P) for CO_2 Conversion

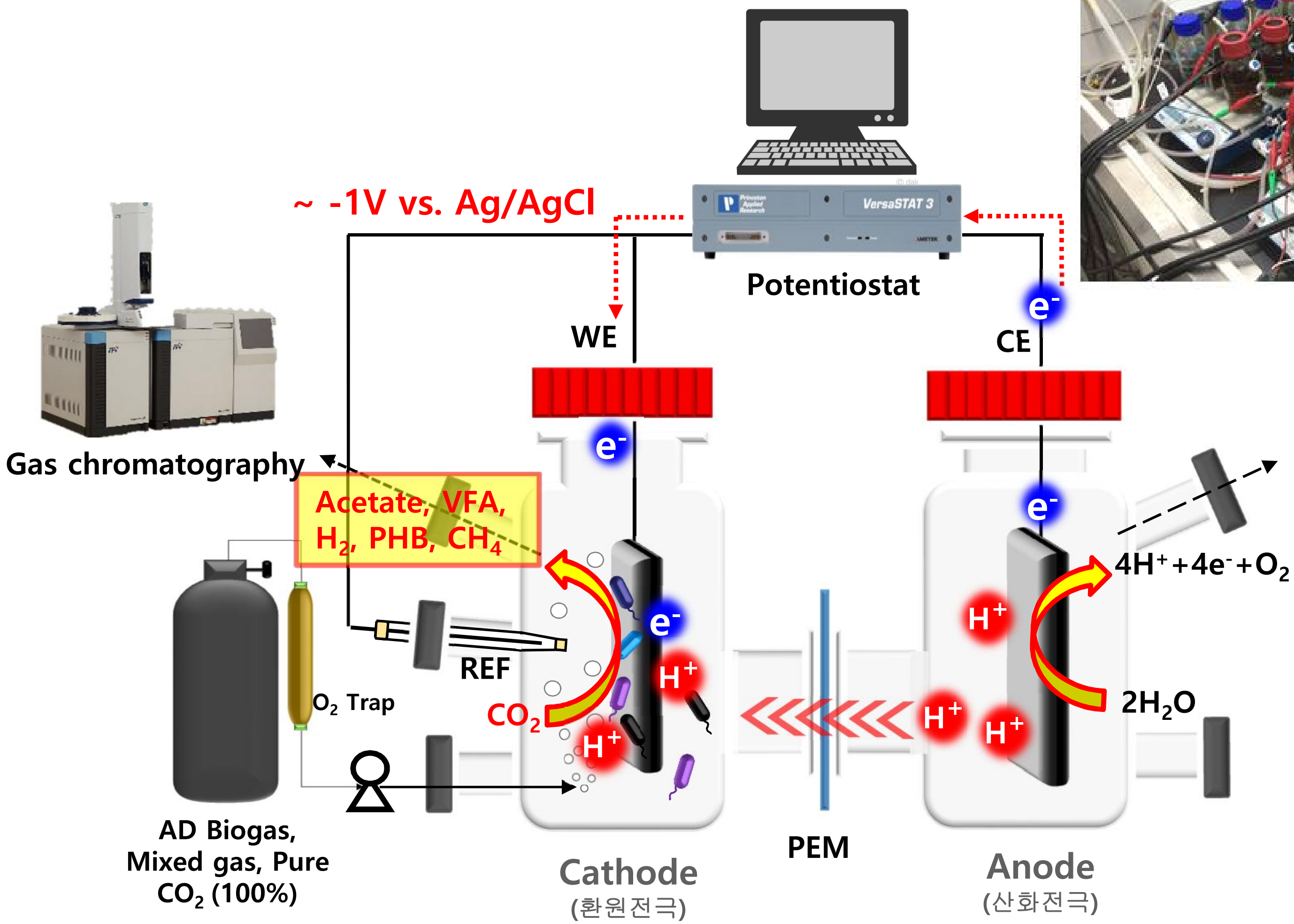
Three different SCP production strategies



PNAS 2021 Vol. 118 No. 26 e2015025118

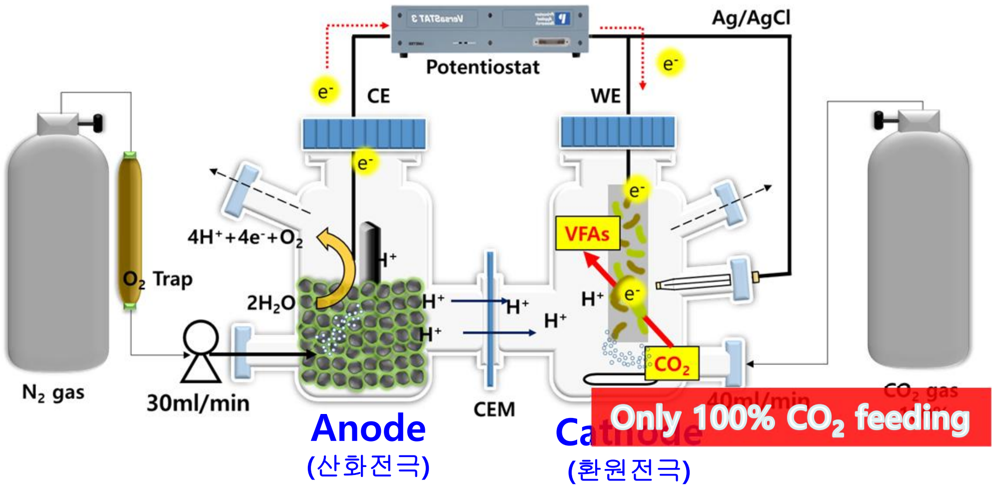
- The PV-driven SCP produces more protein per hectare as compared to sugar beet SCP and conventional soybean agriculture
- The protein yields and amount of people that could be fed from 1 ha
- Assumption of an irradiance of 2,000 $kWh{\cdot}m^{-2}{\cdot}y^{-1}$

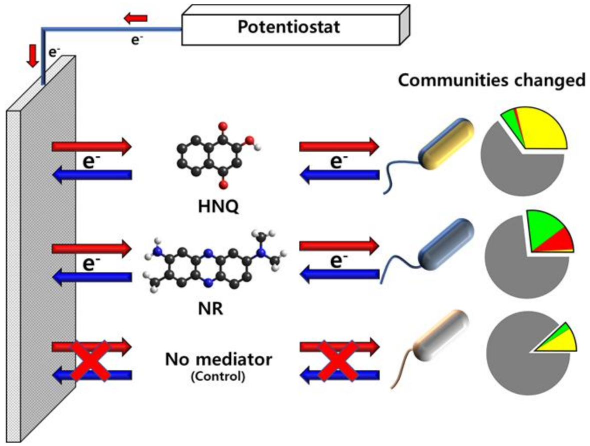
Microbial Electrosynthesis Cell (MEC)

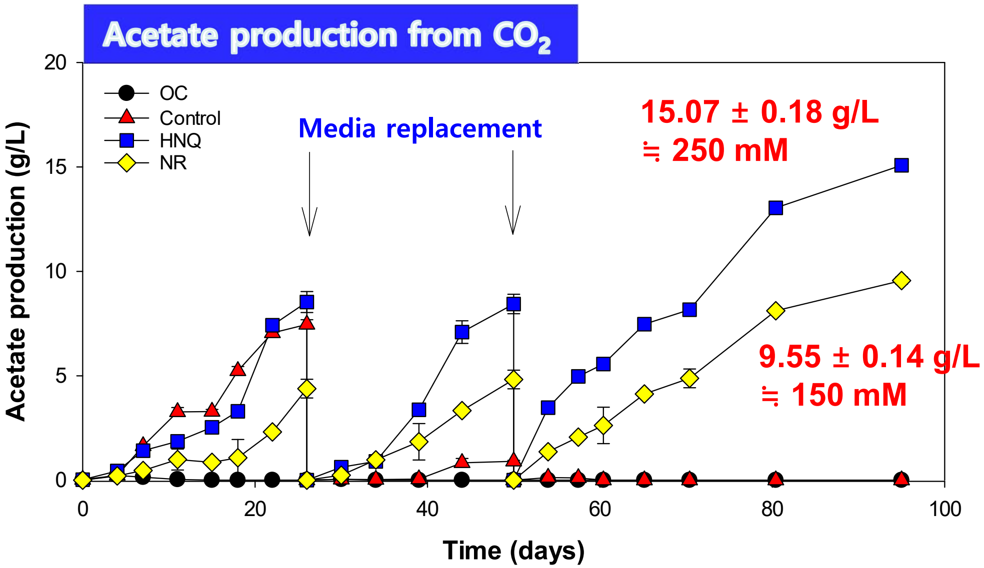


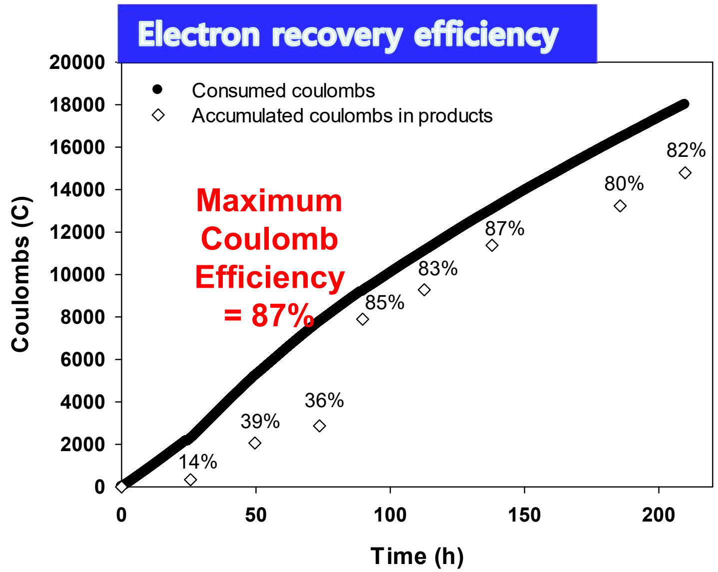
Young Eun Song and Jung Rae Kim. 2022. Chemical Engineering Journal. 427:131885

Acetate Production from CO_2 in MEC









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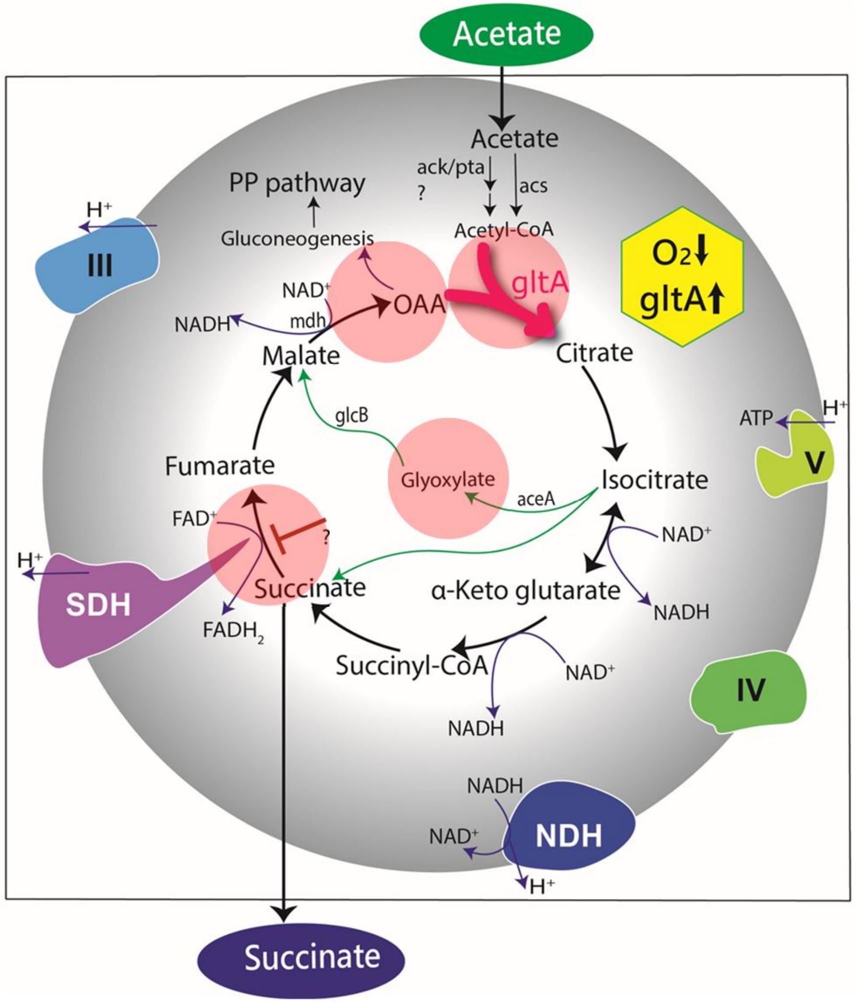
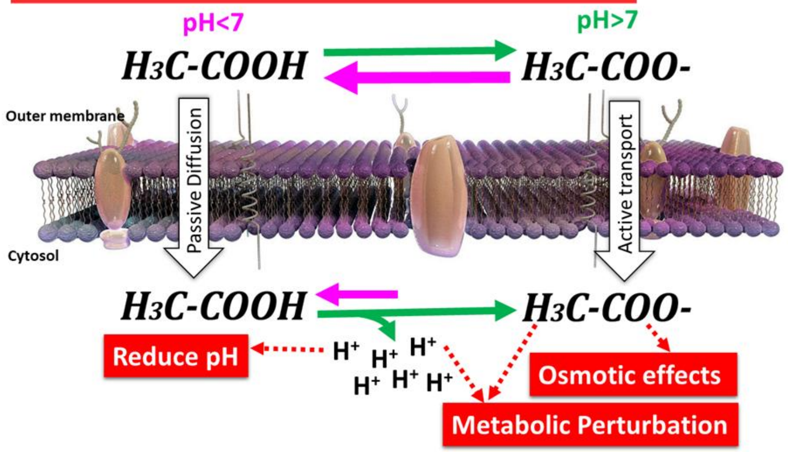
Metabolic Engineering for Acetate Conversion

TCA Cycle for Acetate Influx

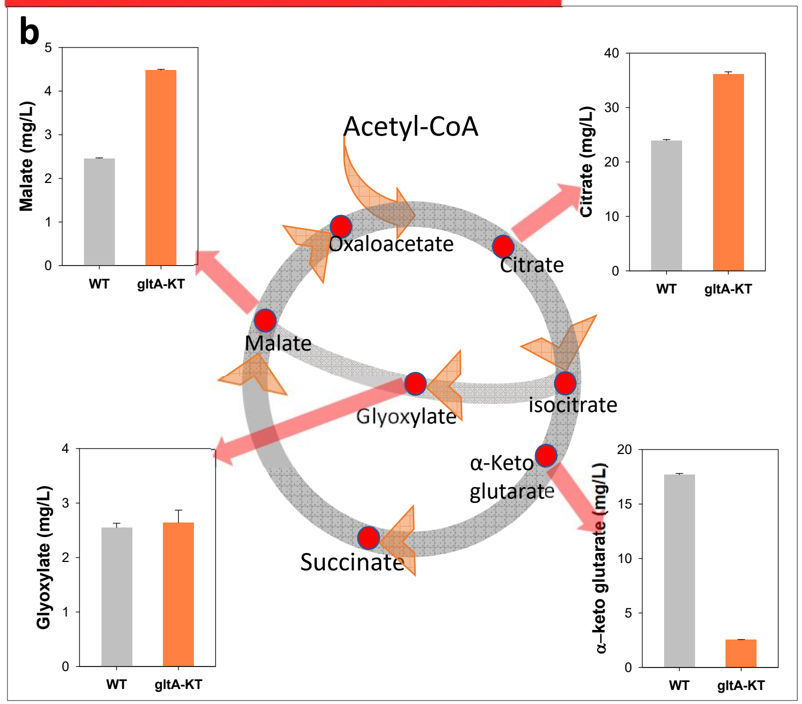


Mutyala and Kim. 2023. ACS Omega. 8:29. 26231–26242

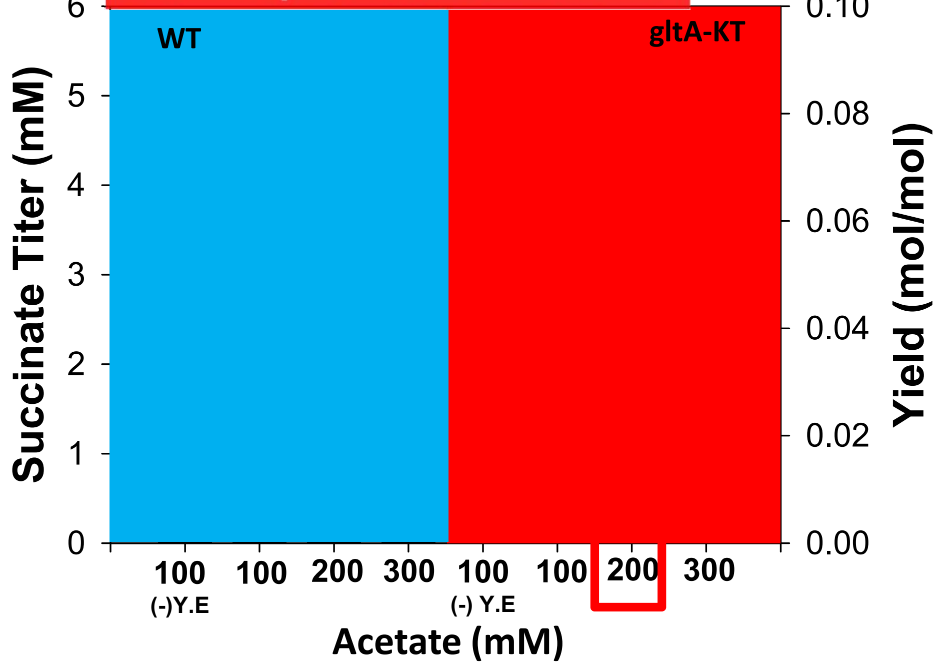
Acetate toxicity at high concentration

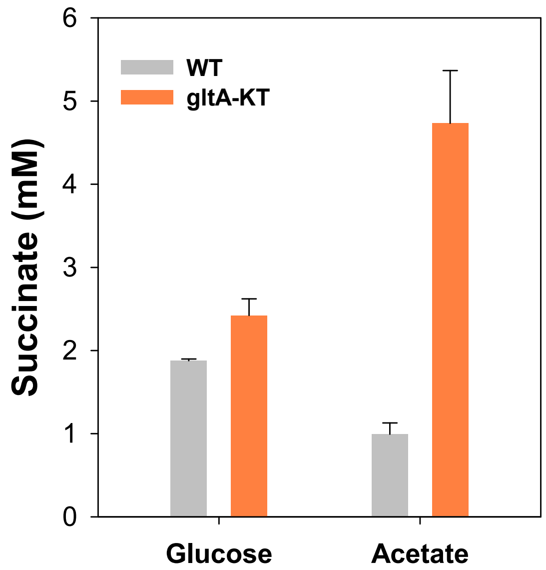


LC-MS metabolites quantification



Succinate production form Acetate



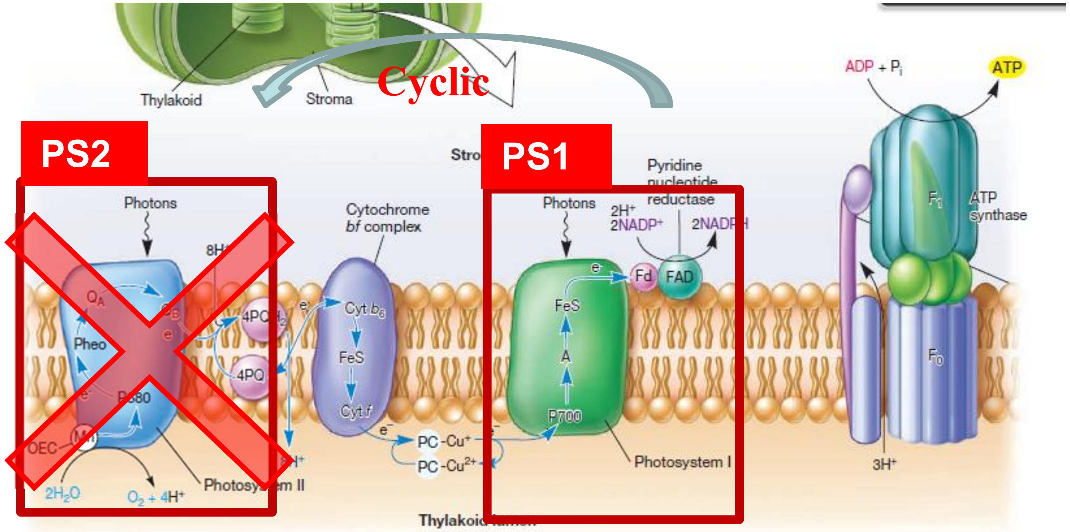


CO_2 to H_2 with *Rhodobacter sphaeroides*

R. sphaeroides

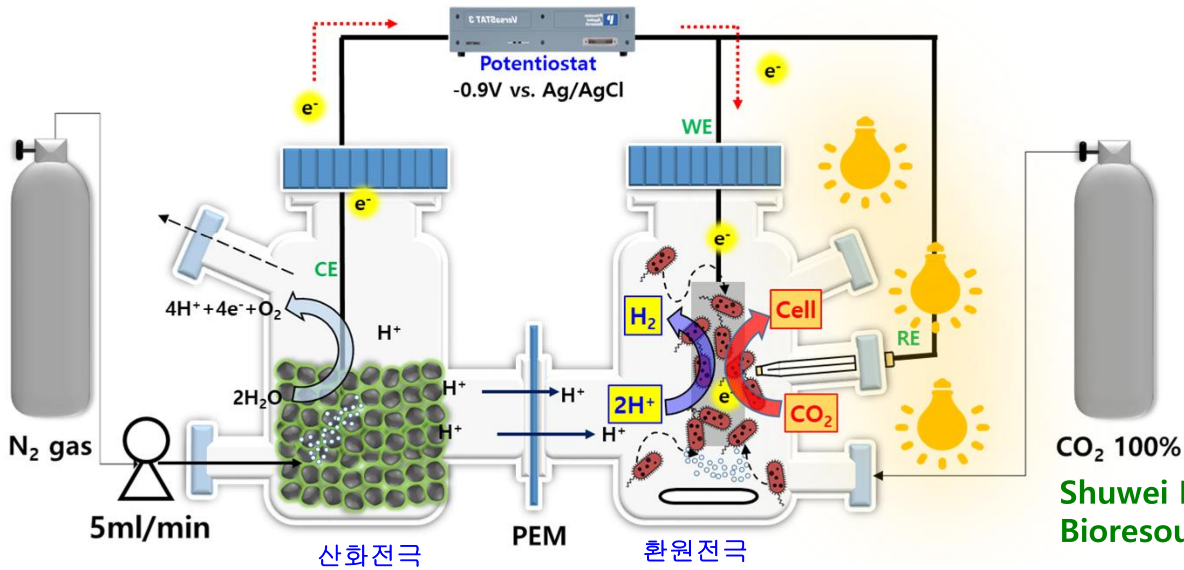
- Photoheterotrophic H_2 production
- No Photosystem II

Light energy → ATP (PS1)



PQ: Plastoquinone， PC: Plastocyanin

Photoautotrophic CO_2 conversion & H_2 production *R. sphaeroides*

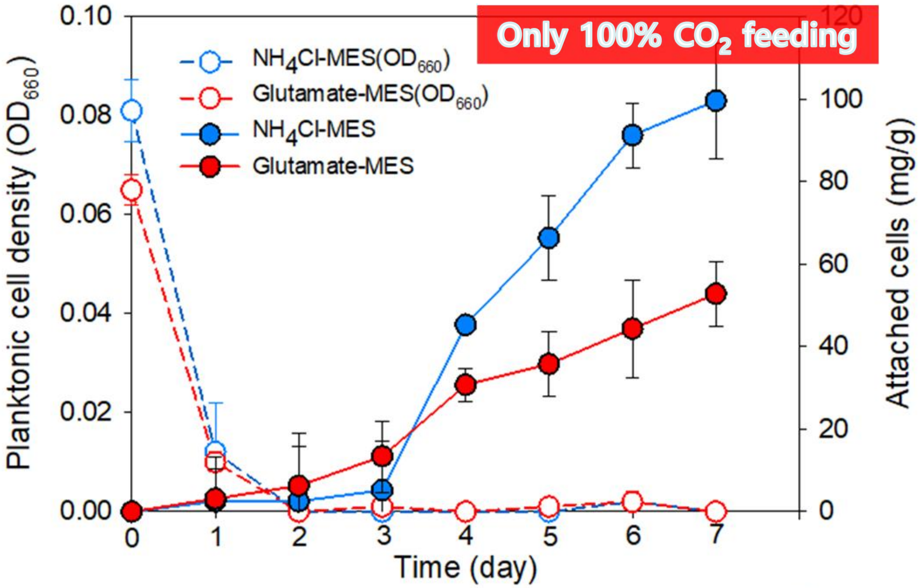


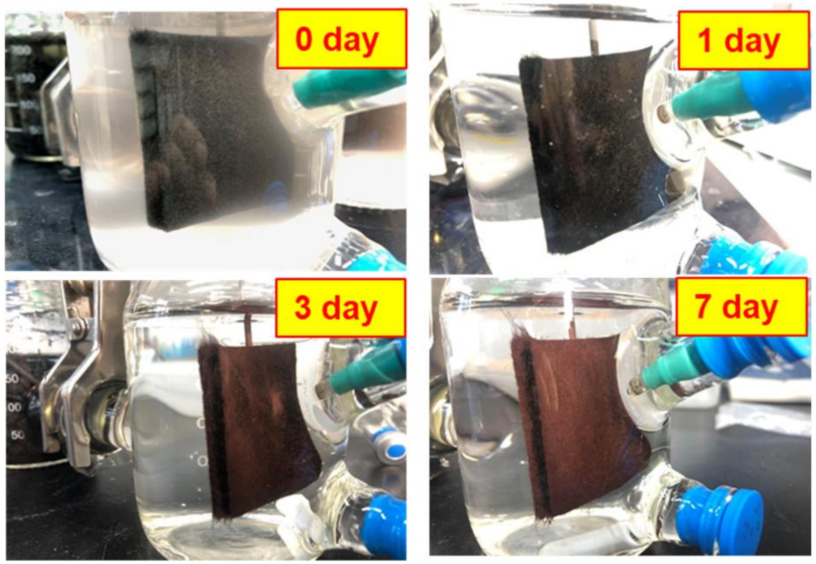
- -0.9V vs. Ag/AgCl applied under light (5000 lux)
- Consumption of CO_2 and simultaneously H_2 production

Shuwei Li and Jung Rae Kim. 2021. Bioresource Technology. 320:124333

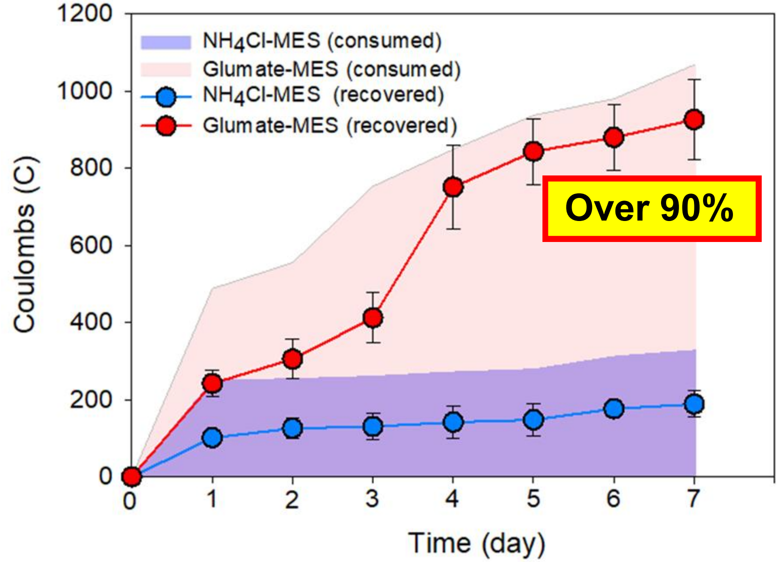
CO_2 to H_2 with *Rhodobacter sphaeroides*

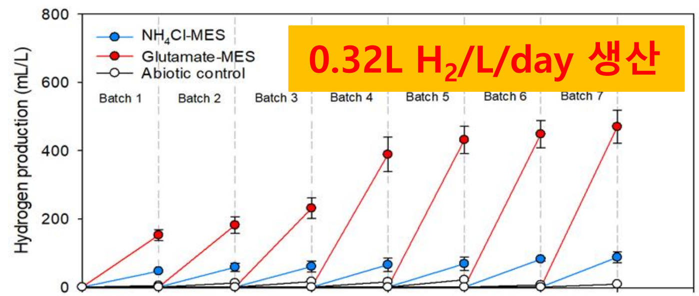
Planktonic cell attach to electrode surface

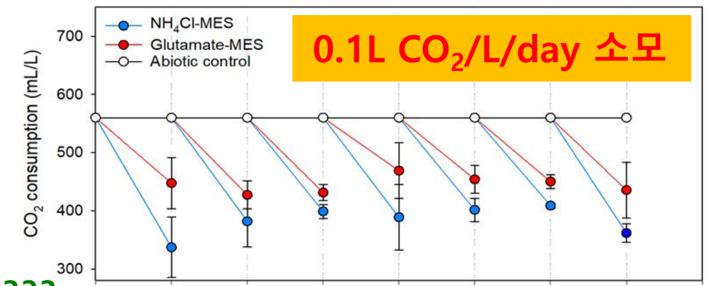




Coulomb Recovery into H_2

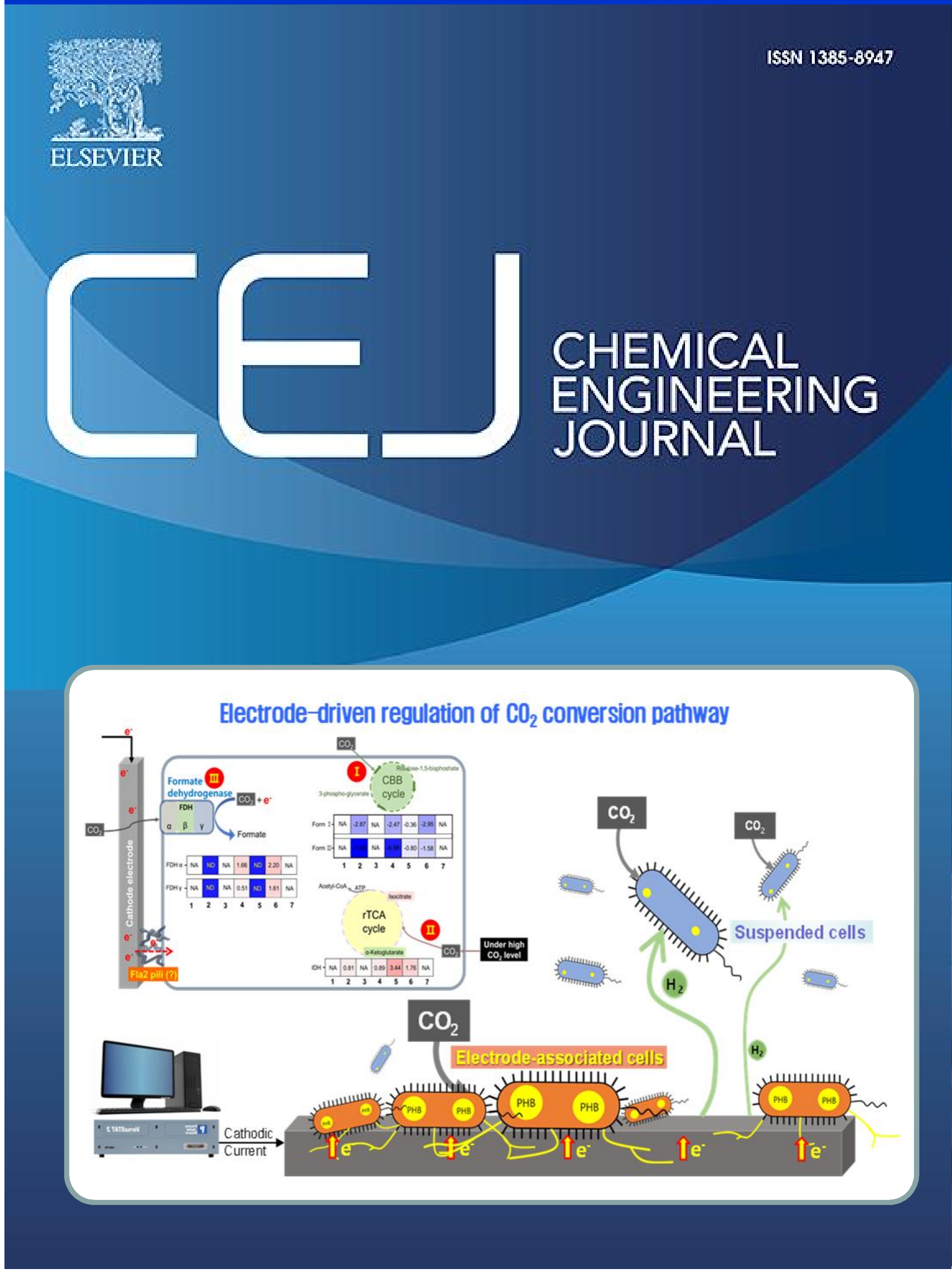






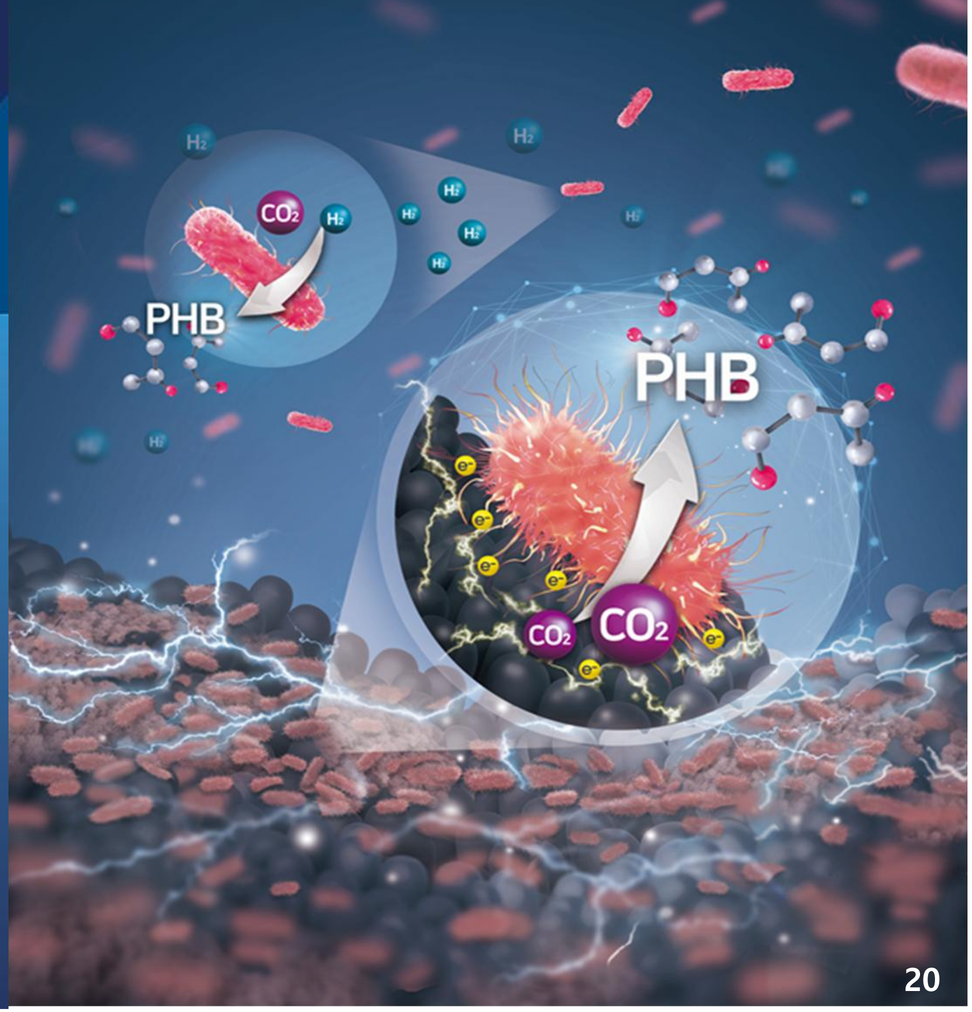
Shuwei Li and Jung Rae Kim. 2021. Bioresource Technology. 320:124333

CO_2 to PHB with *Rhodobacter sphaeroides*

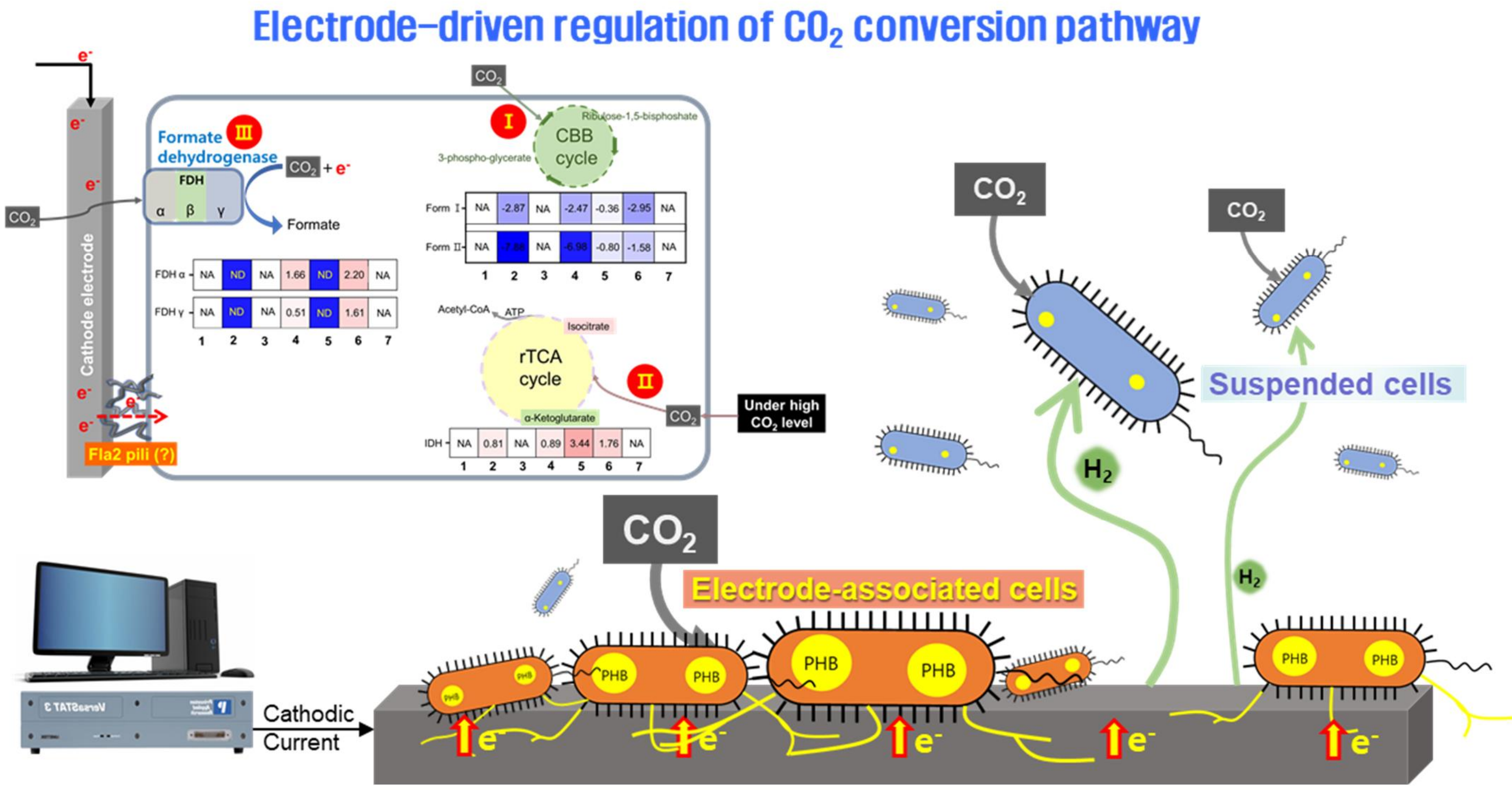


Polyhydroxybutyrate (PHB) Production

Shuwei Li & Jung Rae Kim et al. Electron uptake from solid electrodes promotes the more efficient conversion of CO2 to polyhydroxybutyrate by using *Rhodobacter sphaeroides*. Chemical Engineering Journal 469 (2023) 143785



CO_2 to PHB with *Rhodobacter sphaeroides*



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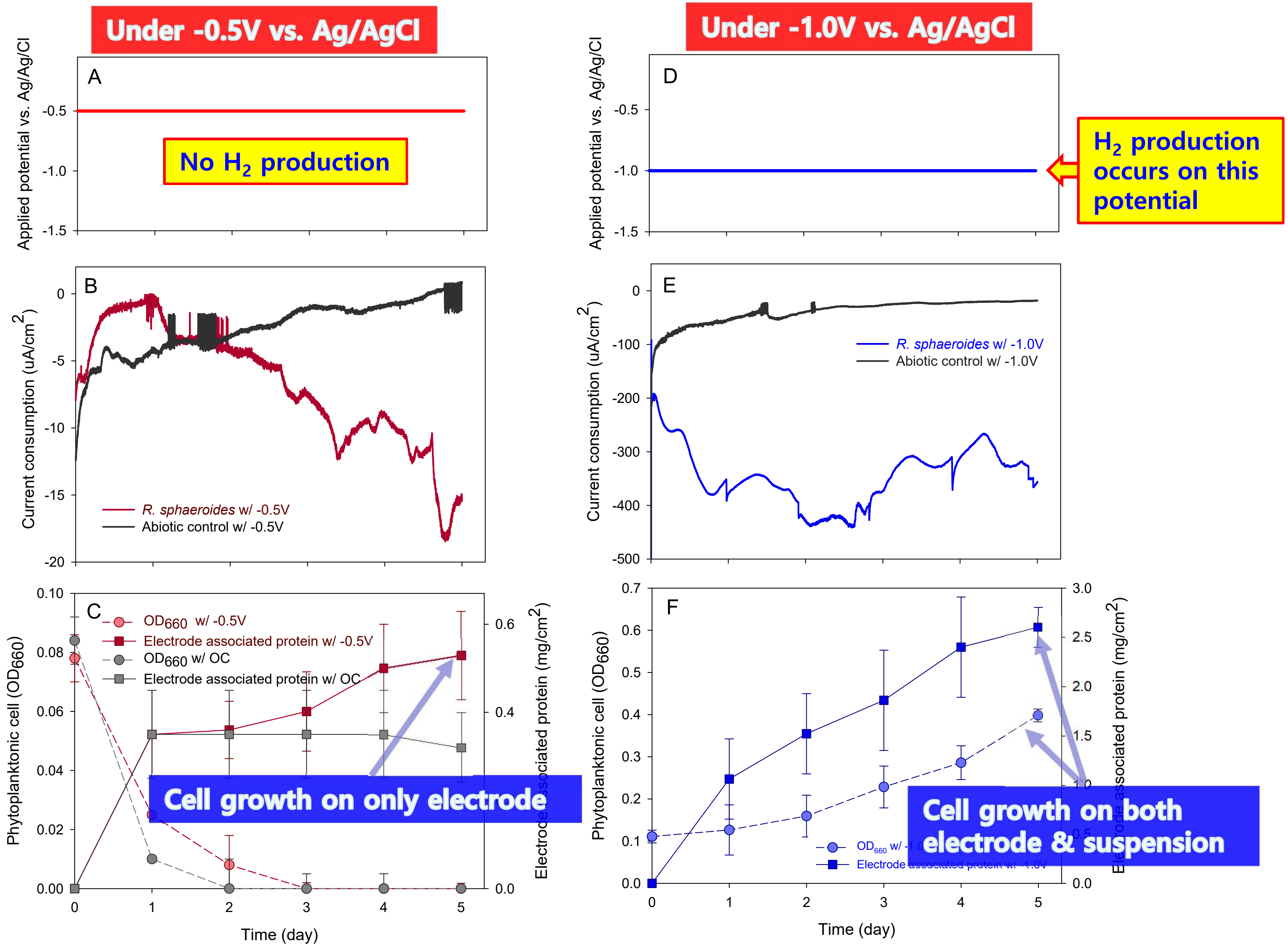
CO_2 to PHB with *Rhodobacter sphaeroides*



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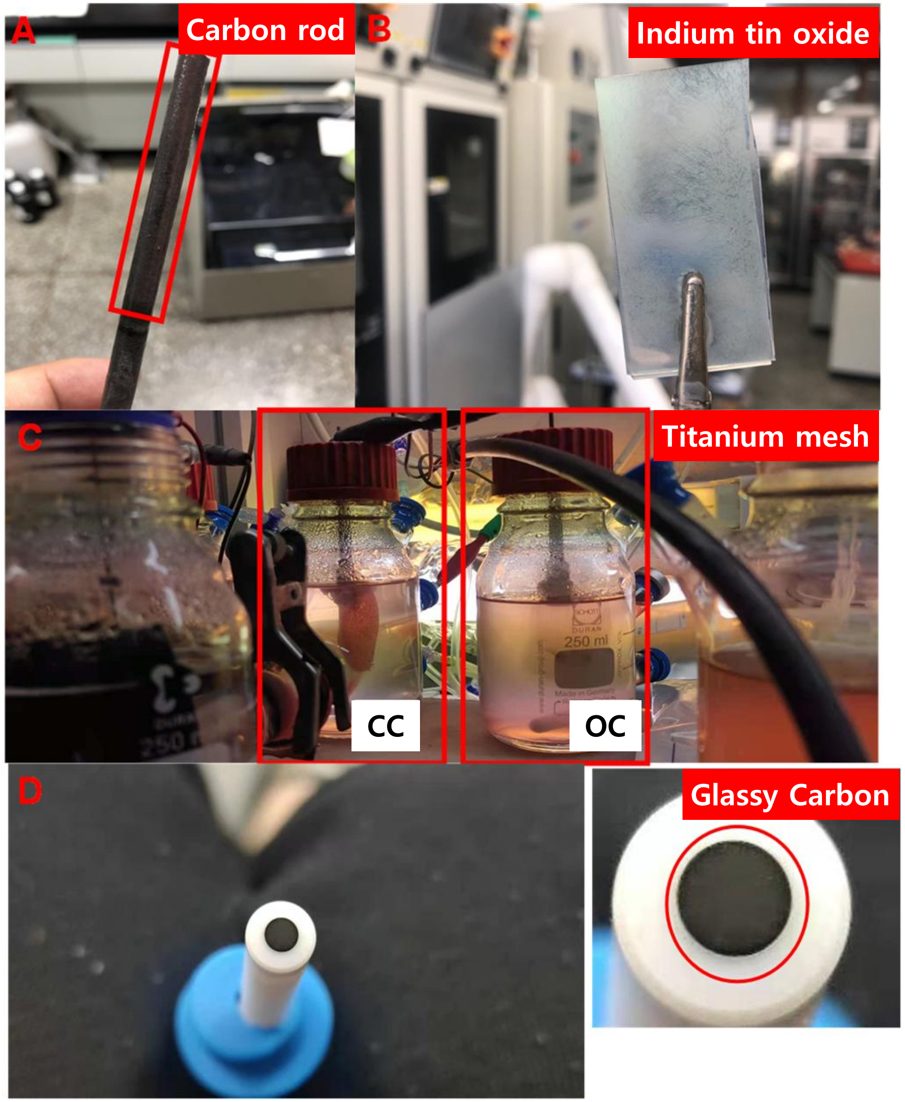
CO_2 to PHB with *Rhodobacter sphaeroides*

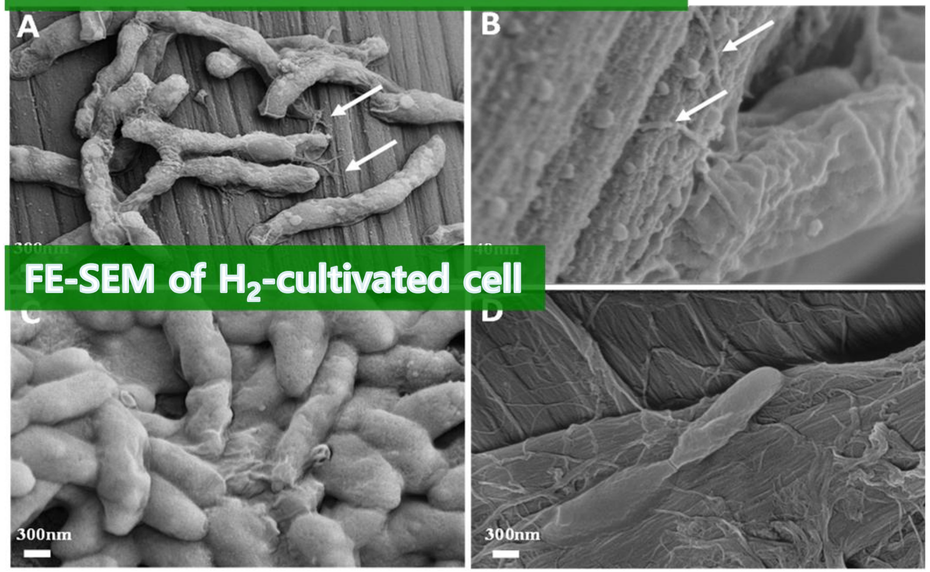
Attachement of cell on electrode surface



R. Sphaeroides **stick to the various carbon surface in MES**

- Carbon rod
- ITO
- Titanium mesh
- Glassy carbon

FE-SEM of electrode-associated cell

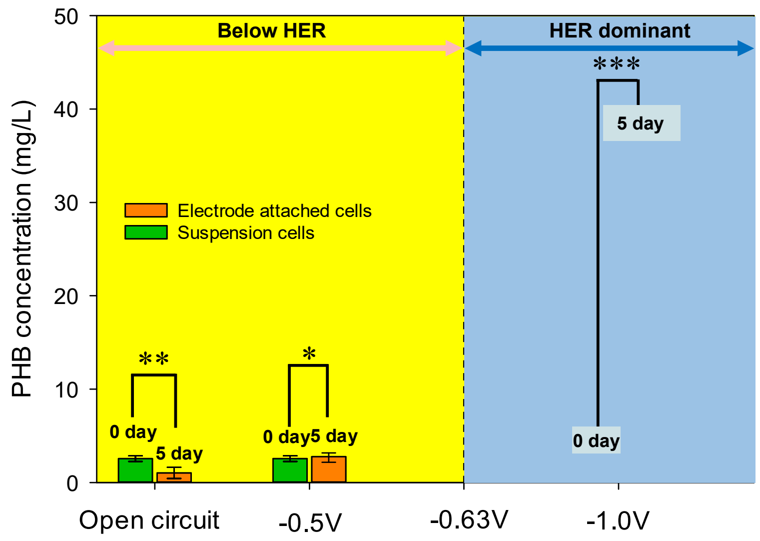


✓ ***R. Sphaeroides*** **may uptake electron directly from the cathode electrode through Fla2 flagella sysem**

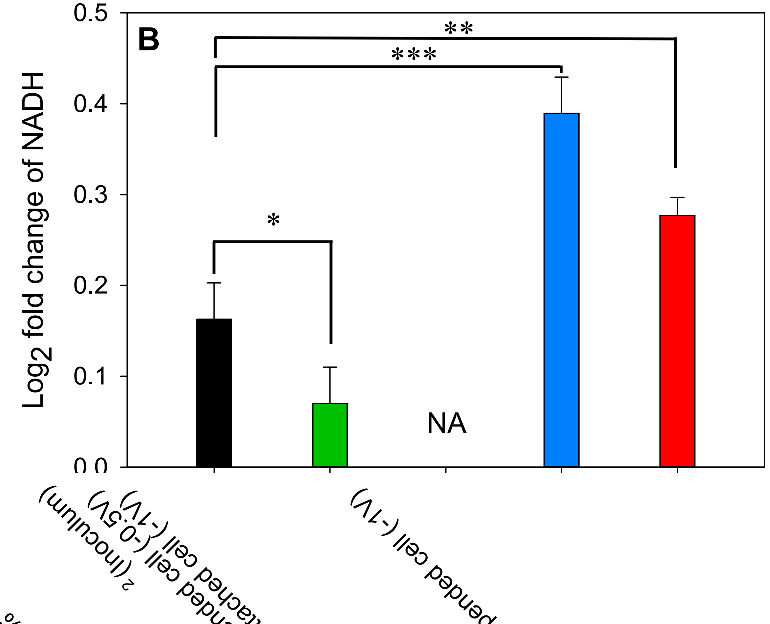
Shuwei Li and Jung Rae Kim. 2023. Chemical Engineering Journal. 469:143785

CO_2 to PHB with *Rhodobacter sphaeroides*

PHB Accumulation under different potentials



NADH level under different potentials



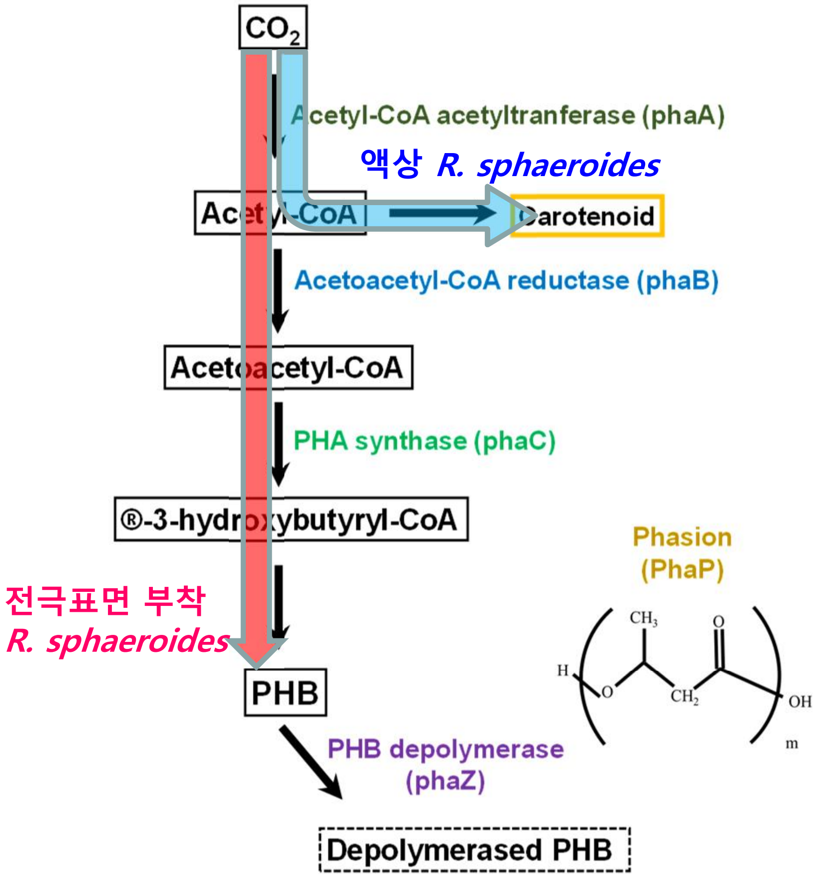
PHB Accumulation in the cell

Sample	Initial inoculum*	-0.5V		-1V	
		Electrode-attached	Suspended	Electrode-attached	Suspended
DCW(g/L)	0.84	0.03	NA**	0.05	0.20
PHB (mg/L)	75.09	2.77	NA**	11.35	19.97
PHB of DCW (%)	8.94±2	9.23±2.3	NA**	23.50±2.8	9.44±3.6

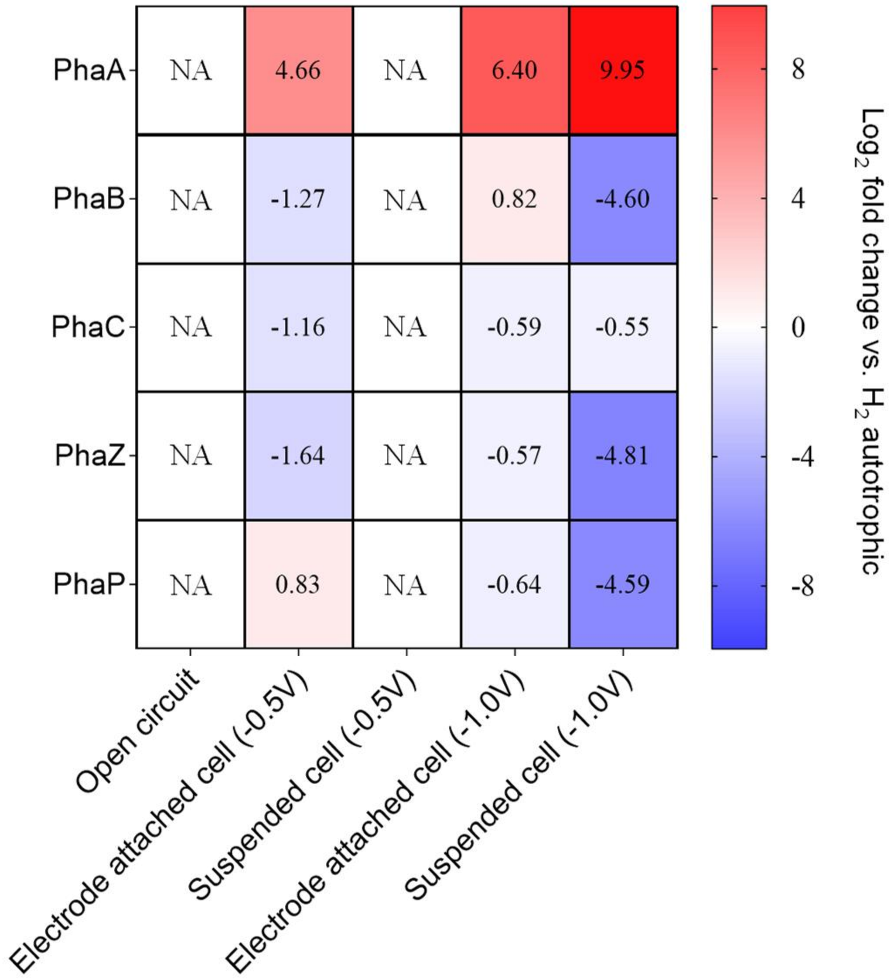
전극 표면부착 *R. sphaeroides*의 세포당 PHB함량이 높음

CO_2 to PHB with *Rhodobacter sphaeroides*

Pathway of PHB synthesis from CO_2



Relative gene expression profile



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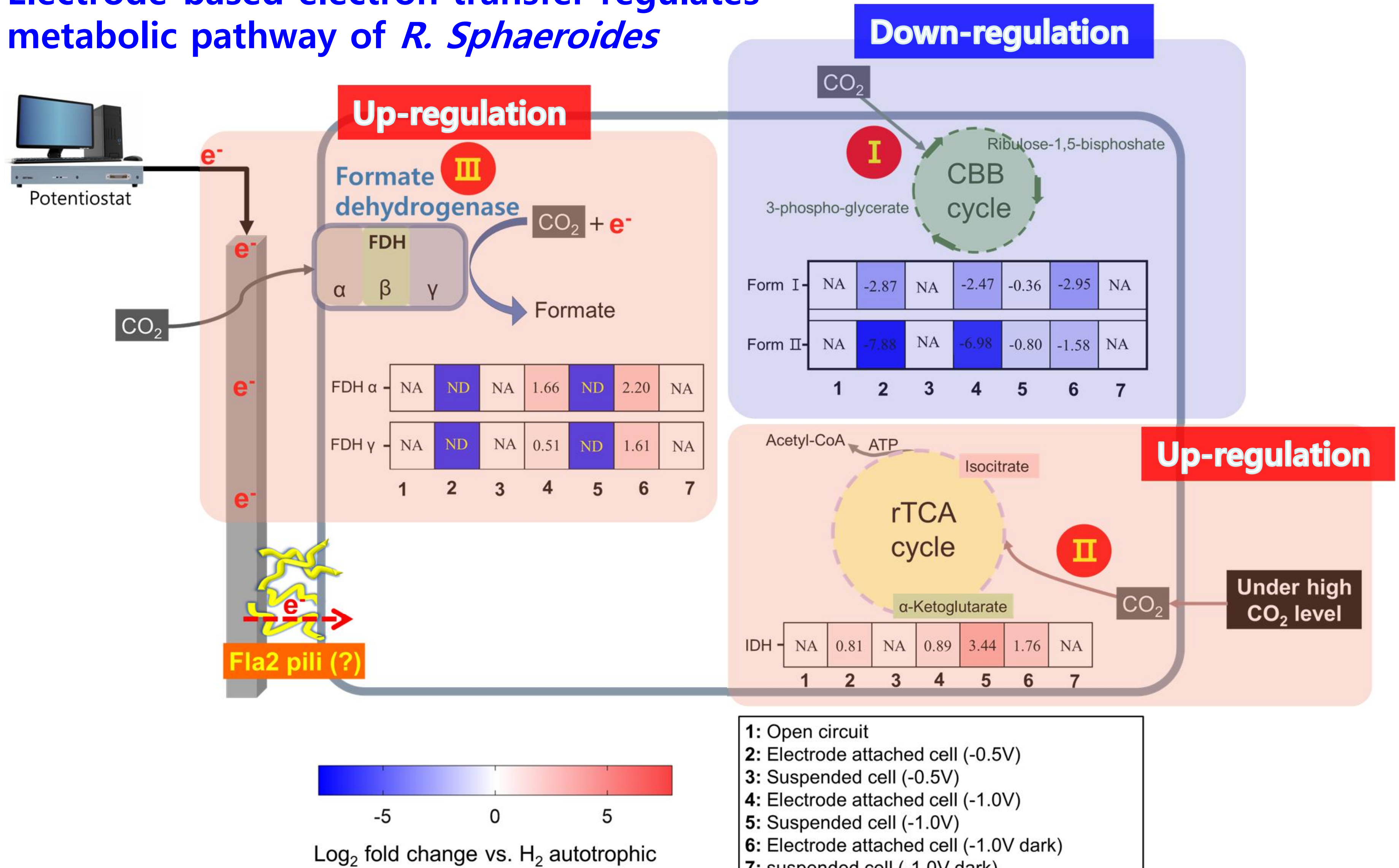
CO_2 to PHB with *Rhodobacter sphaeroides*

Electrode-based electron transfer regulates metabolic pathway of *R. Sphaeroides*



1: Open circuit
2: Electrode attached cell (-0.5V)
3: Suspended cell (-0.5V)
4: Electrode attached cell (-1.0V)
5: Suspended cell (-1.0V)
6: Electrode attached cell (-1.0V dark)
7: suspended cell (-1.0V dark)

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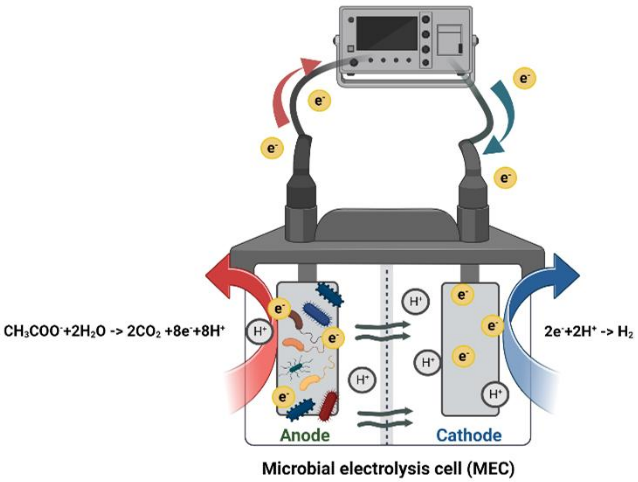
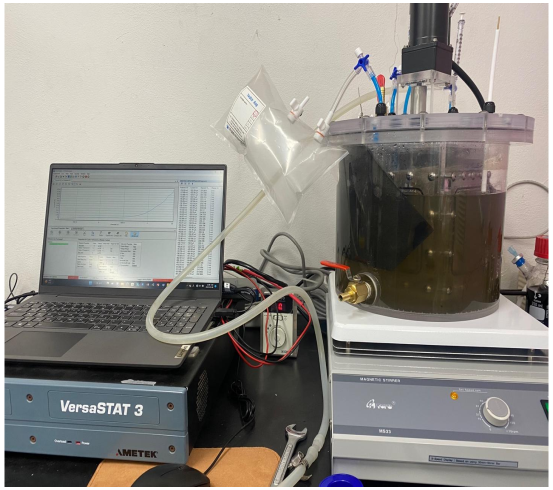
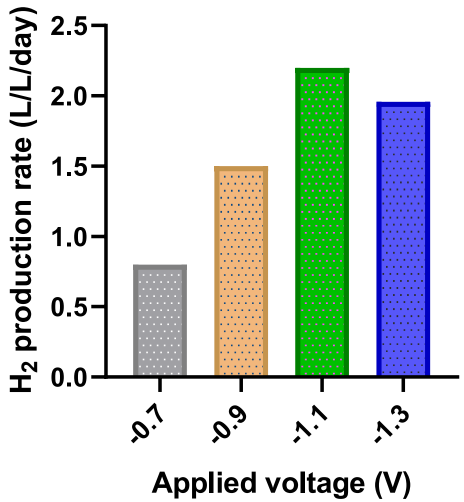
Scaled-up MEC Reactor for H_2 Production

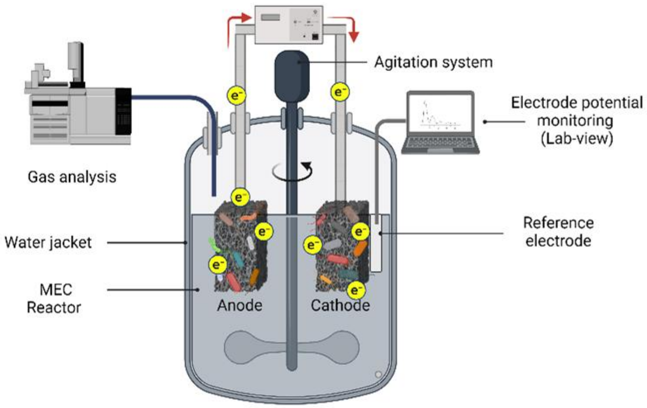
Two-chamber MEC (8L)

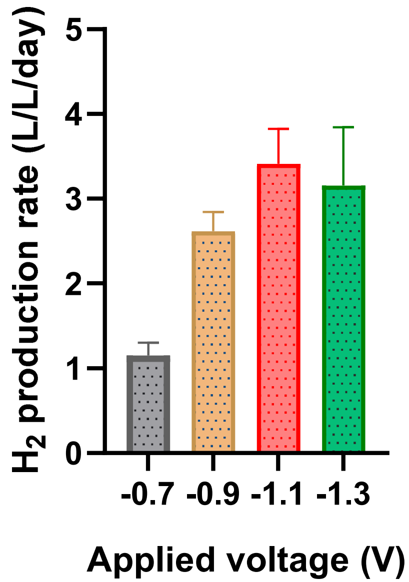






Single-chamber MEC (5L)



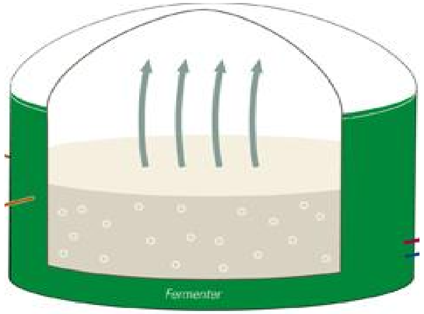


Upgrading AD Biogas with MEC

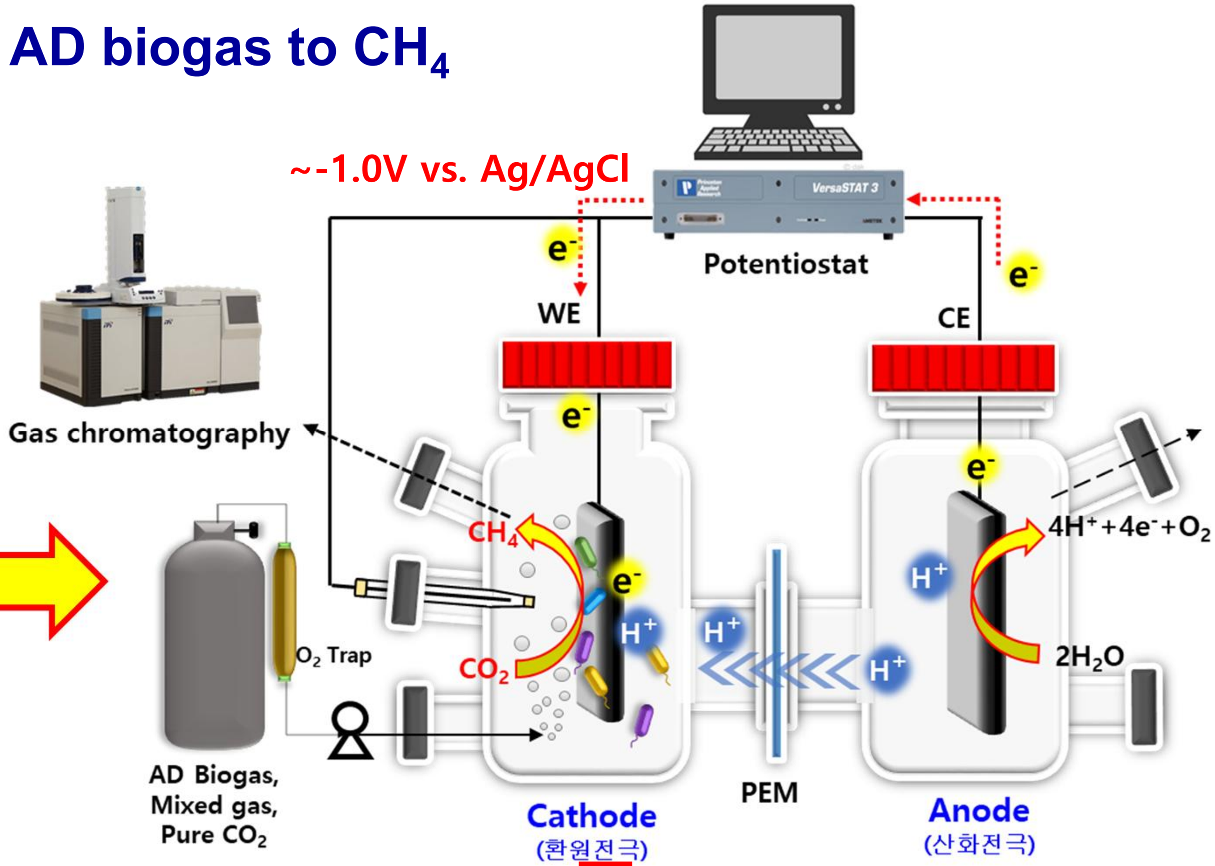
Conversion of CO_2 in AD biogas to CH_4

GS E&C

CH_4: ~60 %
CO_2: ~40 %



Anaerobic digester (AD)



- ✓ Conversion of CO_2 using low quality electricity or idle power
- ✓ Reduction of burden of post separation process of AD
- ✓ Combination with AD as a pretreatment process practically

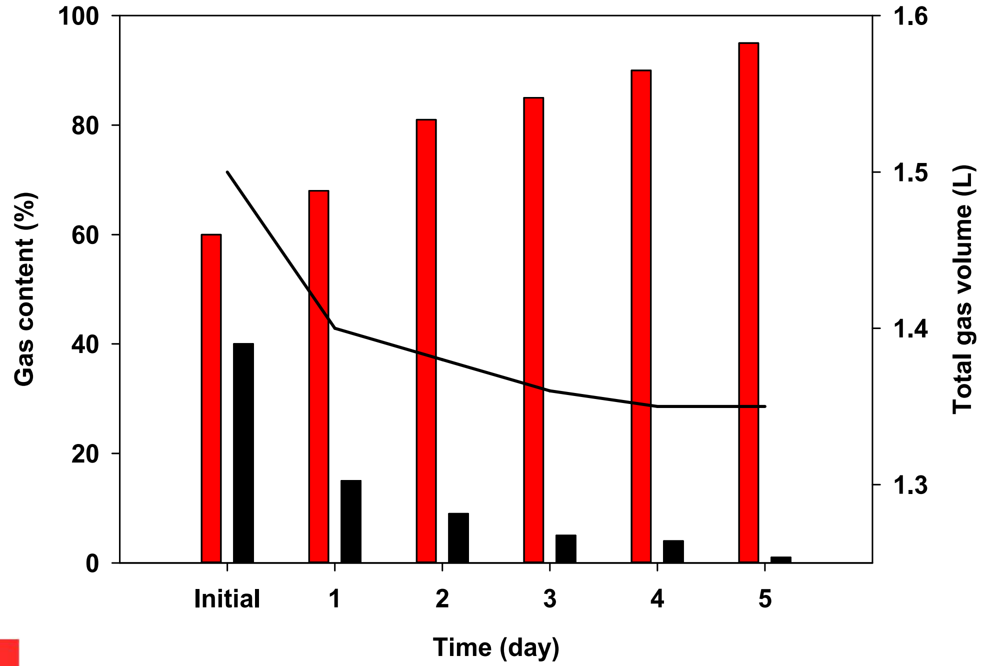
Improve CH_4 purity and production in biogas
CH_4 content ≥ 97%

City Gas Pipeline

Minsoo Kim and Jung Rae Kim. 2022. Chemical Engineering Journal 446:137079

Upgrading AD Biogas with MEC

Conversion of CO_2 to CH_4 in scale-up MEC reactor



Cost estimation of MES CH_4 production

* Below 300 kWh industrial, ~ 6 cent/ kWh

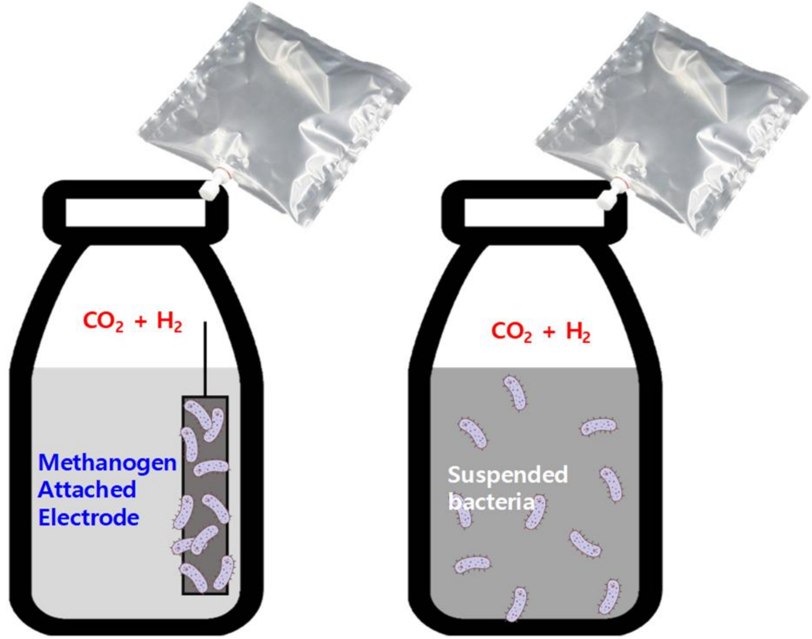
Reactor Volume	Applied Potential (V vs Ag/AgCl)	Temp.	CH_4 Production rate (L CH_4/m^2 cat/hour)	CH_4 Production per energy (L CH_4/kWh)	Cost of CH_4 production (USD/Nm^3 CH_4)
250 + 250 mL	-1.0V	30	2.9	259	0.24 USD
3L + 3L	-1.0V	40	2.29	14.9	4.13 USD

Calculated at standard temperature and pressure (STP)
Calculated with the immersed cathode surface area.
반응기에 인가되는 전압대비, 메탄생성량을 이용하여 계산하였음. (설치비, 운영비, 약품비, 인건비, Utility관리비 제외)

※ Present city gas in Korea: 0.48 USD/Nm^3
LPG : 0.78 USD/Nm^3

CO_2 to CH_4 with MES

전극상 메탄생산 미생물의 고농도 배양

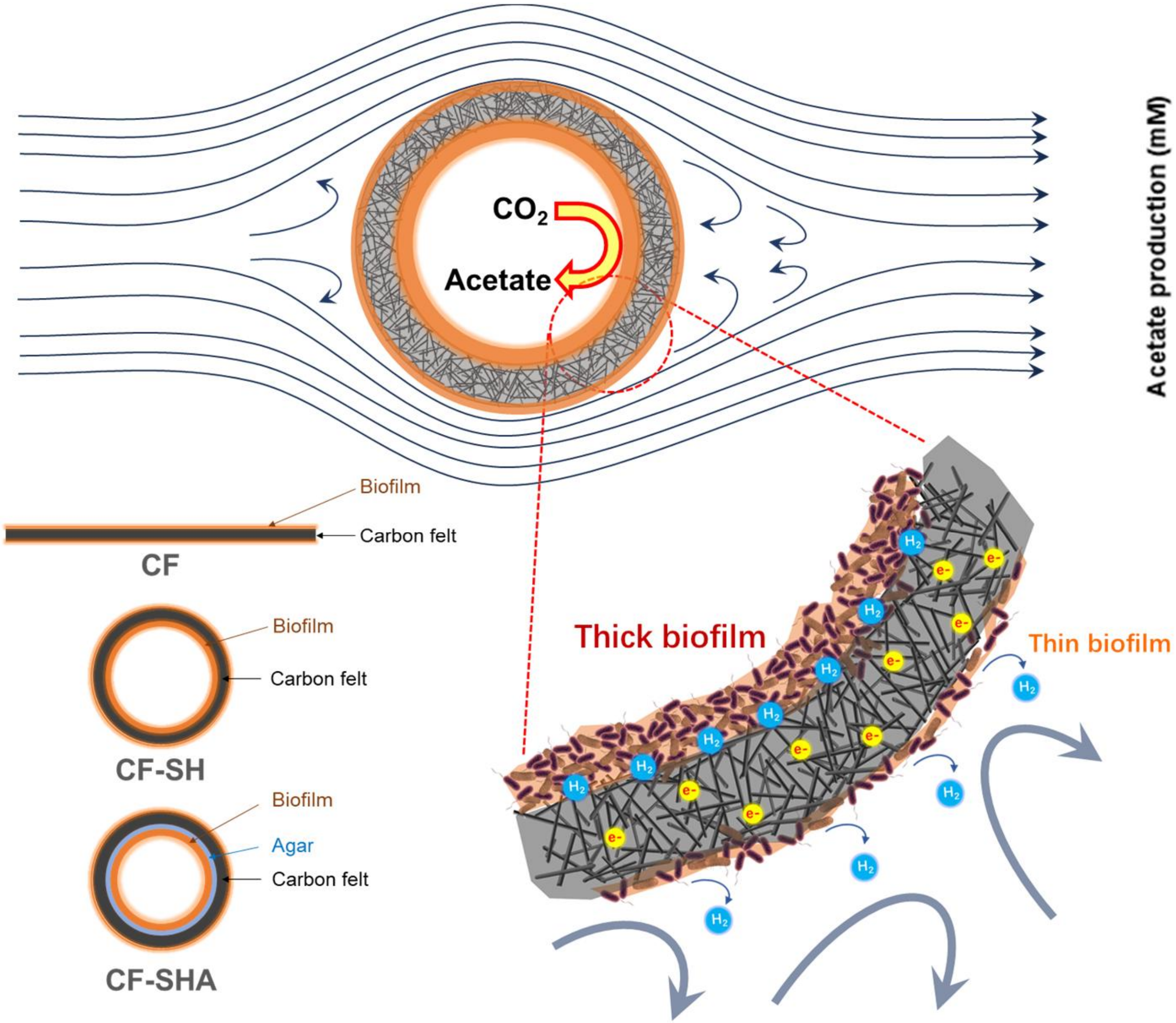


전극상 미생물
CO_2 & H_2 소모됨

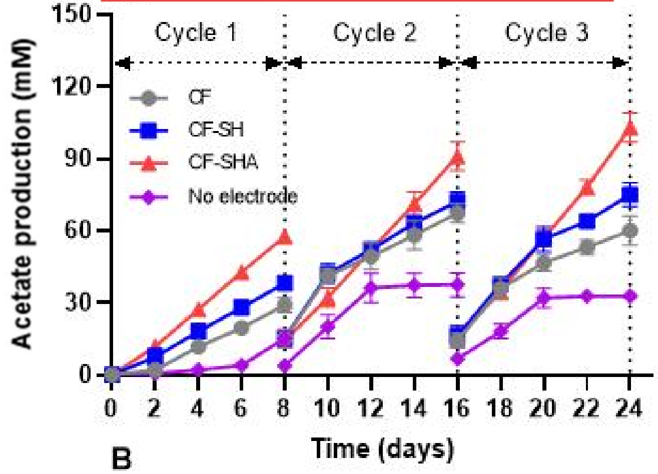
용액상 미생물
CO_2 & H_2 소모 안됨

- CH_4 전환 반응기에서 각각 메탄생성균이 부착된 전극과 배양액을 분리하여 Serum bottle에 배양함.
- Serum bottle 조건의 경우 전자(Electron) 공급을 위해 Potentiostat 대신 H_2 를 공급하였음.
- Methanogen attached electrode만 넣은 Serum bottle에서 CO_2와 H_2의 소모를 확인하였으며, 이는 메탄 생성에서 전극상 부착된 군집이 주요한 역할을 하고 있음을 나타냄.

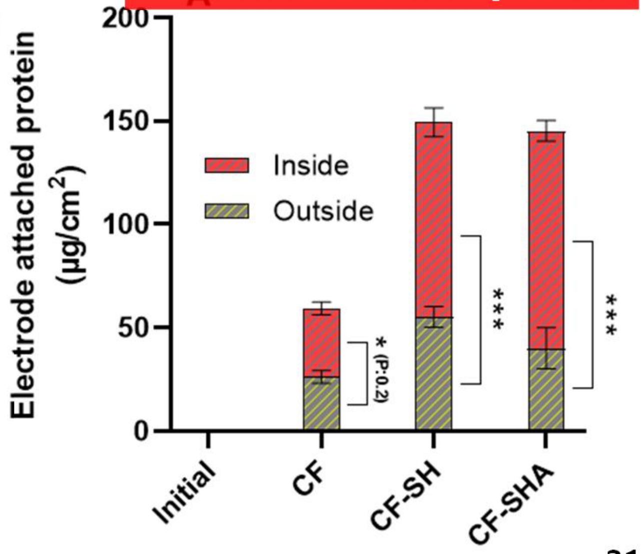
Effect of Hydrodynamic Shear Stress



Acetate production

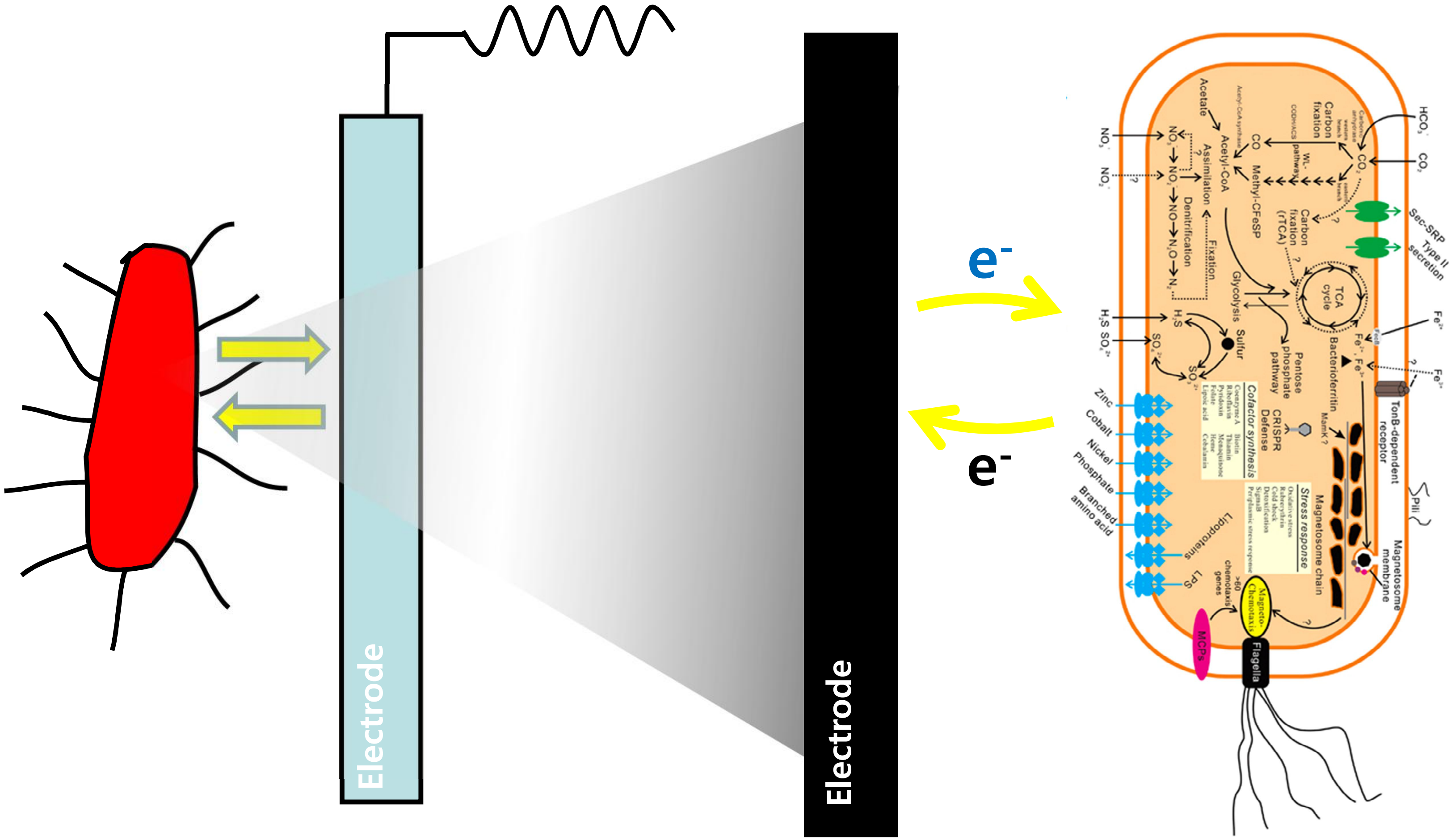


Electrode attached protein



Shuwei Li and Jung Rae Kim. 2023. In preparation

Microbe-Electrode Interaction



Take-Home Message

1. 미생물-전극 반응을 어떻게 분석할 것인가?

2. 생물전기화학시스템으로 무엇을 생산할 것인가?

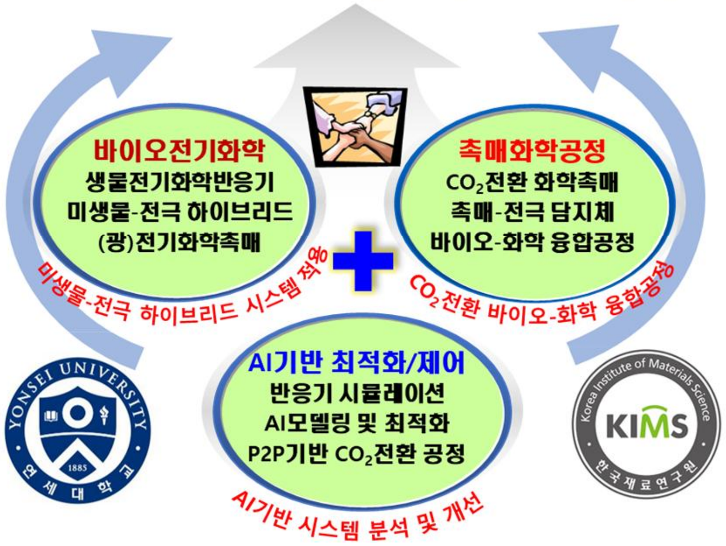
3. 생물전기화학시스템의 실용화 전략은?

→ 미생물-전극 분석 및 제어
→ Carbon capture & utilization (CCU)
→ Electro-fermentation
→ Power to Product (P2P)

한국연구재단 기초연구실 융합연구 (2022-현재)

추진전략

바이오-P2P 융합 CO_2 전환 기초연구실



연구목표

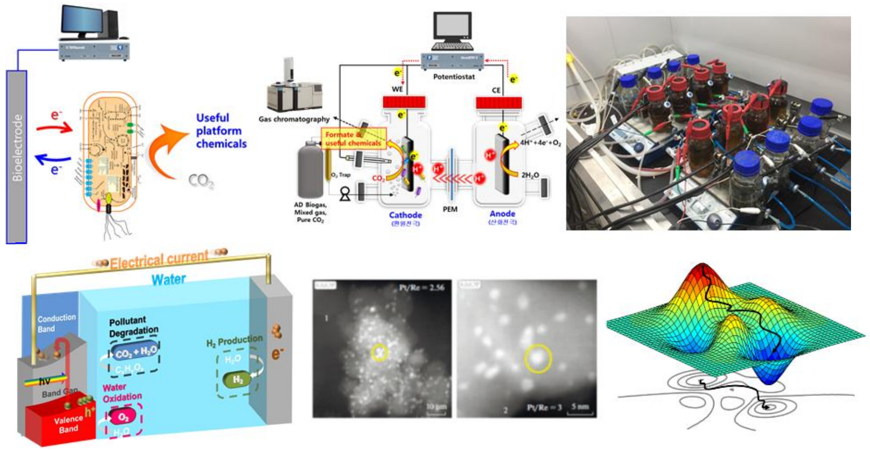
바이오-촉매-전기화학-AI 기술 융합 기초연구실

신재생 전기에너지의 물질화 원천기술 확보

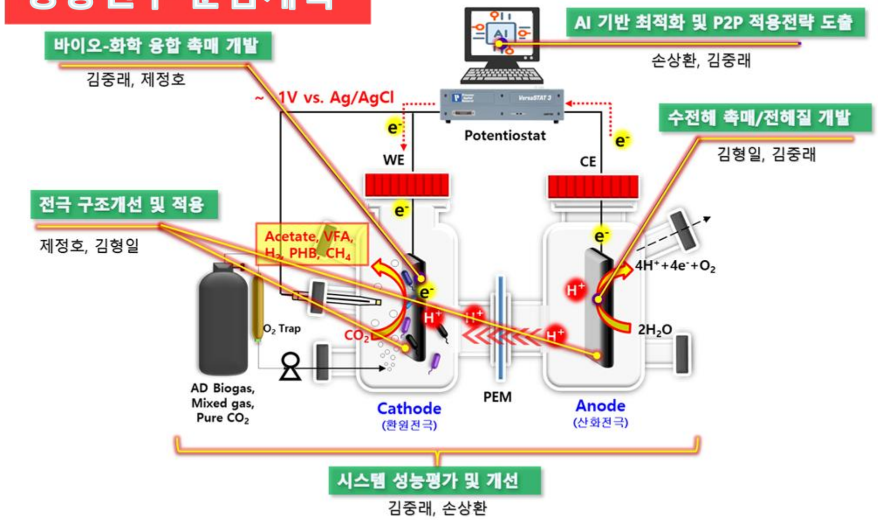
CO_2 전환에 필요한 환원력 제공 플랫폼 개발

석유화학 대체 플랫폼 케미컬 합성

선행 연구 및 결과



공동연구 분담계획



연구진 구성

생물전기화학시스템

연구책임자

김중래

부산대

화공생명공학부

- 전문분야: 생물전기화학반응시스템, 생물공학, 대사공학, 바이오에너지 및 바이오리파이너리 생산
- 담당분야: CO2전환 생물전기화학 반응기설계 및 운전, 미생물-전극 하이브리드 시스템 분석 및 최적화
- SCI(E) 논문 140편 (분야별 상위 10% 50편 포함)
- H-index 40

(광)전기화학촉매

공동연구원 (신진연구자)

김형일

연세대

건설환경공학과

- 전문분야: 광촉매/전기화학 촉매 개발 및 적용. (광)전기화학적 에너지 생산 및 수처리공정 개발
- 담당분야: 산화전극 개발, 산화환원 촉매 분석, 환원전극 담지체 개발
- SCI(E) 논문 46 편 (분야별 상위 10% 32편)
- h-index 27

화학촉매공정

공동연구원

제정호

부산대

화공생명공학부

- 전문분야: 바이오매스/C1 가스 전환 불균일촉매 설계, 산/염기/금속 복합나노구조체 촉매
- 담당분야: CO_2전환 화학촉매 및 담지체 개발, 바이오-화학 융합공정 분석 및 적용
- SCI(E) 논문 100편 (분야별 상위 10% 50편)
- h-index 37

AI기반 최적화/제어

공동연구원 (신진연구자)

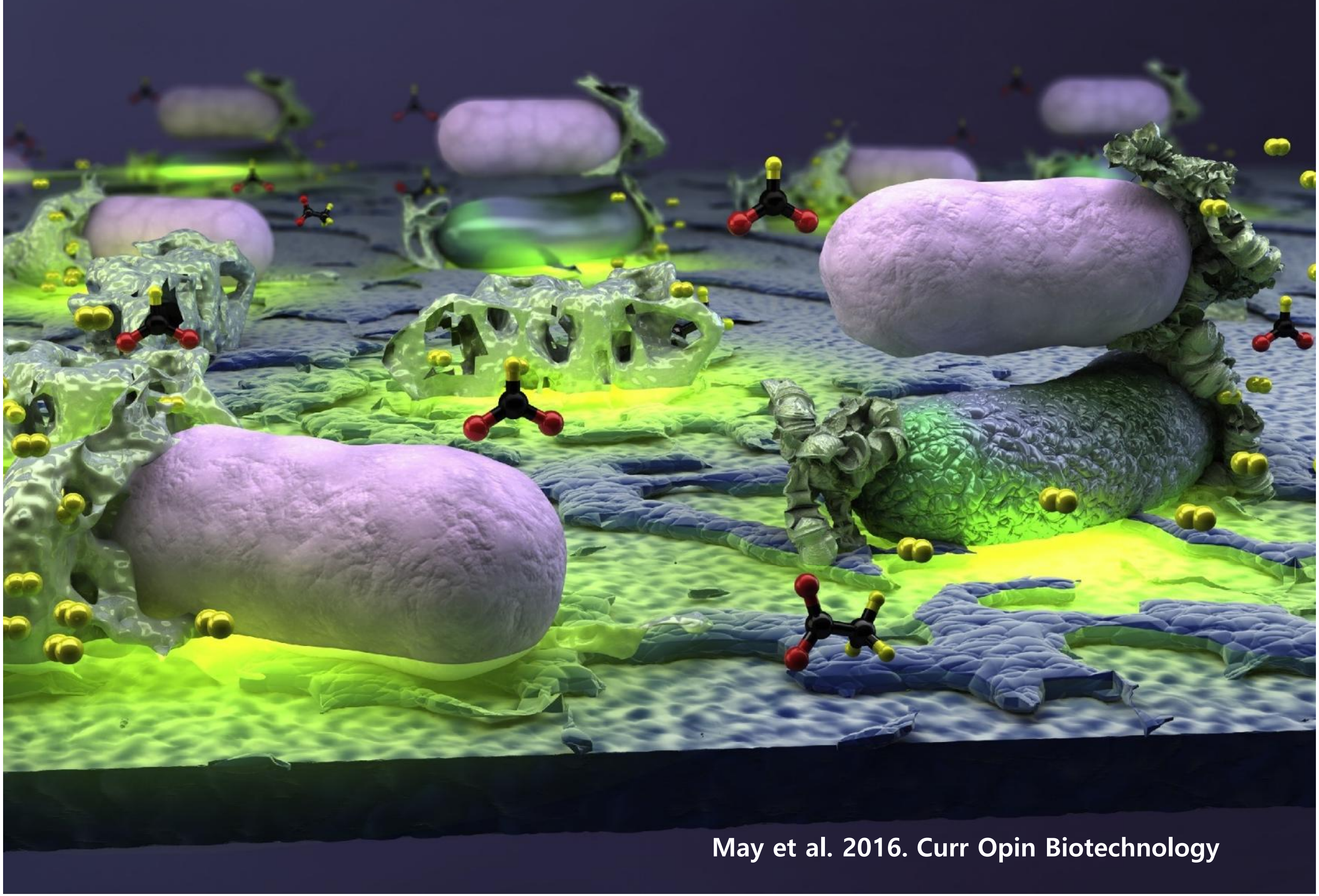
손상환

부산대

화공생명공학부

- 전문분야: 화학공정시스템 모델링 및 최적화, 모델링 및 AI기반 최적 제어
- 담당분야: 생물전기화학반응시스템 모델링 및 분석, 반응기 운전조건 최적화, 최적 제어 전략 개발
- SCI(E) 논문 16 편
- h-index 6

Biofunctionalization of Electrode Surface by Live Cell



May et al. 2016. Curr Opin Biotechnology

PNU Bioenergy & Bioprocess Engineering Lab (BBE Lab)

http://bioenergy.pusan.ac.kr/

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- **Researcher** Dr. Eun-Hee Seol
- **PhD Students** Ms. Sakuntala M.
  Mr. Shuwei Li
  Mr. Minsu Kim
  Ms. Dasuel Kong
  Mr. Himanshu Kandelwal
  Ms. Eun Su Kim
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  Ms. Eun Ju Park
  Ms. Wonkyung Park

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- Bio P2P-based CO_2 Valorization Lab, **Basic Research Laboratory Program (BRL),** National Research Foundation of Korea & Ministry of Science and ICT, Korea
- Bio-Electrosynthetic CO_2 valorization for value-added chemical production **Korea-Sweden Research Cooperation Program (STINT)**. National Research Foundation of Korea
- **BK21 PLUS** Center for Advanced Chemical Technology, Pusan National University, National Research Foundation of Korea
- Bioelectrochemical System for Biogas upgrading Project, GS E&C

과학기술정보통신부 Ministry of Science and ICT

NRF National Research Foundation of Korea

BrainKorea21 PLUS

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감사합니다!
Thank you!