



# **CATALYST DESIGN FOR THE DIRECT ELECTROCATALYTIC CO<sub>2</sub> REDUCTION REACTION (e-CO<sub>2</sub>RR)**

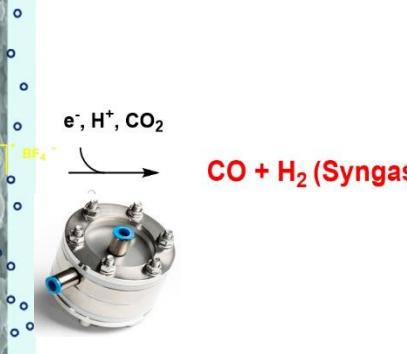
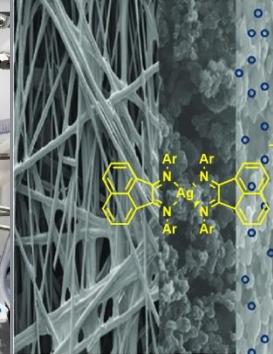
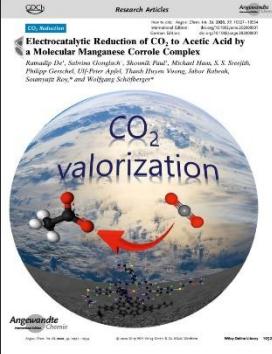
Prof. Dr. Wolfgang Schöfberger

Institute of Organic Chemistry, Johannes Kepler University Linz (JKU)  
Altenberger Straße 69, 4040 Linz, Austria.

Email: wolfgang.schoefberger@jku.at

<https://www.jku.at/institut-fuer-organische-chemie/team/schoefberger-lab/>





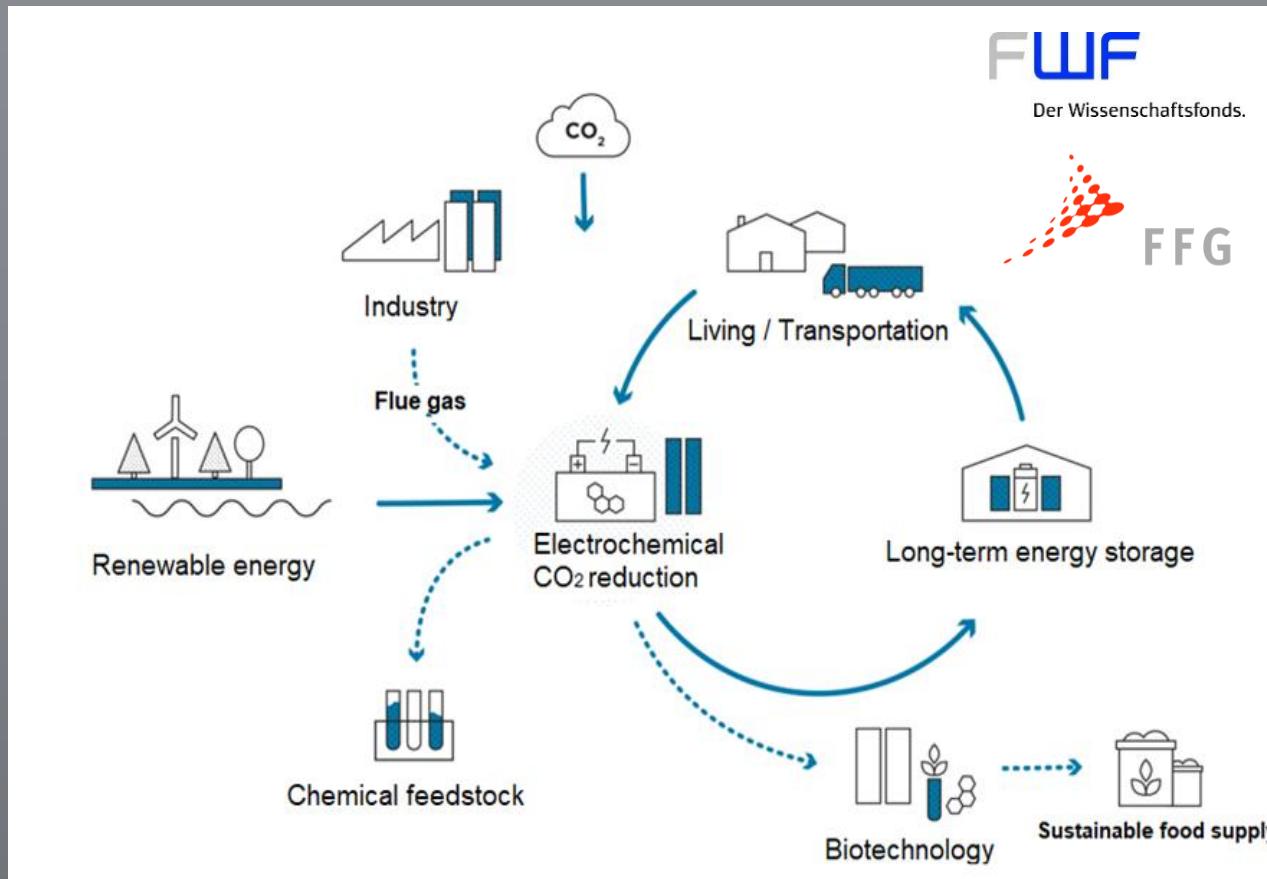
# RESEARCH

## Catalyst Design for Heterogeneous (photo-)electrocatalysis

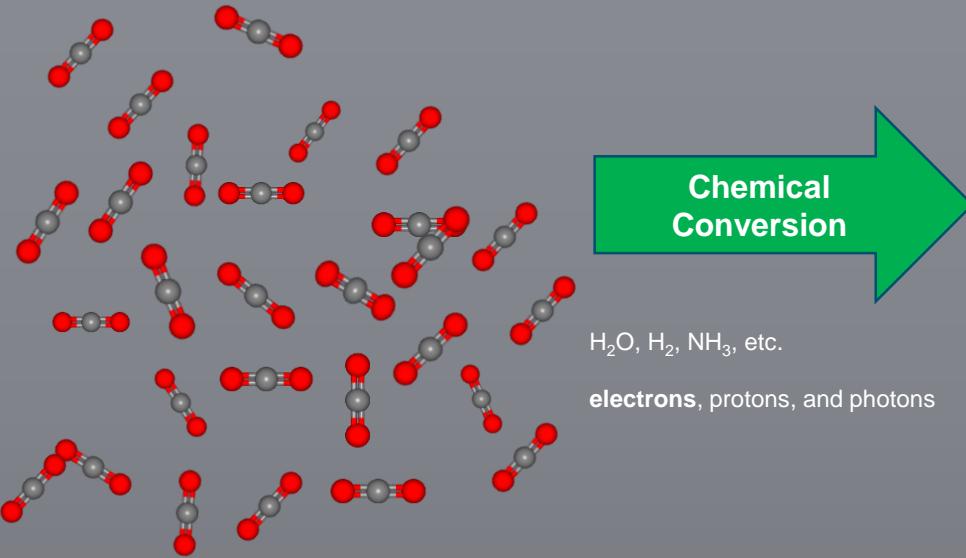
- Water Oxidation Reaction (WOR)
- Oxygen Reduction Reaction (ORR)
- Hydrogen Evolution Reaction (HER)
- Nitrogen Reduction Reaction (NRR)
- **Electrocatalytic  $\text{CO}_2$  Reduction Reaction ( $\text{e}-\text{CO}_2\text{RR}$ ) - from flue-gas to Syngas, Ethylene, Formic acid, Methanol, Ethanol, Acetic acid**



# ELECTROCATALYTIC CO<sub>2</sub> REDUCTION REACTION (e-CO<sub>2</sub>RR)

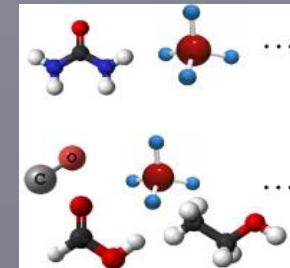


# CATALYTIC CONVERSION OF CO<sub>2</sub> TO VALUE ADDED COMPOUNDS



- Cyclic Carbonates, Polycarbonates, Carboxylates, Lactones

Carbamates  
Urea or isocyanates  
Biodegradable polymers



- Fuels

Syngas, methane, etc.

Formic acid, methanol, ethanol, C<sub>n</sub> products (n ≥ 2), etc.

## Publications

1. Electrocatalytic Reduction of CO<sub>2</sub> to Acetic Acid by a Molecular Manganese Corrole Complex, R. De, S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreekumar, P. Gerschel, U.-P. Apfel, H. Vuong, J. Rabéah, S. Roy\*, and W. Schöfberger\*, *Angew. Chem.* 2020, 59, 26, 10527-10534. <https://doi.org/10.1002/anie.202000601>
2. Co-function of protons as dopant and reactant activate the electrocatalytic hydrogen evolution in emeraldine-polyguanine, H. Coskun\*, A. Aljabour, W. Schöfberger, A. Hinterreiter, D. Stifter, N. S. Sariciftci, and P. Stadler, *Adv. Mat. Interfaces* 2019, 1901364. <https://doi.org/10.1002/admi.201901364>
3. Molecular Cobalt Corrole Complex for the Heterogeneous Electrocatalytic Reduction of Carbon Dioxide, S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreekumar, S. Barman, R. De, S. Müllegger, P. Gerschel, U.-P. Apfel, H. Coskun, A. Aljabour, P. Stadler, W. Schöfberger\*, and S. Roy\*, *Nat. Commun.* 2019, 3864. <https://doi.org/10.1038/s41467-019-11868-5>
4. Biofunctionalized conductive polymers enable efficient CO<sub>2</sub> electroreduction, H. Coskun, A. Aljabour, A. P. de Luna, D. Farka, T. Greunz, D. Stifter, M. Kus, X. Zheng, M. Liu, A. W. Hassel, W. Schöfberger, E. H. Sargent, N. S. Sariciftci, P. Stadler, *Sci. Adv.* 2017, 3:e1700686 <https://doi.org/10.1126/sciadv.1700686>
5. CO<sub>2</sub> Fixation with Epoxides under Mild Conditions with a Cooperative Metal Corrole - Quaternary Ammonium Salt Catalyst System, M. Tiffner, S. Gonglach, M. Haas, W. Schöfberger\*, and M. Waser\*, *Chem. Asian J.* 2017, 12(10), 1048-1051. <https://doi.org/10.1002/asia.201700354>

# ELECTROCATALYTIC CONVERSION OF CO<sub>2</sub> TO VALUE ADDED FUELS

## MARKET VALUE

Ethylene = \$ 182B

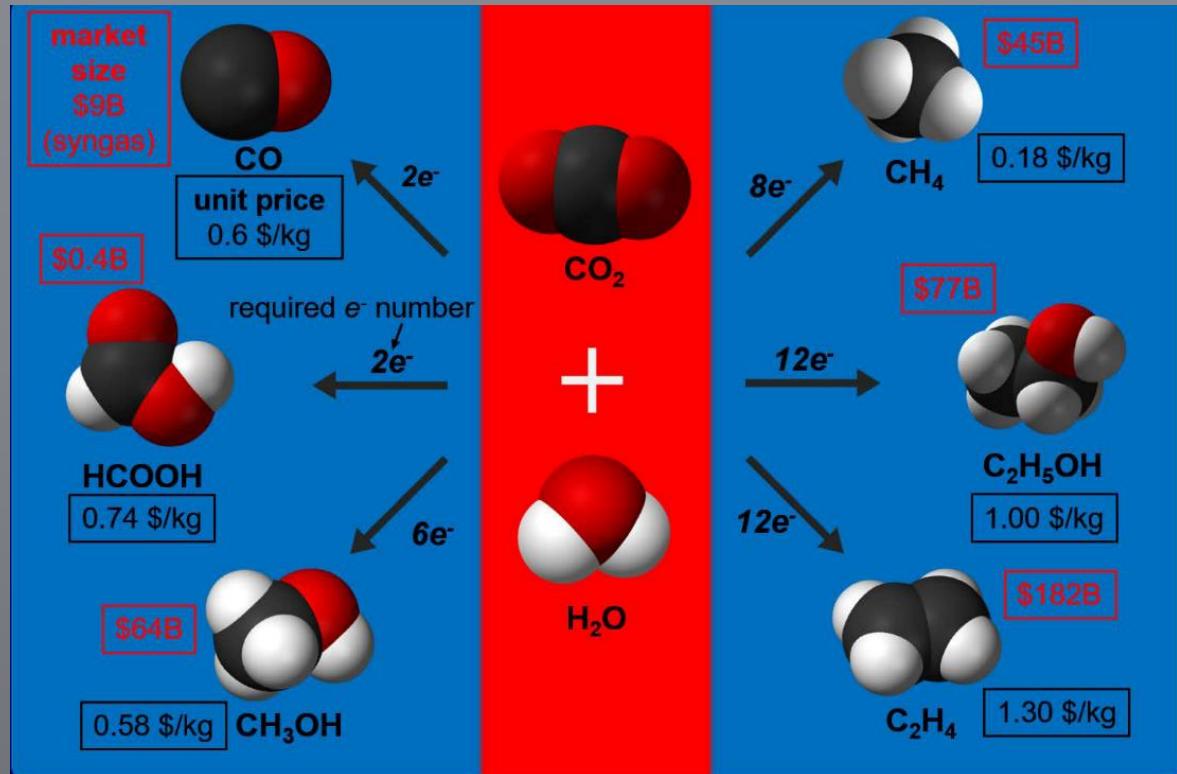
Ethanoic Acid = \$ 77B

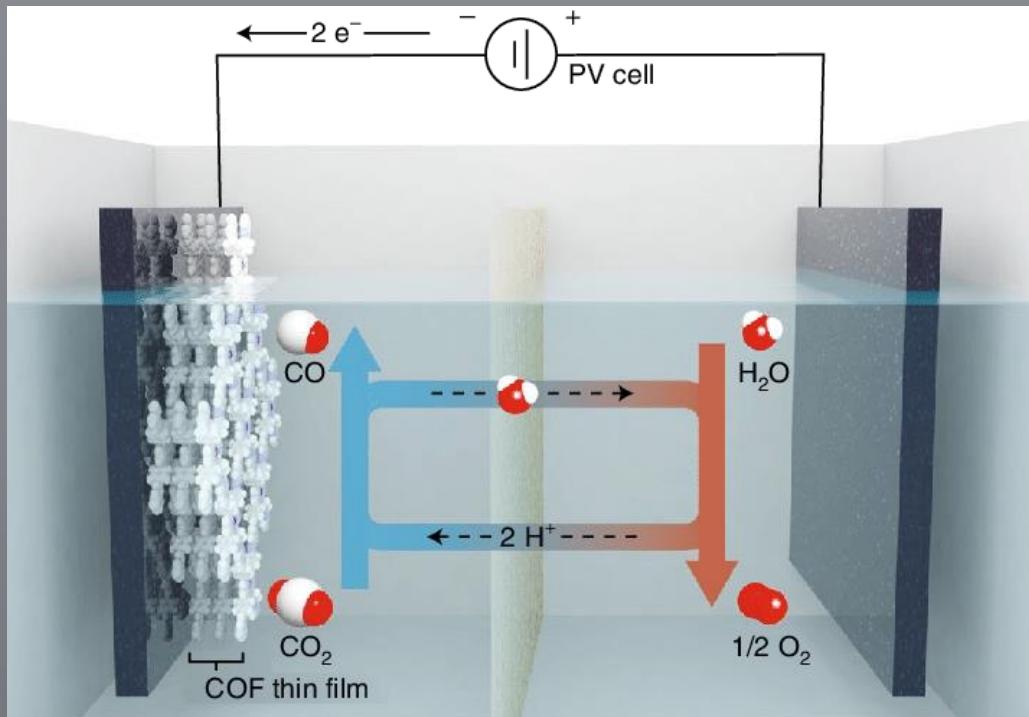
Methanol = \$ 64B

Methane = \$ 45B

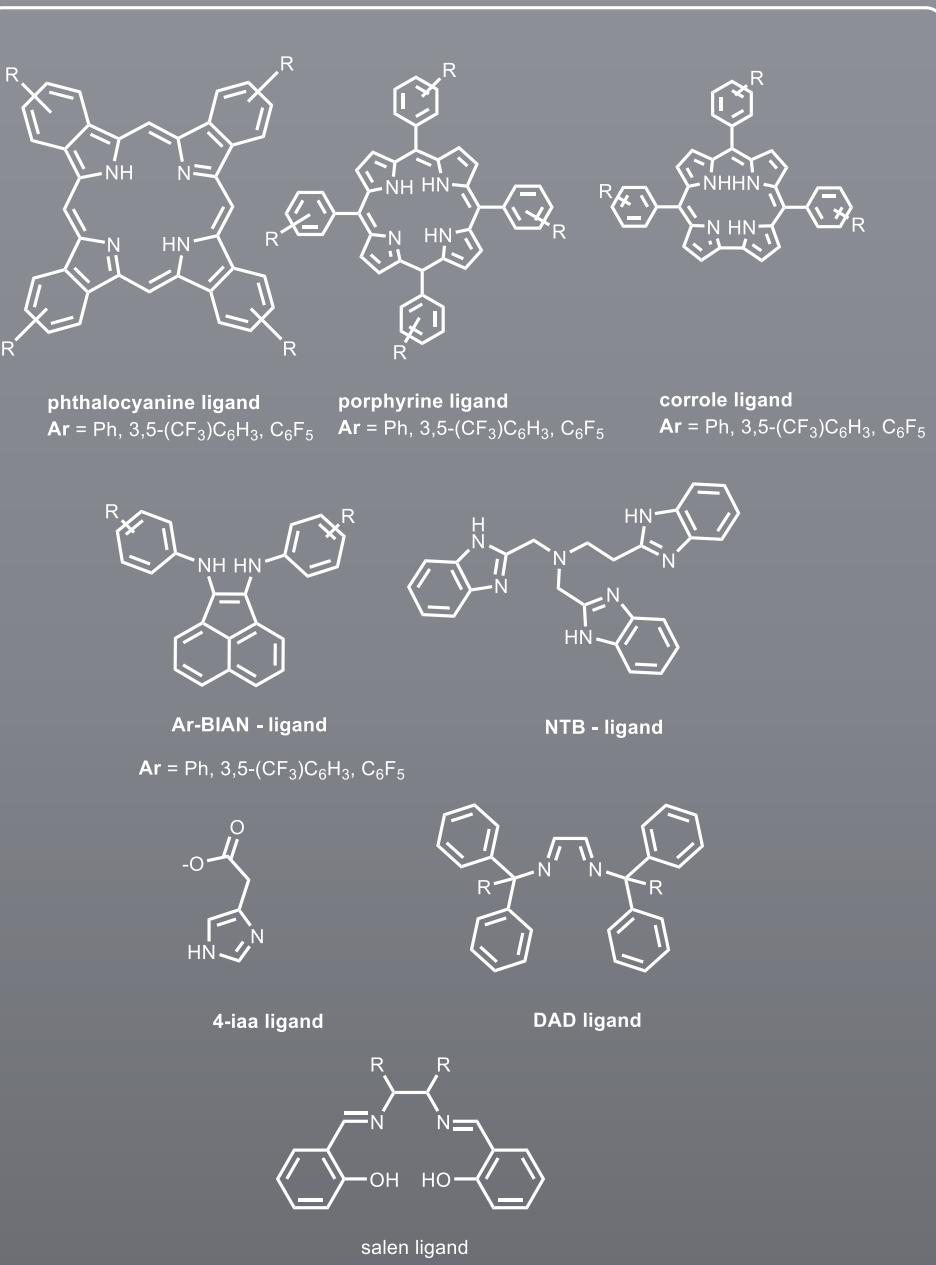
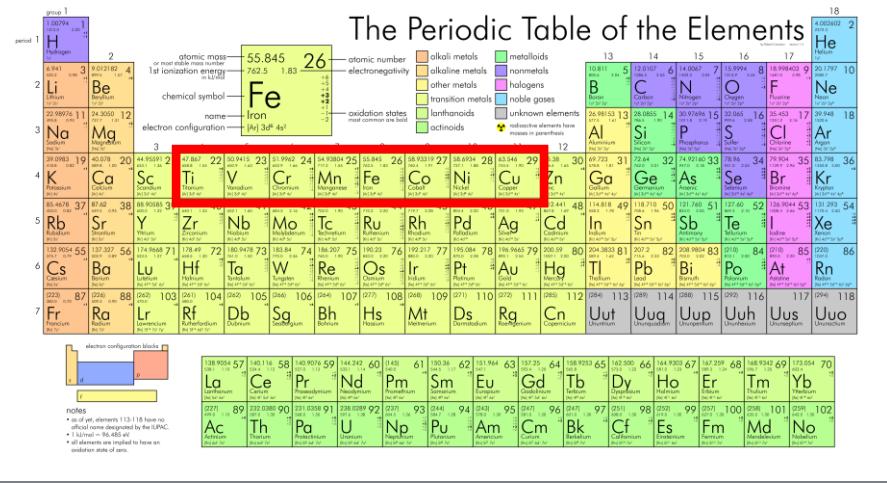
Carbon Monoxide = \$ 9B

Formic Acid = \$ 400M

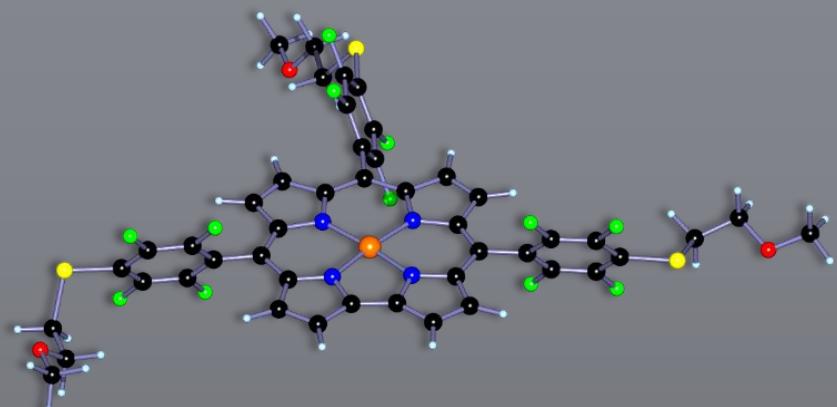
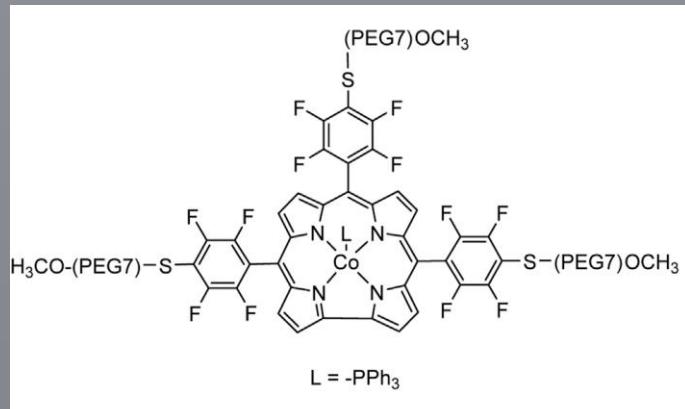
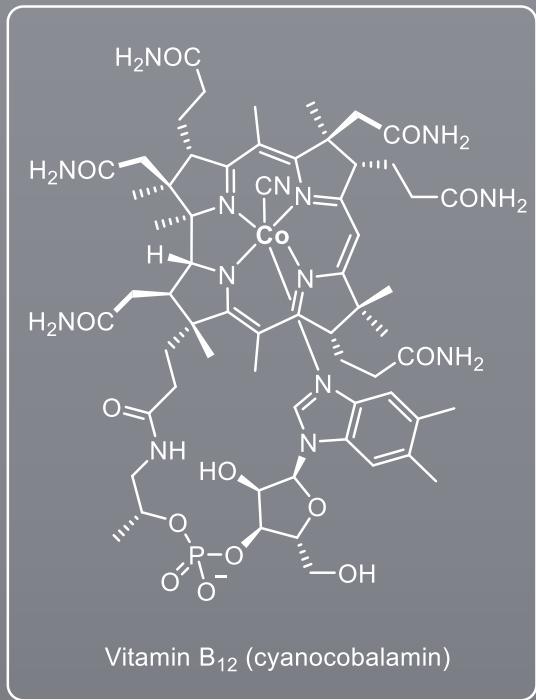




# CATALYST DESIGN



# CATALYST DESIGN

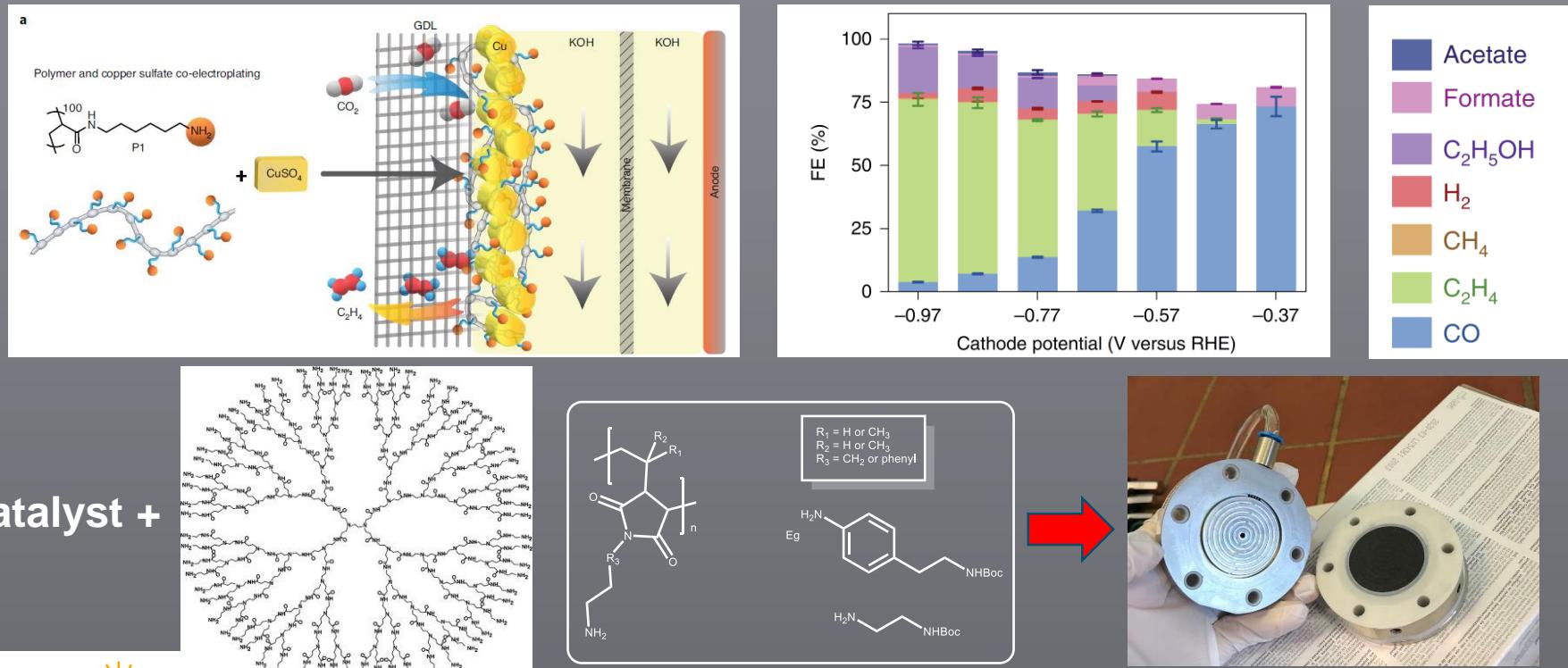


# METAL-POLYMER ELECTRODES

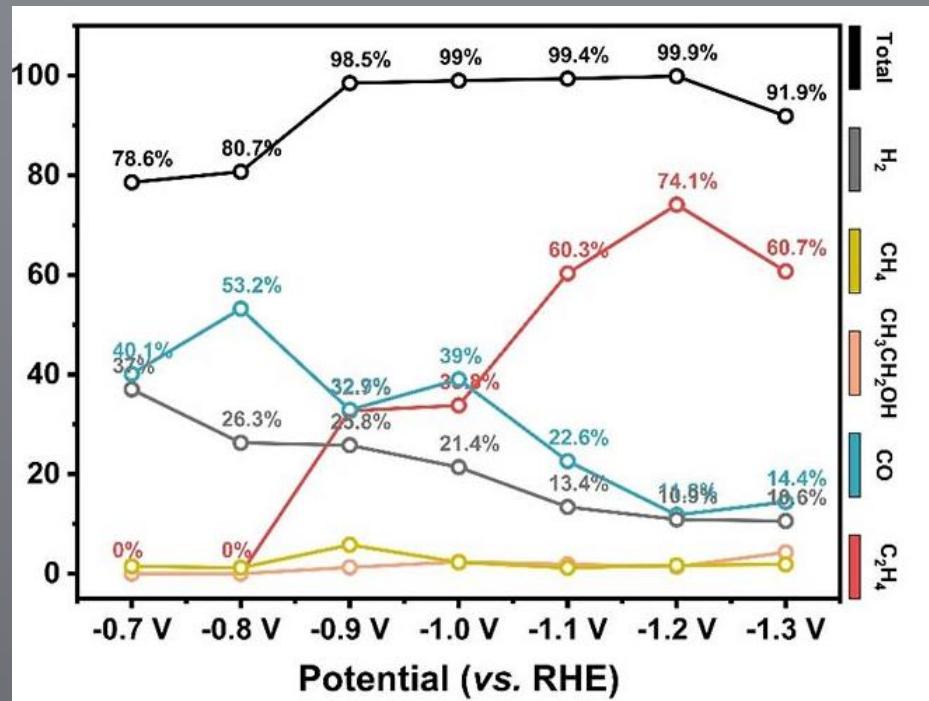
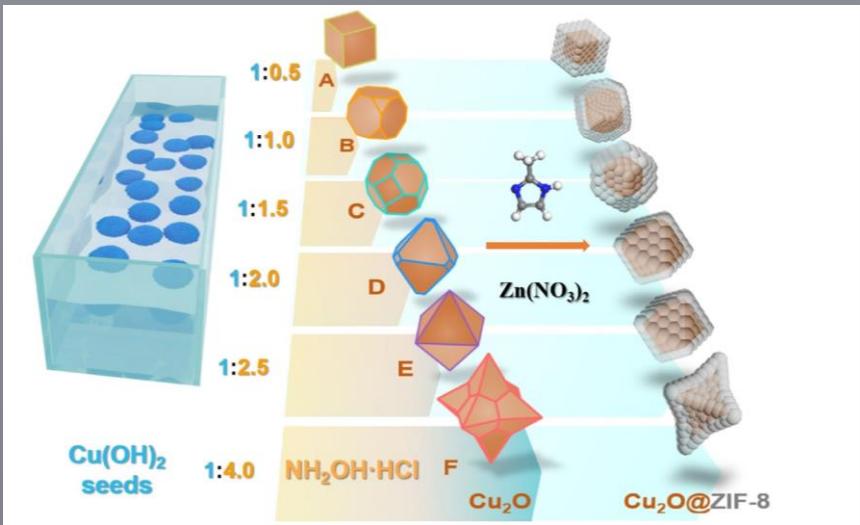
prepared by co-electrodeposition.

Each electrode comprises a carbon-fibre-paper-based gas diffusion layer (GDL) substrate on which the catalyst is electrodeposited.

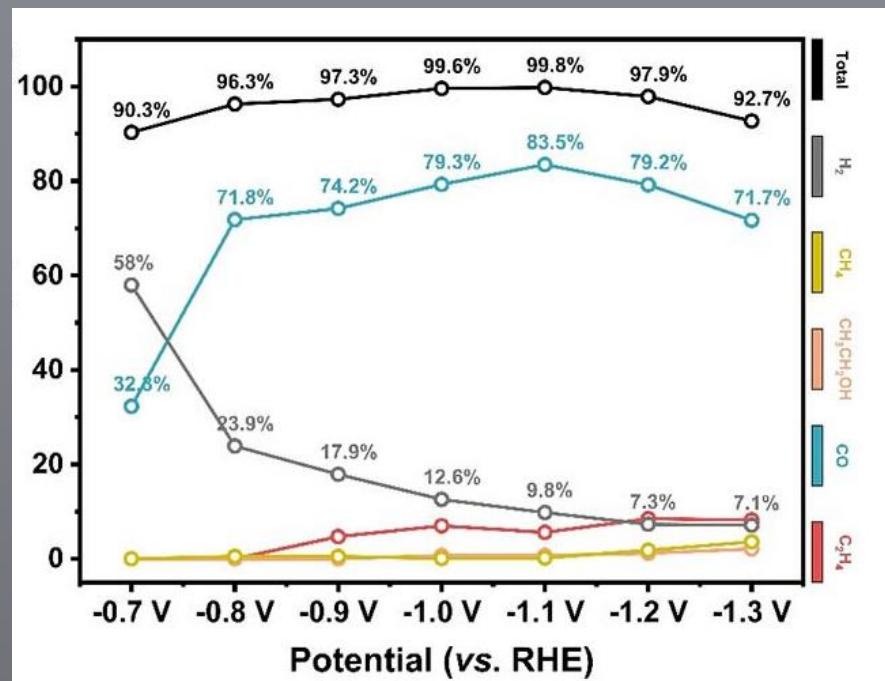
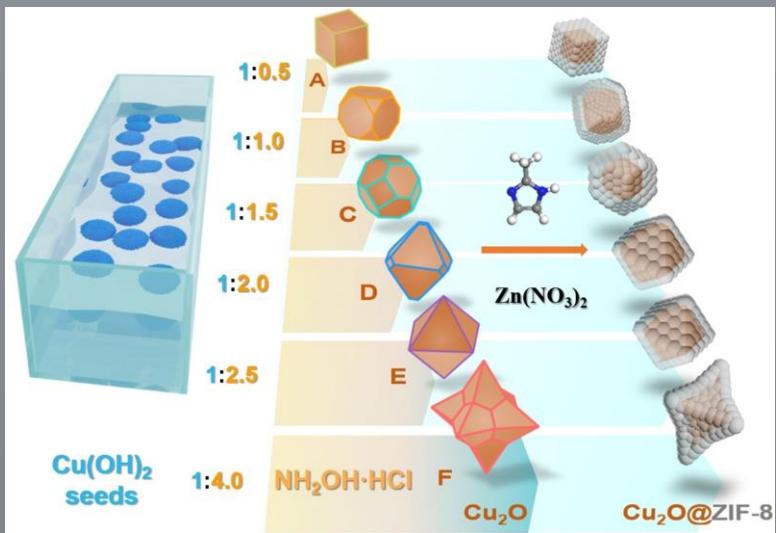
Cu–Pi electrode is prepared in a plating bath containing e.g. 3 mM CuSO<sub>4</sub>, 12 µM Pi, 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>.



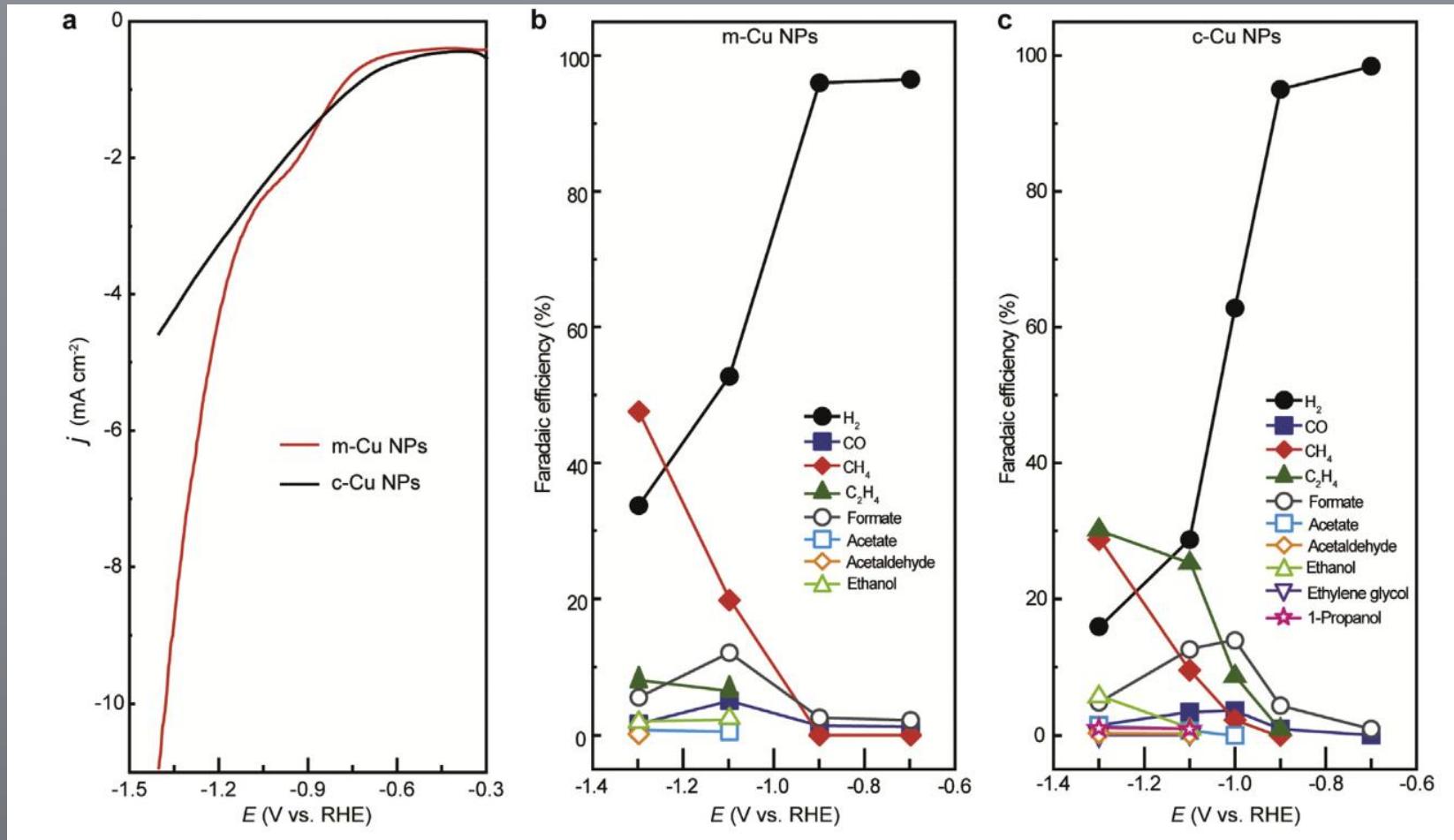
Catalyst +



Electrochemical properties and ECO<sub>2</sub>RR performance of Cu<sub>2</sub>O nanoparticles. e) FE values of the products on F-Cu<sub>2</sub>O.



Electrochemical properties and ECO<sub>2</sub>RR performance of F-Cu<sub>2</sub>O@ZIF-8. FE values of all products for F-Cu<sub>2</sub>O@ZIF-8.

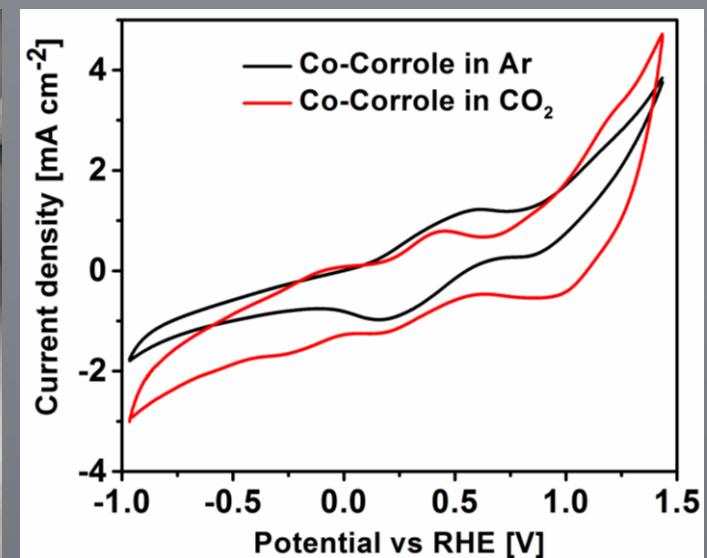
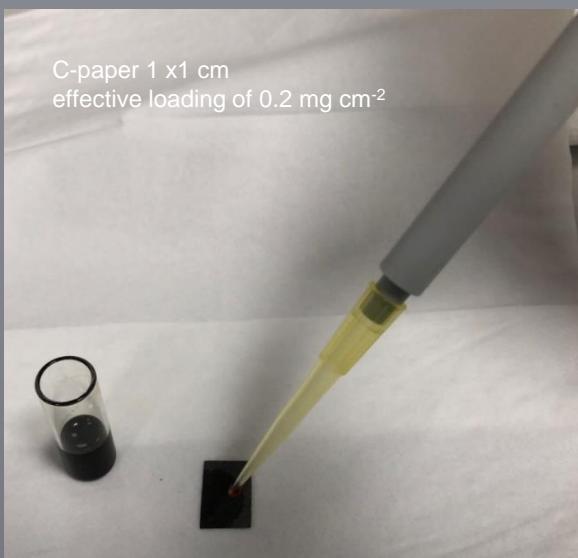
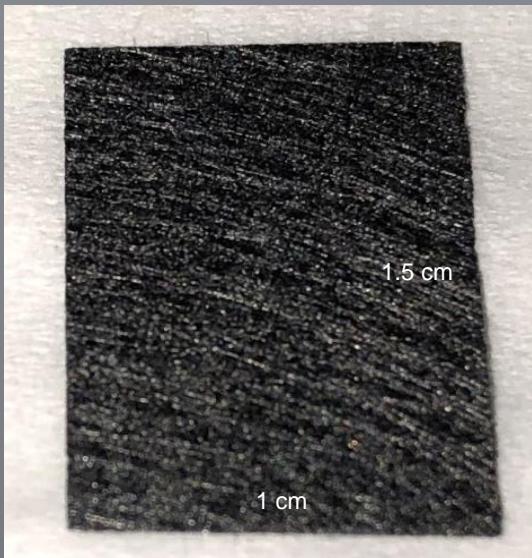


Electrochemical activities of m-Cu NP and c-Cu NP (a) LSV curves of c-Cu and m-Cu nanoparticles. (b) Faradaic efficiencies (FE) of the m-Cu NP, and (c) FE of c-Cu NP electrode for different products at the applied  $V$ .

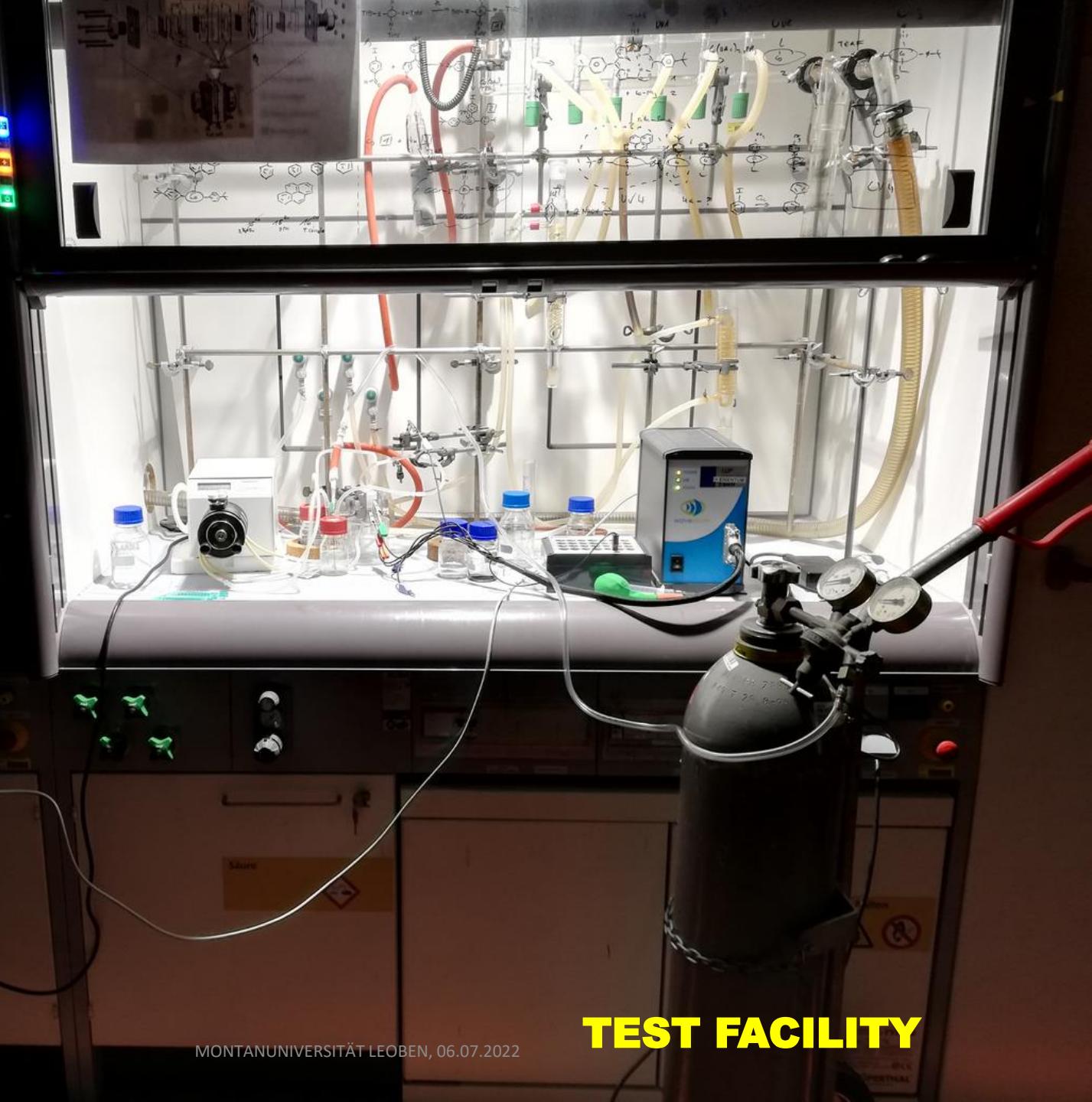
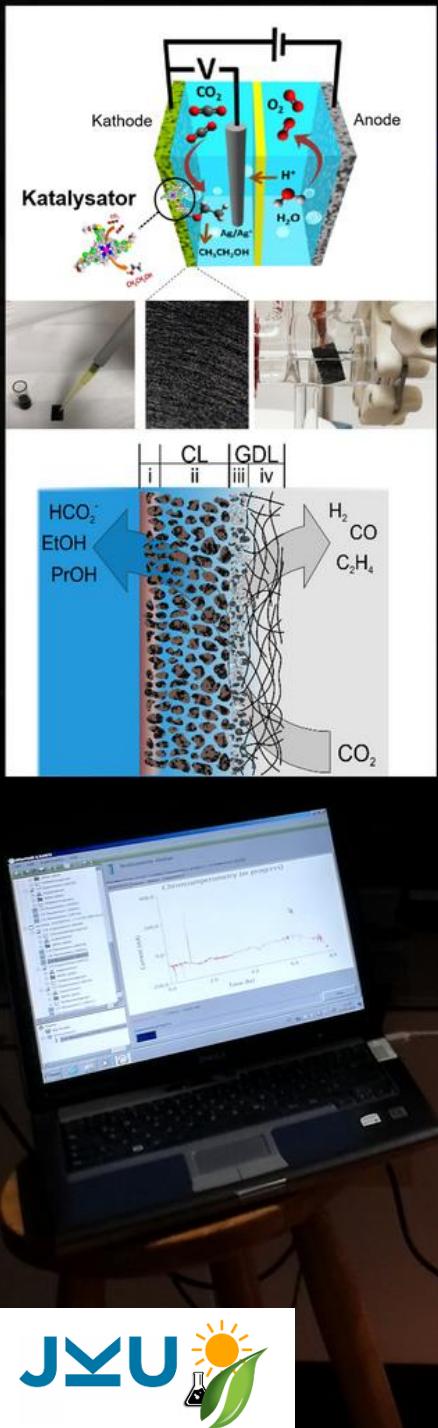


# HETEROGENEOUS CO<sub>2</sub> ELECTROREDUCTION

- Preparation of the working electrode: drop coating



Co-Corrole modified carbon paper/ Ag/AgCl/ Pt, 0.1 M NaClO<sub>4</sub>,  
phosphate buffer, pH=6, 100 mV s<sup>-1</sup>

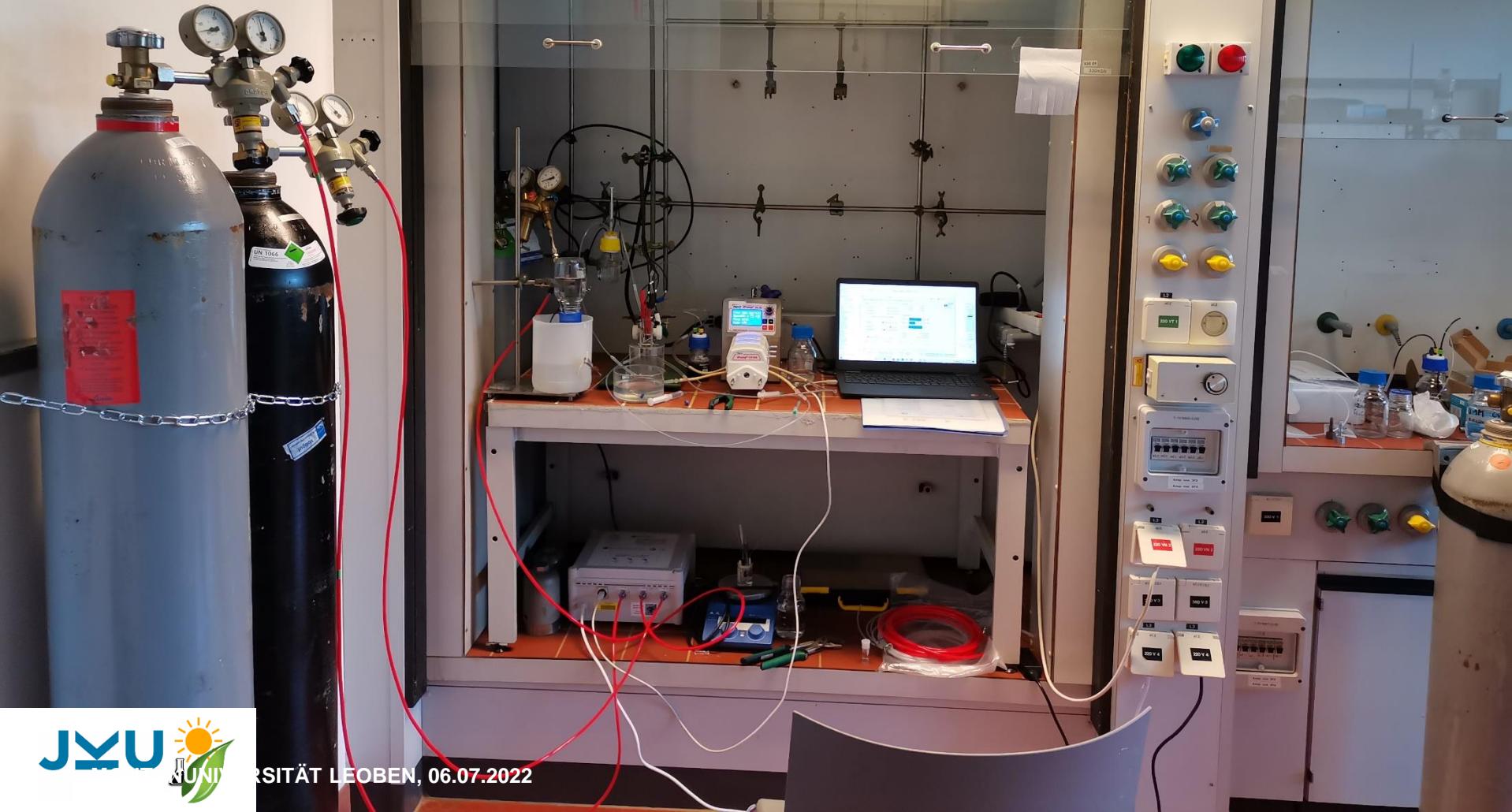


**TEST FACILITY**

MONTANUNIVERSITÄT LEOBEN, 06.07.2022

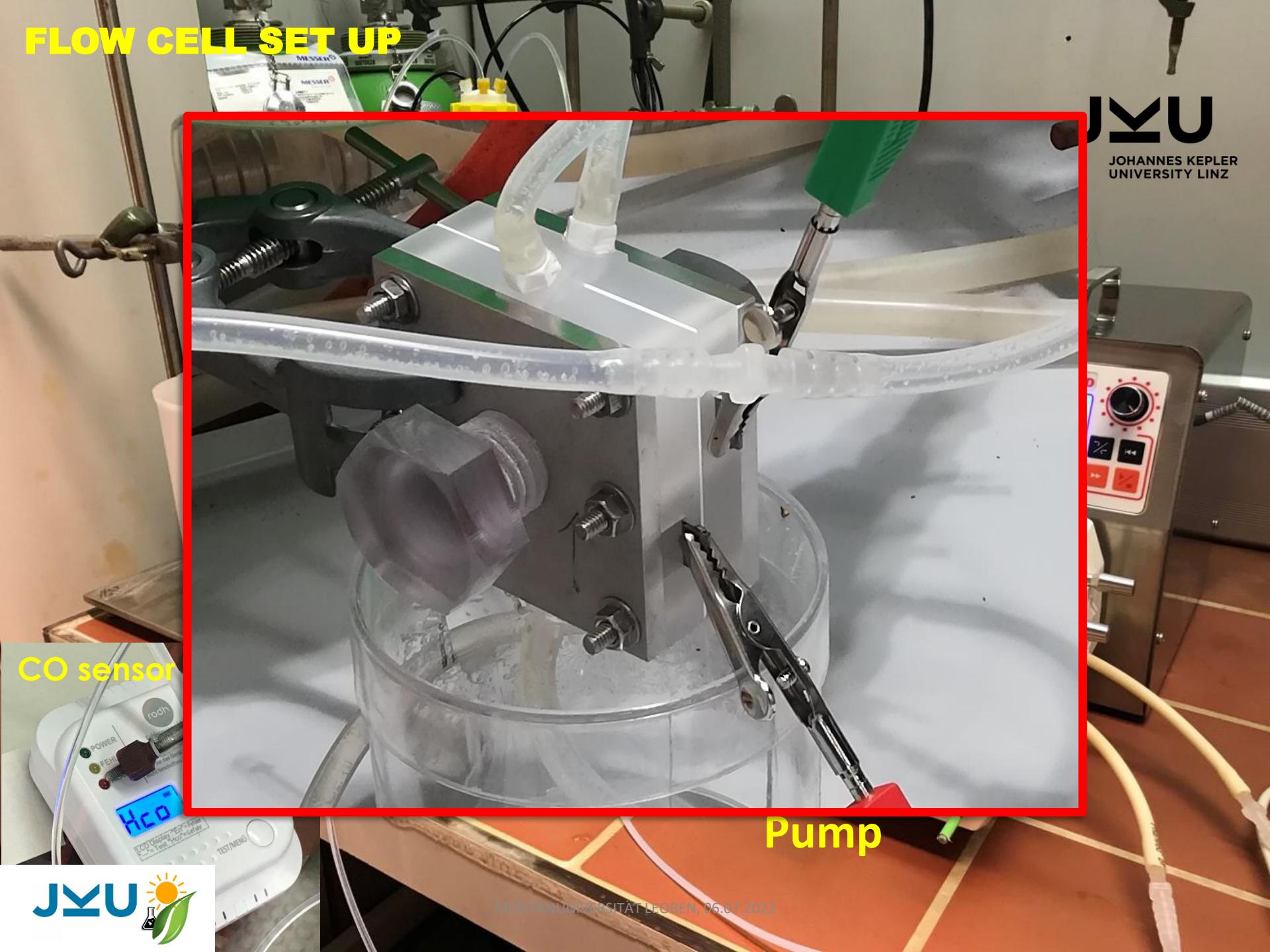
# TEST FACILITY

**JKU**  
JOHANNES KEPLER  
UNIVERSITY LINZ



# FLOW CELL SET UP

**JKU**  
JOHANNES KEPLER  
UNIVERSITY LINZ

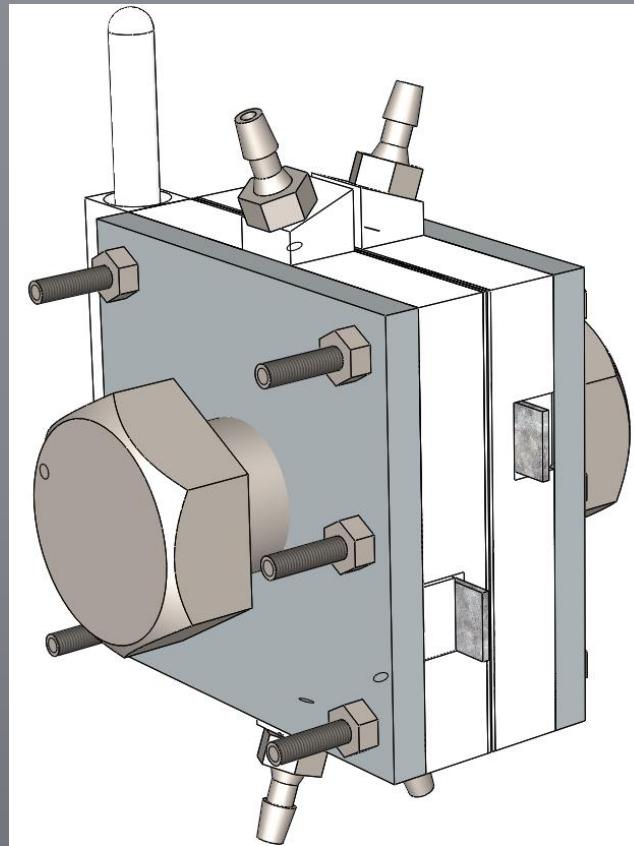


CO sensor

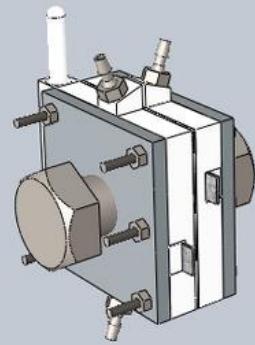
Pump



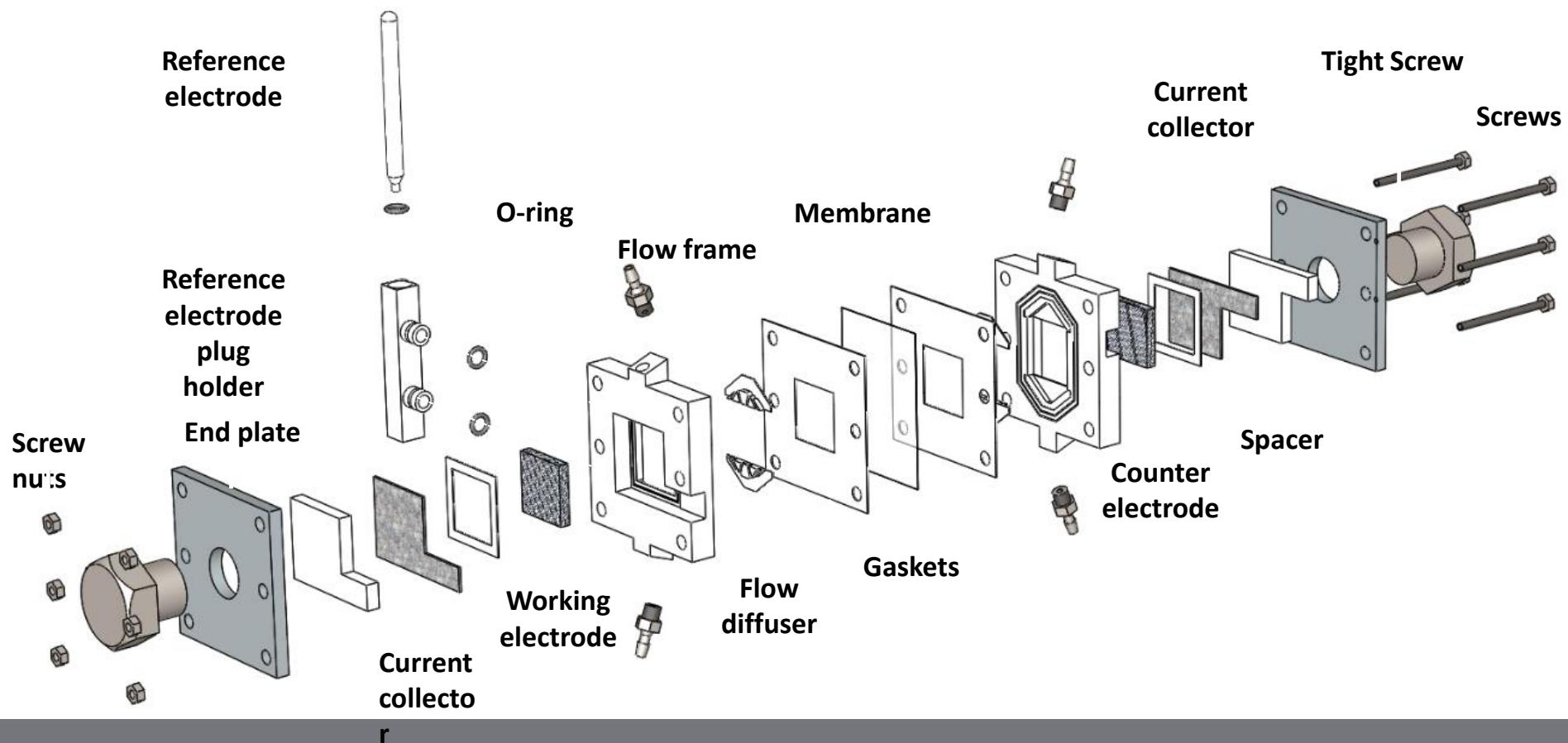
## **OPTION 1: FLOW CELL**



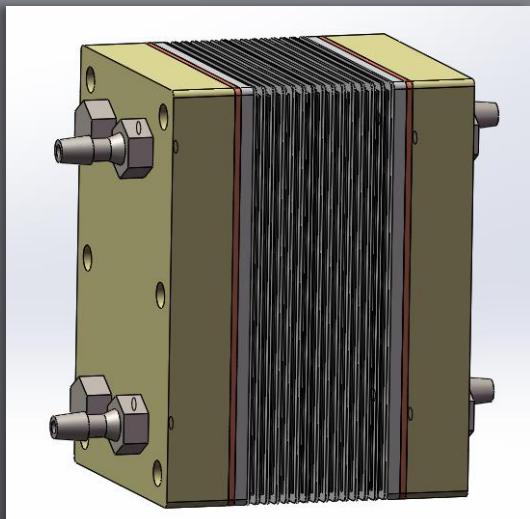
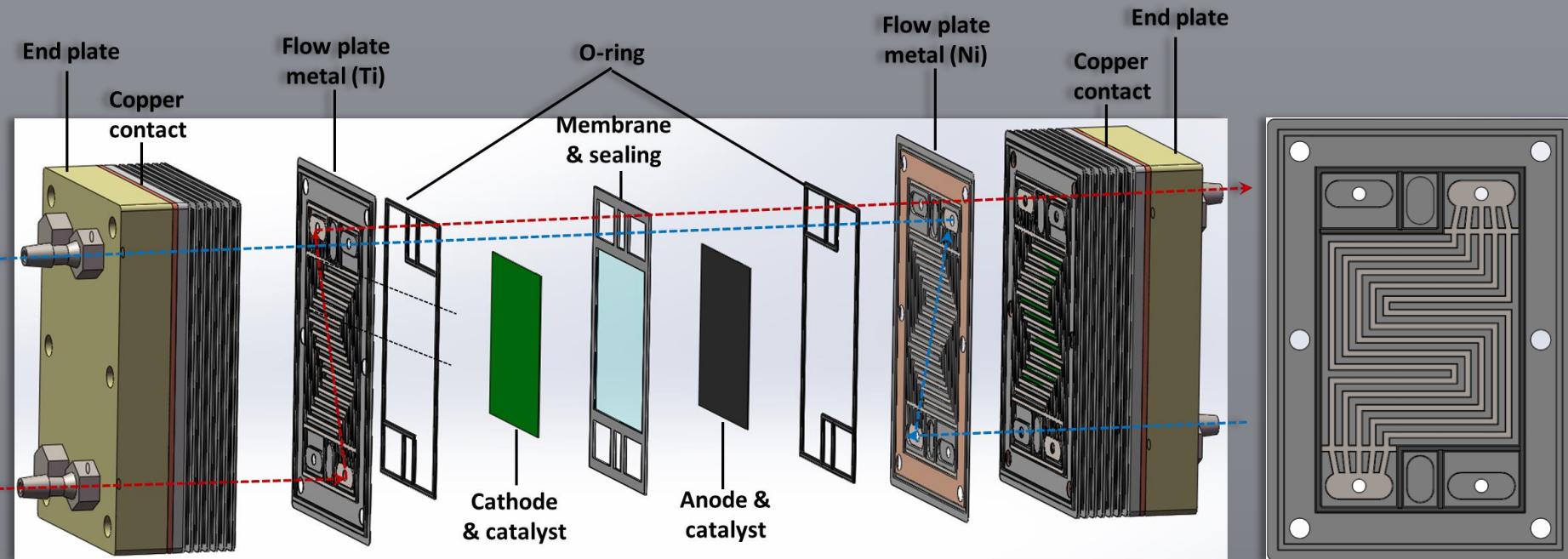
## **OPTION 1: FLOW CELL**



## **OPTION 1: FLOW CELL**



# CELL STACK TO INCREASE EFFICIENCY

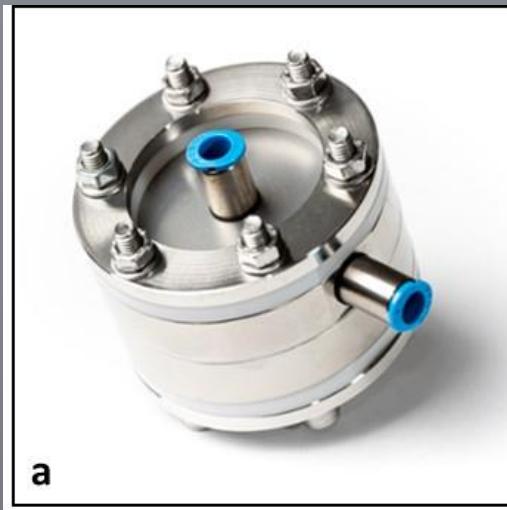


MONTANUNIVERSITÄT LEOBEN, 06.07.2022  
Full cell stack

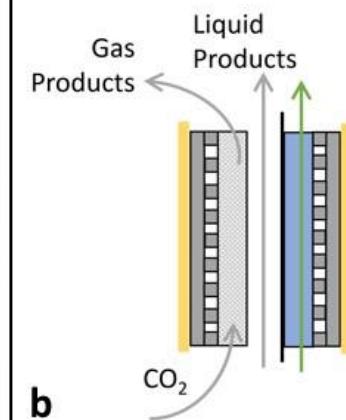


## OPTION 2: ZERO-GAP CELL

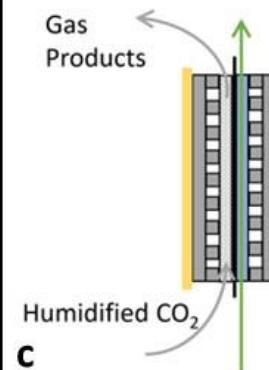
### ELECTROCATALYTIC REDUCTION OF HUMIDIFIED CO<sub>2</sub> GAS



Three components cell with GDL:



Two components cell with MEA  
(membrane electrode assembly):



## ANALYTICS: NMR SPECTROSCOPY OF LIQUID SAMPLES

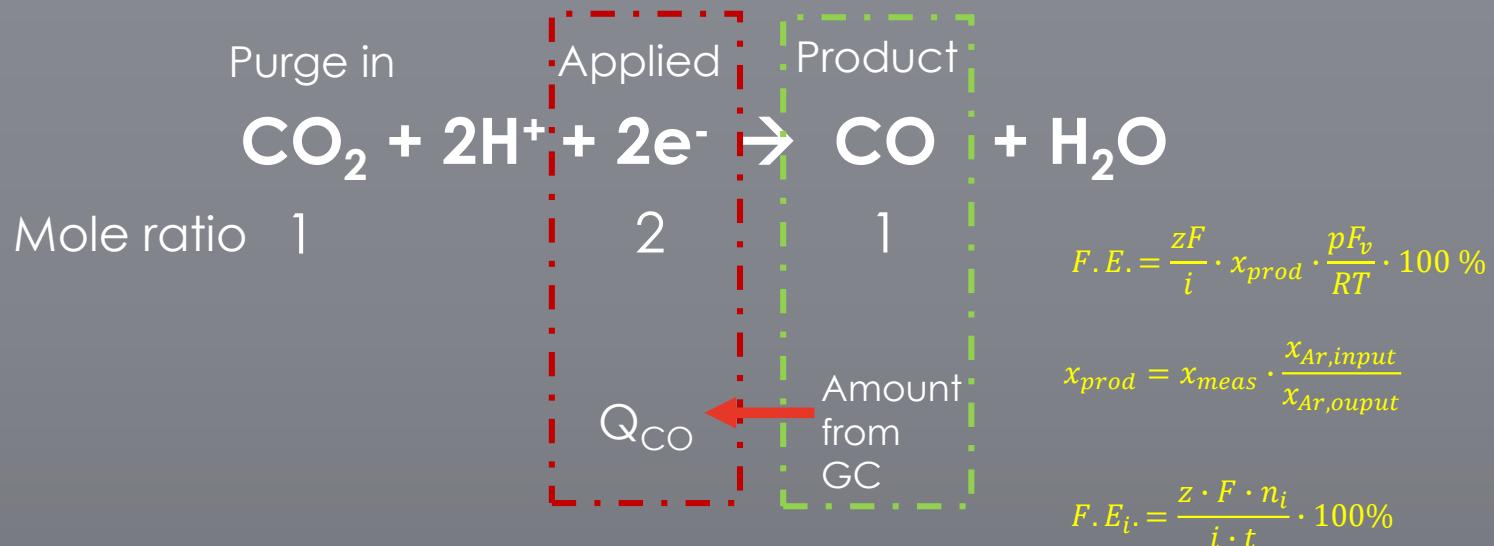


# ANALYTICS: GASCHROMATOGRAPHY OF GASEOUS SAMPLES



# FARADAIC EFFICIENCY (FE) CALCULATION

Faraday efficiency (also called faradaic efficiency, faradaic yield, coulombic efficiency or current efficiency) describes the efficiency with which charge (electrons) are transferred in a system facilitating an electrochemical reaction.

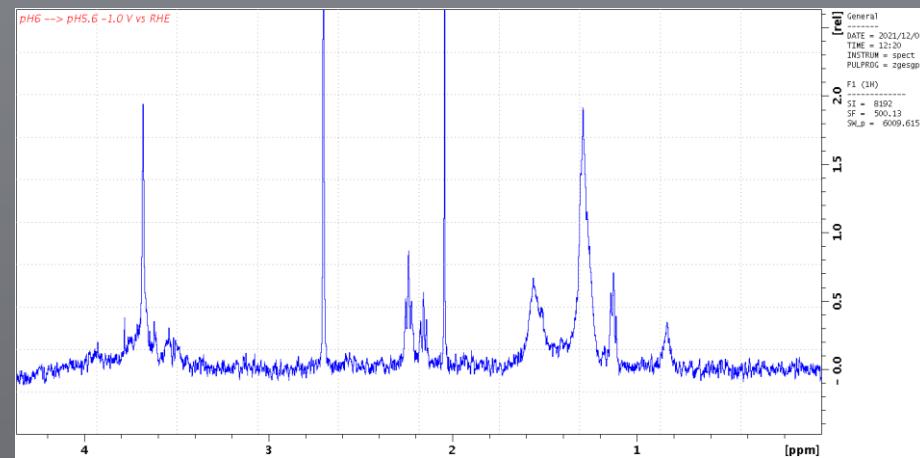
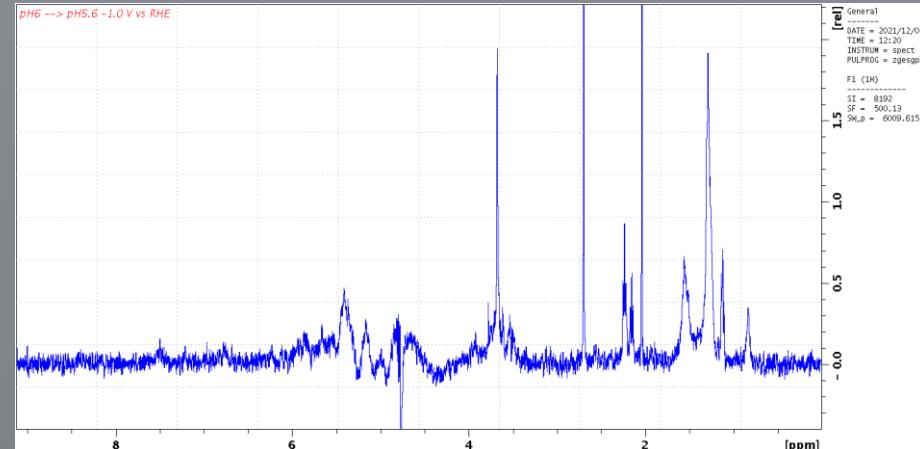
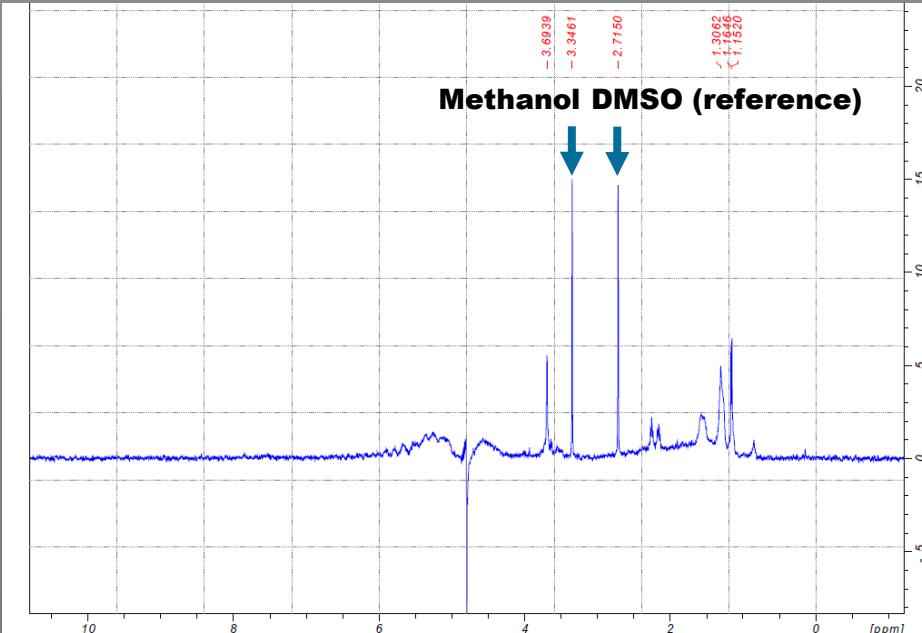


$Q_{total}$ : total electric quantity (C)  
I: applied current (A)  
t: time (s)

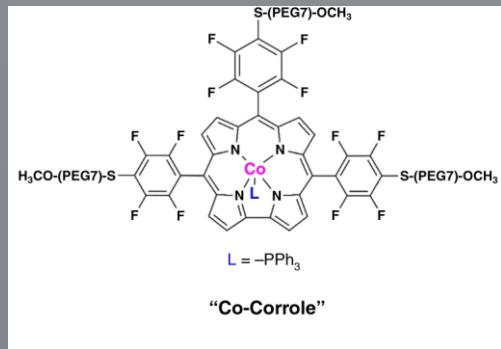
$FE_{CO}$ : faradaic efficiency of CO  
 $Q_{CO}$ : CO consumed electric quantity

# **<sup>1</sup>H NMR SPECTRUM OF LIQUID PRODUCTS:**

**4 HOURS ELECTROCATALYSIS**



# RESULTS: COBALT CORROLE



**nature communications**

Explore content ▾ About the journal ▾ Publish with us ▾

nature | nature communications | articles | article

Article | Open Access | Published: 27 August 2019

**Molecular cobalt corrole complex for the heterogeneous electrocatalytic reduction of carbon dioxide**

Sabrina Gonglach, Shounik Paul, Michael Haas, Felix Pillwein, Sreekumar S. Sreeith, Soumitra Barman, Ratnado De, Stefan Müllegger, Philipp Gerschel, Ulf-Peter Apfel, Halime Coskun, Abdalaziz Aljabour, Philipp Stadler, Wolfgang Schöfberger<sup>✉</sup> & Soumyajit Roy<sup>✉</sup>

*Nature Communications* 10, Article number: 3864 (2019) | [cite this article](#)

12k Accesses | 37 Citations | 43 Altmetric | Metrics

**Abstract**

Electrochemical conversion of  $CO_2$  to alcohols is one of the most challenging methods of conversion and storage of electrical energy in the form of high-energy fuels. The challenge lies in the catalyst design to enable its real-life implementation. Herein, we demonstrate the synthesis and characterization of a cobalt(III) triphenylphosphine corrole complex, which contains three polyethylene glycol residues attached at the meso-phenyl groups. Electron-donation and therefore reduction of the cobalt from cobalt(III) to cobalt(II) is accompanied by removal of the axial ligand, thus resulting in a square-planar cobalt(II) complex. The cobalt(II) as an electron-rich supernucleophilic  $d^8$ -configured metal centre, where two electrons occupy and fill up the antibonding  $d_{z^2}$  orbital. This orbital possesses high affinity towards electrophiles, allowing for such electronically configured metals reactions with carbon dioxide. Herein, we report the potential dependent heterogeneous electroreduction of  $CO_2$  to ethanol or methanol of an immobilized cobalt A<sub>3</sub>-corrole catalyst system. In moderately acidic aqueous medium ( $pH \approx 6.0$ ), the cobalt corrole modified carbon paper electrode exhibits a Faradaic Efficiency (FE)% of 48% towards ethanol production.

From: Molecular cobalt corrole complex for the heterogeneous electrocatalytic reduction of carbon dioxide

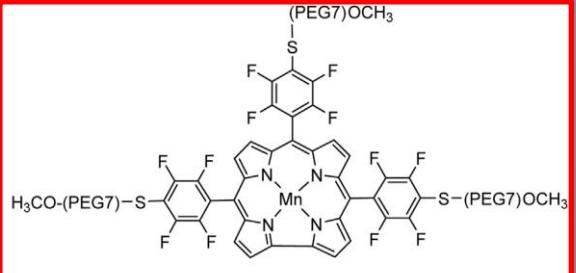
Potential V vs. RHE	Faradaic Efficiency of each reduced products on Co-corrole-carbon paper electrode after 5 h of controlled potential electrolysis at the mentioned potentials <sup>a</sup>							Total FE%	Charge passed (Coulomb)
	CH <sub>3</sub> CH <sub>2</sub> OH		CH <sub>3</sub> OH		HCOO <sup>-</sup>		CH <sub>3</sub> COO <sup>-</sup>		
	FE%	FE%	FE%	FE%	FE%	FE%	(CHO) <sub>2</sub>		
-0.515	—	59	12	—	17	10	—	98	35
-0.585	5	52	10	—	22	6	3	98	36
-0.650	10	45	8	1	27	5	2	98	39
-0.700	23	32	6	4	27	5	2	99	40
-0.730	39	23	5	5	20	3	3	98	42
-0.770	44	14	4	8	26	2	1	99	43
-0.800	48	8	1	10	28	1	3	99	44
-0.855	47	5	—	12	33	—	2	99	47
-0.905	45	3	—	12	37	—	1	98	50
-0.955	47	2	—	13	36	—	—	98	53

<sup>a</sup>In 0.1 M NaClO<sub>4</sub> (0.1 M pH = 6.0 phosphate buffer)

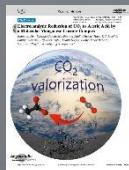
S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreeith, S. Barman, R. De, S. Müllegger, P. Gerschel, U.-P. Apfel, H. Coskun, A. Aljabour, P. Stadler, W. Schöfberger\*, and S. Roy\*, *Nat. Commun.* 2019, 3864.

<https://doi.org/10.1038/s41467-019-11868-5>

# RESULTS: MANGANESE CORROLE



Potential vs Ag/AgCl	FE % of each CO <sub>2</sub> reduced products at different potential with Mn-Cor-CP electrode after 5h of electrolysis								Total FE%	Charge passed (Coulomb)		
	Acetate		Methanol		CO		H <sub>2</sub>			average	SD	
	FE%	SD	FE%	SD	FE%	SD	FE%	SD				
-1.1	40	4.3	23	3	31	5	-	-	94	6.3	0.2	
-1.2	55	4	20	3	20	4			95	9	0.25	
-1.25	63	3.75	16	3.5	-	-	18	4.5	97	14.4	0.3	
-1.3	60	3.55	19	2.5	-	-	19	5	98	17.1	0.5	
-1.4	61	4	9	3	-	-	25	6	95	19.8	0.8	



R. De, S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreekumar, P. Gerschel, U.-P. Apfel, H. Vuong, J. Rabeah, S. Roy\*, and W. Schöfberger\*, *Angew. Chem.* 2020, 59, 26, 10527-10534.

<https://doi.org/10.1002/anie.202000601>

# RESULTS: Cu AND Ag BIANS IN ZERO-GAP CELLS

- Electrode Fabrication



## 1) Ink

10  $\mu\text{L ml}^{-1}$  Nafion117

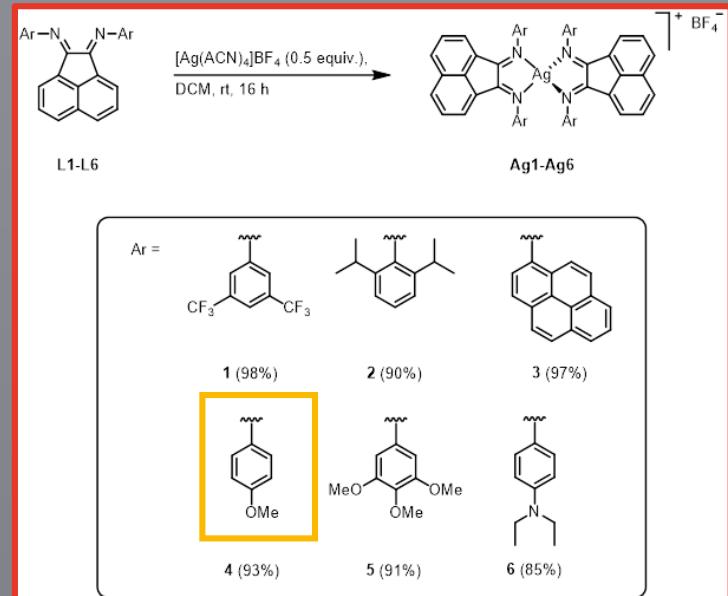
2 mg  $\text{ml}^{-1}$  BIAN Catalyst

1mg  $\text{ml}^{-1}$  ENSACO 250G

## 2) Processing

- Ultrasonication of 30 min
- Constant stirring of solution

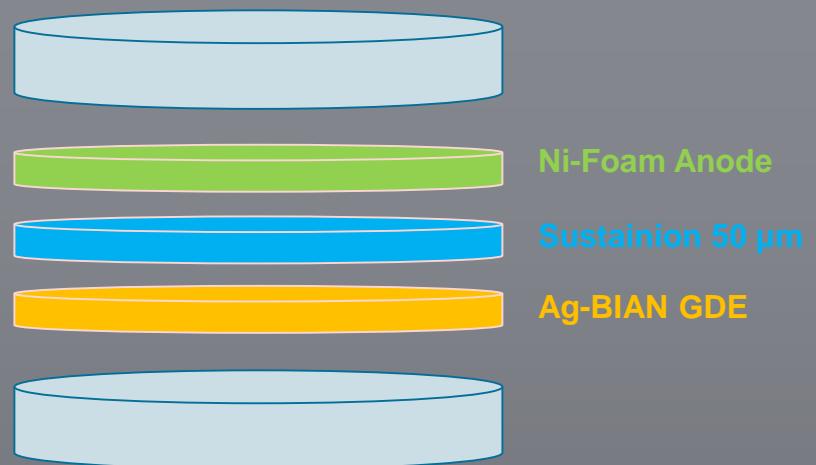
## 3) Spray coat



# Ag-BIANS in Zero-gap Cells

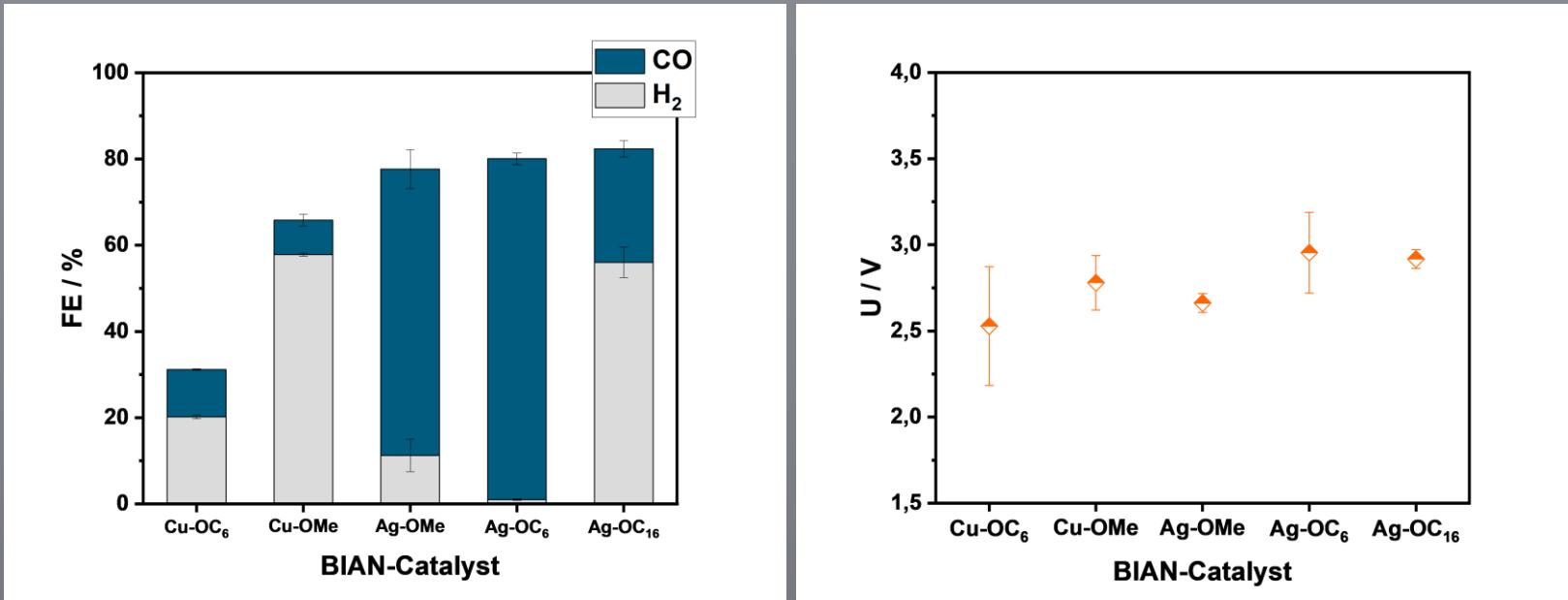
- Cell

- Conditions
- All RT – 100% wetted CO<sub>2</sub>
- 1M KOH Anolyte
- BIAN GDE – BIAN loading of 0.4 mg cm<sup>-2</sup>
- 100 mA cm<sup>-2</sup>



# BIANs in Zero-gap Cells

- BIANs in Zero-gap Cells



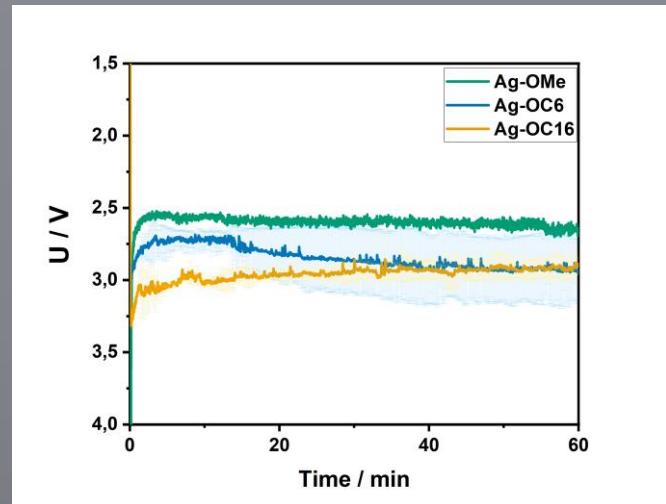
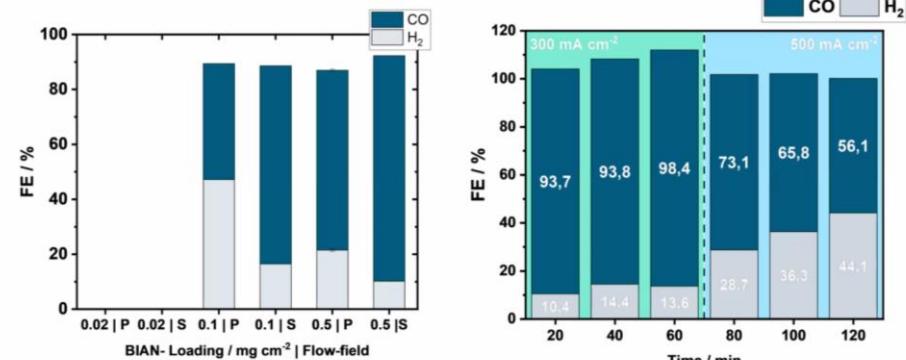
Differences in cell voltage between metal centers not so significant

Conditions: Zero Gap Electrode | Ag-BIAN| 0.4 mg cm<sup>-2</sup> | 100 mA cm<sup>-2</sup> | 1h | RT | 1 M KOH

# BIANs in Zero-gap Cells

## Ag-BIAN GDEs

Implementation into industrial conditions – Parameter variations



- Electrode & Material properties affect the GDE performance
- BIAN-Electrodes show stable cell voltage during electrolysis

Conditions: Zero Gap Electrode | Ag-BIAN| 0.1-0.4  $\text{mg cm}^{-2}$  | 100 - 500  $\text{mA cm}^{-2}$  | 1-72 hrs | RT | 1 M KOH

# **EXPERIMENTS WITH GAS MIXTURE (GM)**

## **TO MIMIC FLUE-GAS CONVERSION**

<b>Gas composition</b>	<b>GM</b>	<b>Contents (Vol.%)</b>
N <sub>2</sub>	71.8	
O <sub>2</sub>	11	
CO	0.11	
NO <sub>x</sub>	0.035	
SO <sub>2</sub>	0.001	
CO <sub>2</sub> /N <sub>2</sub> additional	17	

# ELECTROLYSIS IN CO<sub>2</sub> GAS MIXTURE

## 4 HOURS ELECTROCATALYSIS

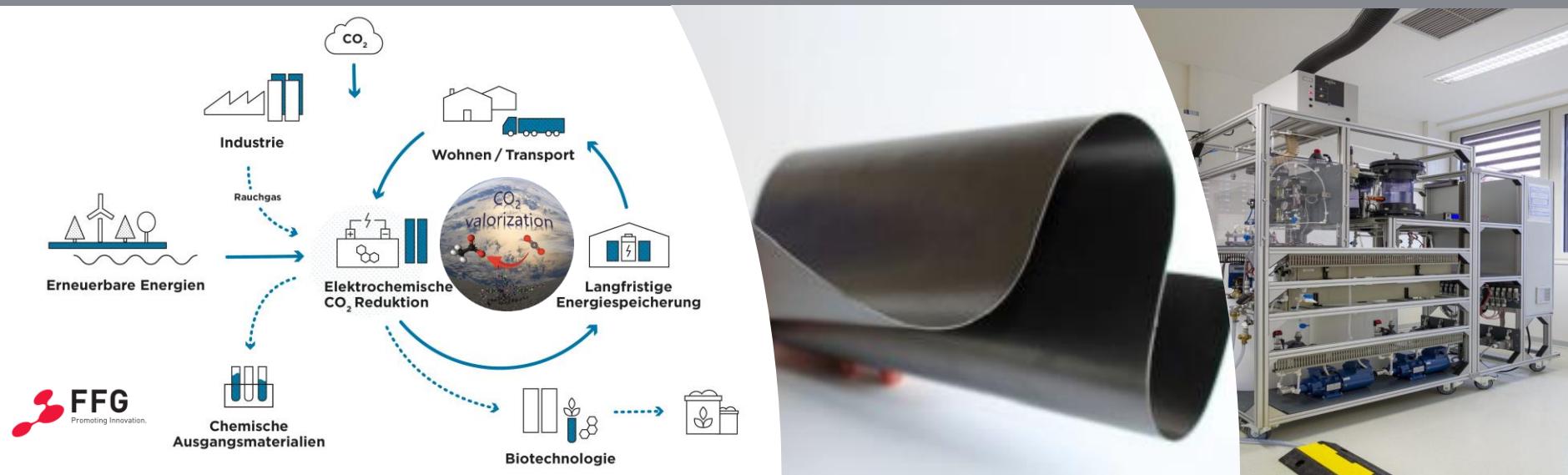
Experimental Parameters	H <sub>2</sub> FE %	CO FE %	Liquid FE %	ORR
Cat. CO <sub>2</sub> GM 20 mA 10 mL/min	30	15	-	55
Cat. CO <sub>2</sub> GM 40 mA 10 mL/min	30	60	-	10
Cat. C CO <sub>2</sub> GM 60 mA 100 mL/min	20	45	0.5 (after 4h) methanol	24.5



Syngas production!

# WORK IN PROGRESS

## DEVELOPMENT AND CONSTRUCTION OF A LABORATORY SYSTEM FOR ACTIVATION AND ELECTROCATALYTIC REDUCTION FROM CARBON DIOXIDE TO C<sub>1</sub> AND C<sub>2</sub> PRODUCTS (AKTUROS)



# Team



## Institute of Organic Chemistry

Dr. Sabrina Gonglach

Dr. Luyang Song

DI Dominik Krisch

DI Jessica Michalke

DI Daniel Timelthaler

Dr. Christoph Topf

Dr. Sun He

Assoc. Univ.-Prof. Dr. Wolfgang Schöfberger



# Scientific Collaborations



## Institute of Catalysis, INCA

Univ.-Prof. Dr. Marko Hapke

Dr. Christoph Topf



## Institute of Semiconductor and Solid State Physics

Univ.-Prof. Dr. Stefan Müllgger



Ruhr-University Bochum: Faculty of Chemistry and Biochemistry – Inorganic Chemistry I, Fraunhofer UMSICHT – Oberhausen



## Leibniz Institute of Catalysis

Dr. Jabor Rabaeh

Prof. Dr. Angelika Brückner



University of Natural Resources and Life Sciences, Vienna

Dr. Michael Egermeier



# THANK YOU!

