

# Structural Evolution and Durability of NiFe-based Catalysts in Water Oxidation at High Current Densities

Yuan Sheng<sup>1,2</sup>, Markus Kraft<sup>1,2,3\*</sup>, and Rong Xu<sup>1,2\*</sup>

## Introduction

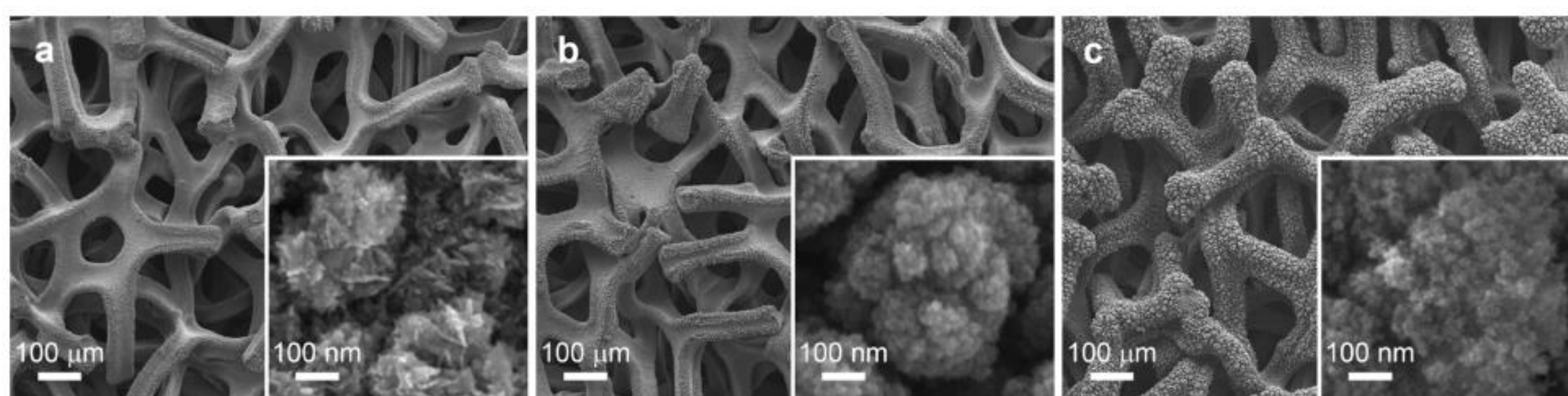
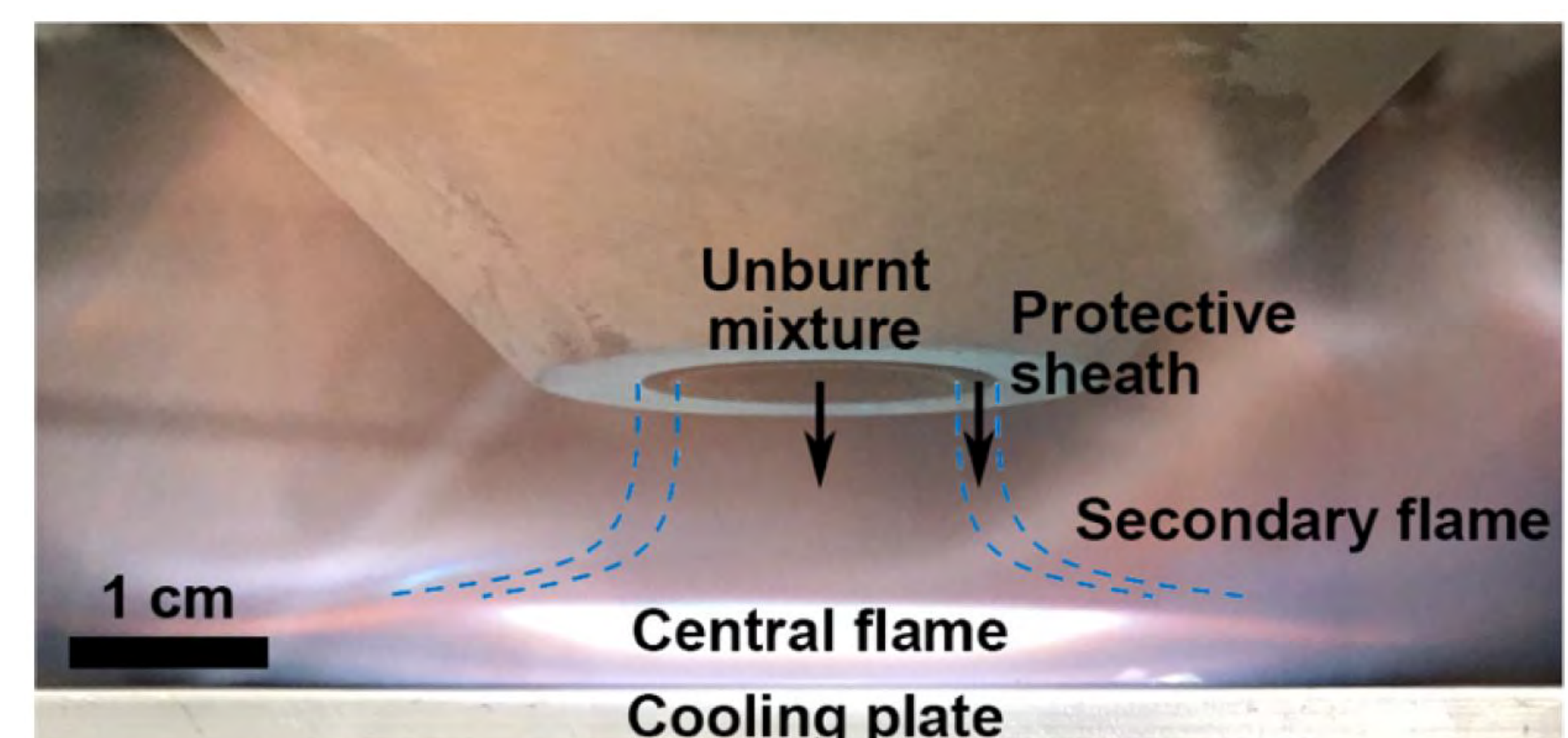
Producing hydrogen through renewable energy-driven water electrolysis is a promising solution for decarbonization, but the slow oxygen evolution process at the anode poses a significant challenge. NiFe-based catalysts are highly active materials for the oxygen evolution reaction. This study introduces the first-ever one-step flame aerosol synthesis of NiFe-P, analyzing compositional and structural changes during high-current water oxidation. It also assesses the electrochemical stability and metal composition of NiFe-LDH films during prolonged electrolysis in highly alkaline conditions at 500 mA/cm<sup>2</sup> and 60°C.

## Durability of NiFe-P Nanoparticle/Carbon Composite Films in Water Oxidation at High Current Densities

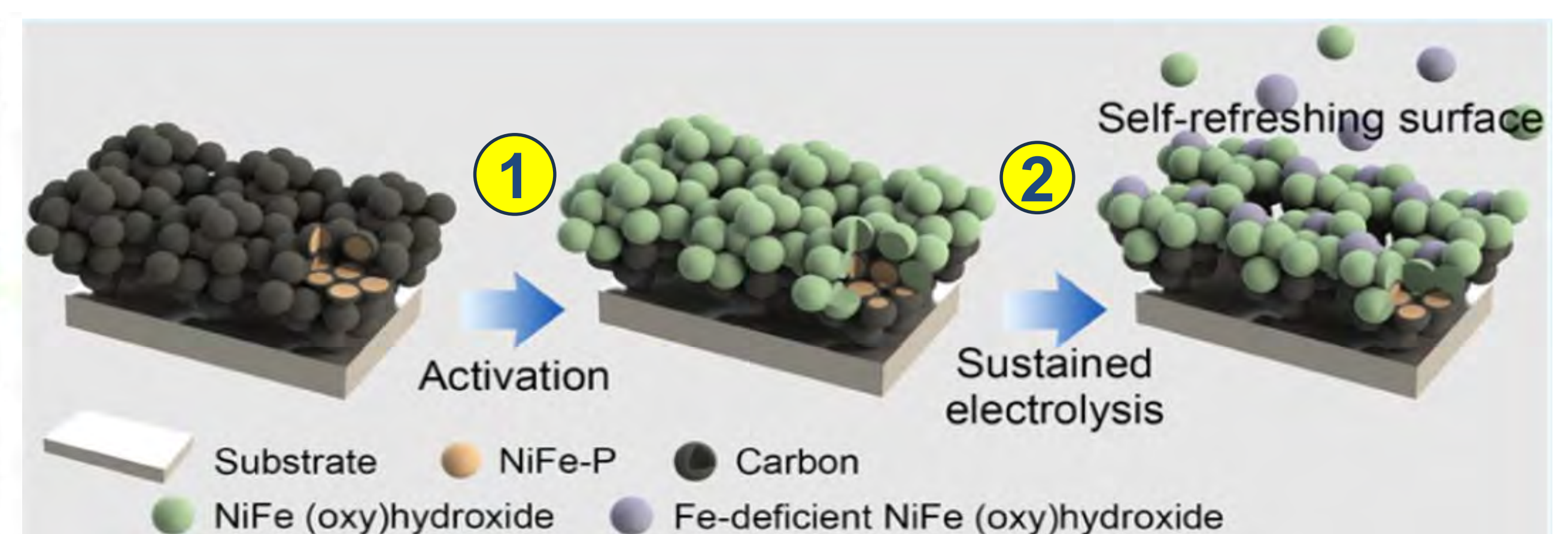
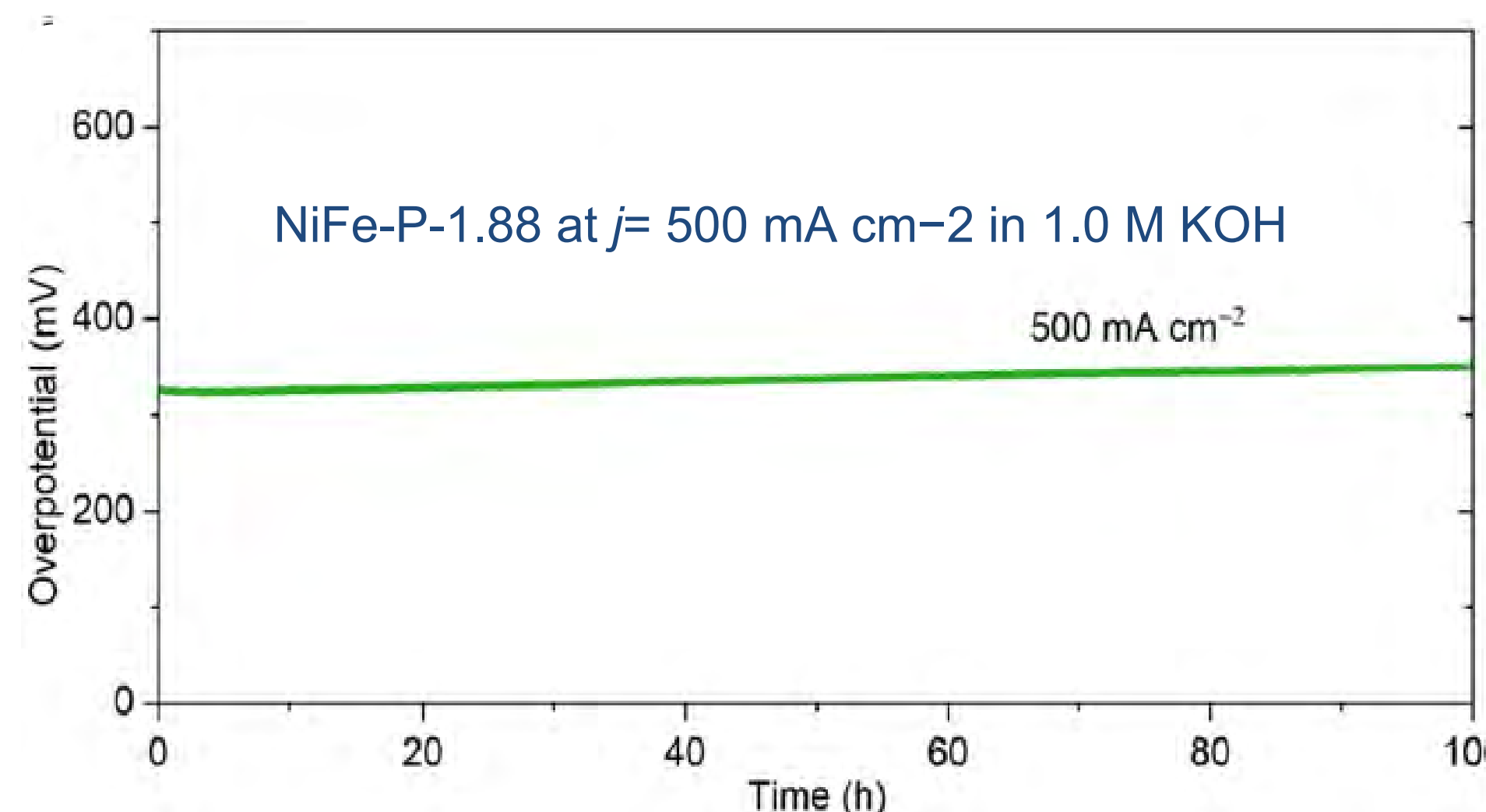
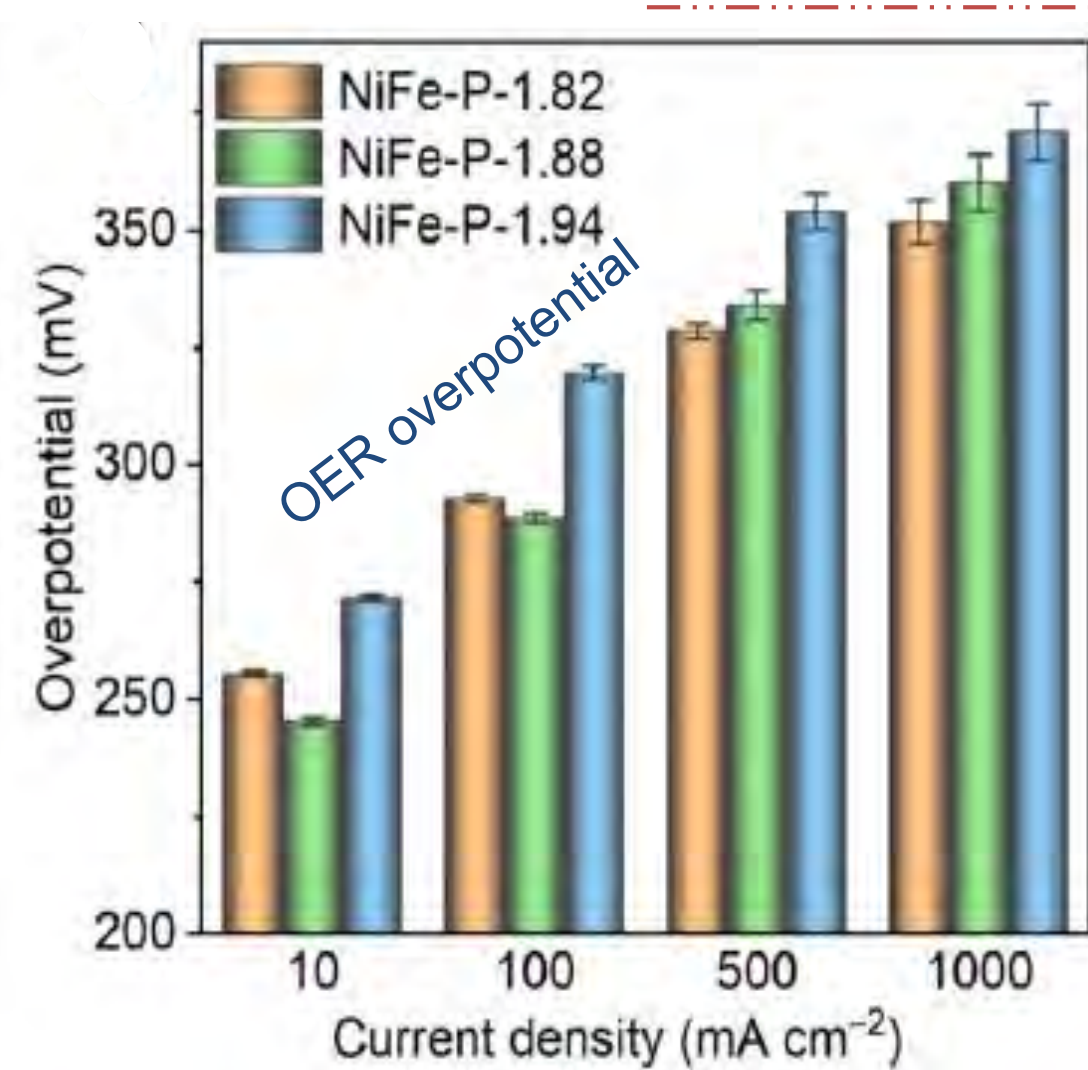
### Electrode synthesis in flames

NiFe-P is prepared by flame aerosol synthesis (FAS). FAS is a process where precursor vapors or microdroplets are fed to a flame, pyrolyzed, and form nanoparticles as an aerosol. Electrodes were synthesized in 10 min by feeding Ni/Fe/P precursor vapors to premixed flame.

Precursors: Nickelocene, Ferrocene, and Triethyl phosphate  
Fuel: C<sub>2</sub>H<sub>4</sub>    Oxidant: O<sub>2</sub>    Temperature: 2200°C



NiFe-P films were synthesized with an equivalence ratio  $\phi$  of a) 1.82, b) 1.88, and c) 1.94. The thickness of the film increases with  $\phi$ , especially from  $\phi = 1.88$  to  $\phi = 1.94$ .



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### Proposed mechanism for long time durability

#### 1 Activation step

- Electrochemical oxidation of carbon, more hydrophilic surface and wetting
- Removal of carbon species and increase in accessible active sites

#### 2 Long term electrolysis step

- In alkaline OER, Fe oxyhydroxides dissolves much faster than Ni oxyhydroxides
- Top layer of particles detach, so that a relatively fresh, Fe-rich Surface is exposed over the course of stability test

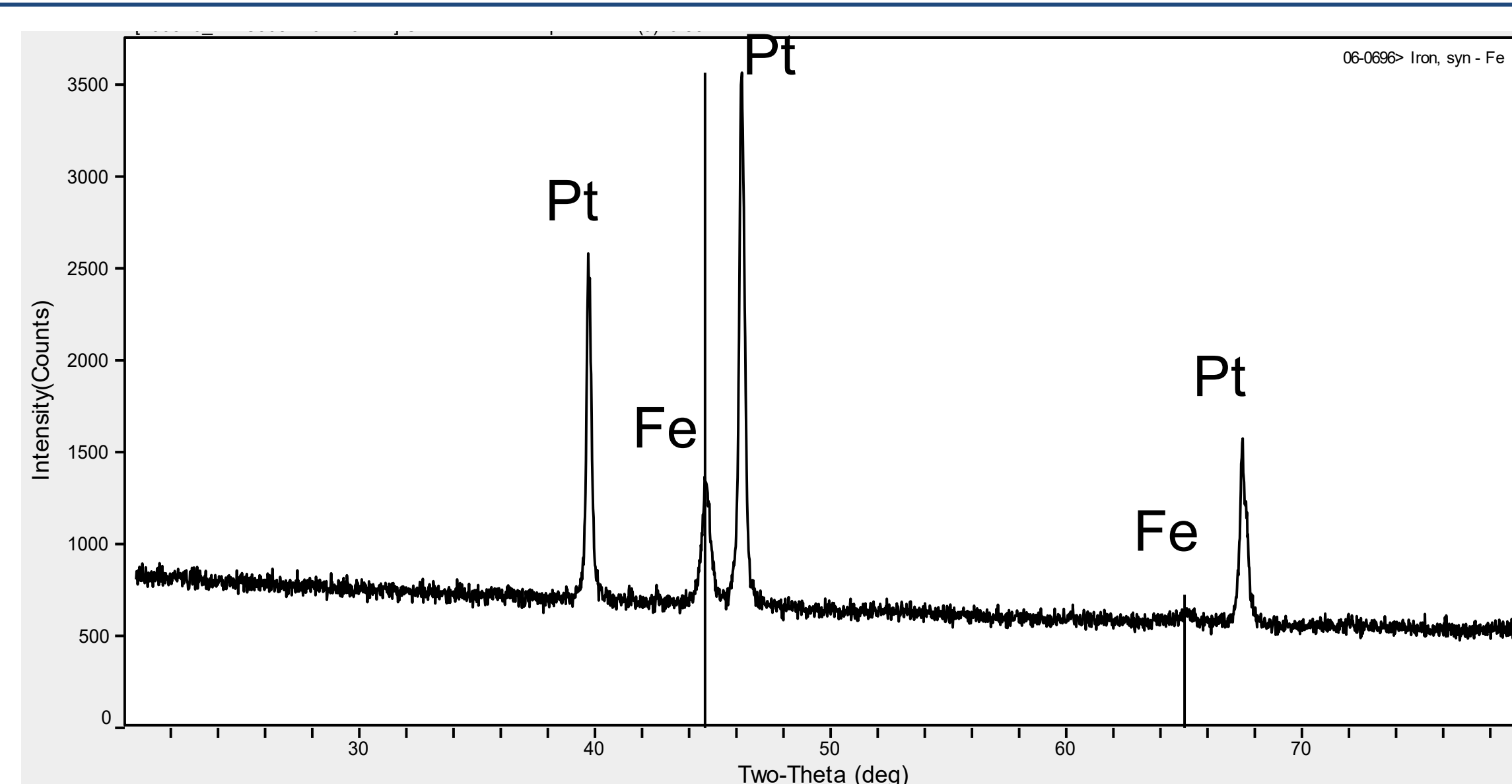
## Enhancing OER stability of NiFe LDH in industrial conditions

### ELECTRODE SYNTHESIS

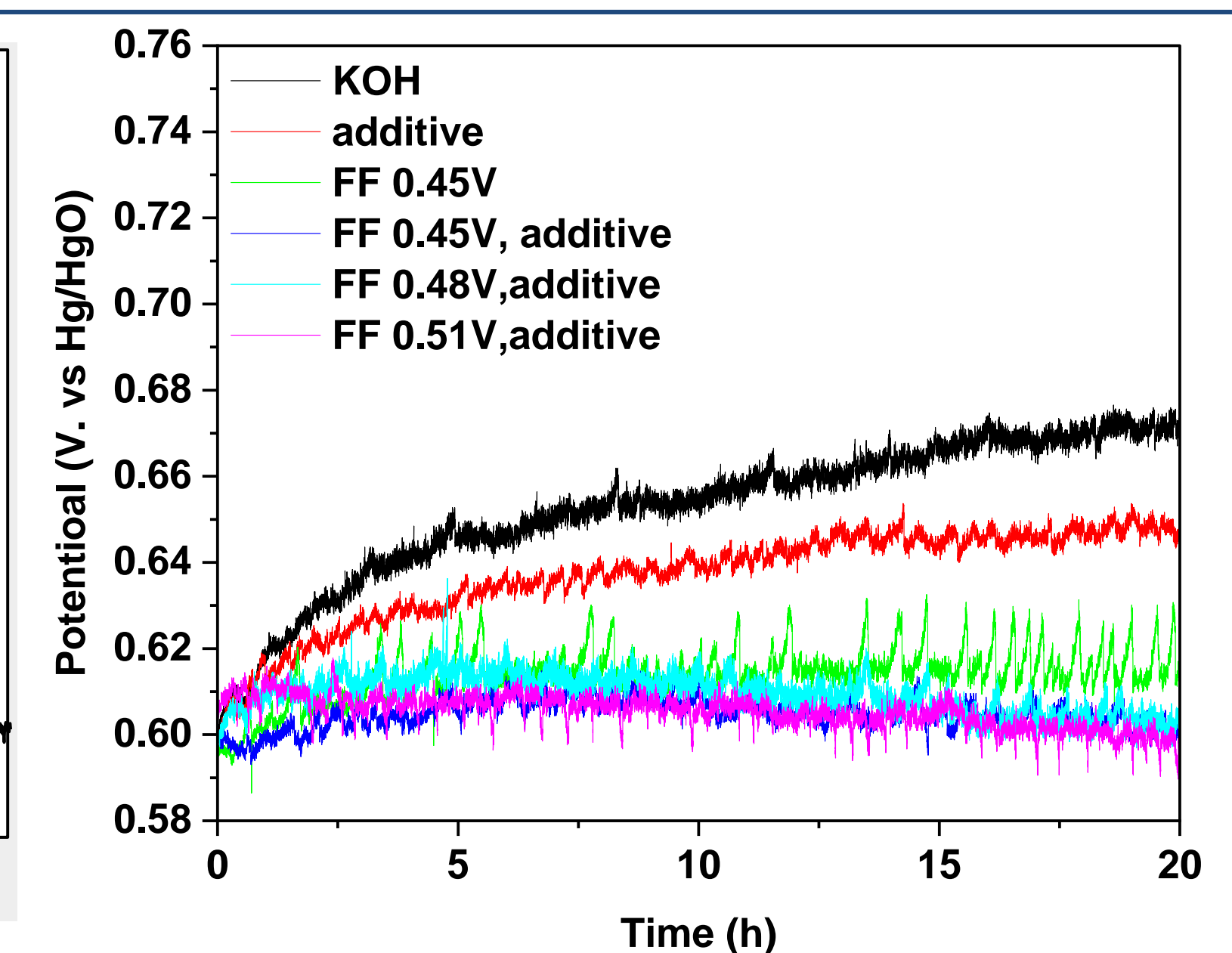
NiFe LDH prepared by cathodic electrodeposition on Ni foam.

Electrolyte: 3mM Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 3mM Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O.

Constant potential: -1.0V (versus Ag/AgCl)



XRD of the spent cathode with FF 0.45 V



OER stability @ 0.5 A/cm<sup>2</sup>, 6 M KOH, 60 °C

- Two distinct diffraction peaks situated at 44.8° and 65° are attributed to the Iron deposition on the surface of Pt.
- OER stability outcomes of NiFe-LDH demonstrate the improved stability of the catalyst resulting from the presence of the additives.

TD in consideration

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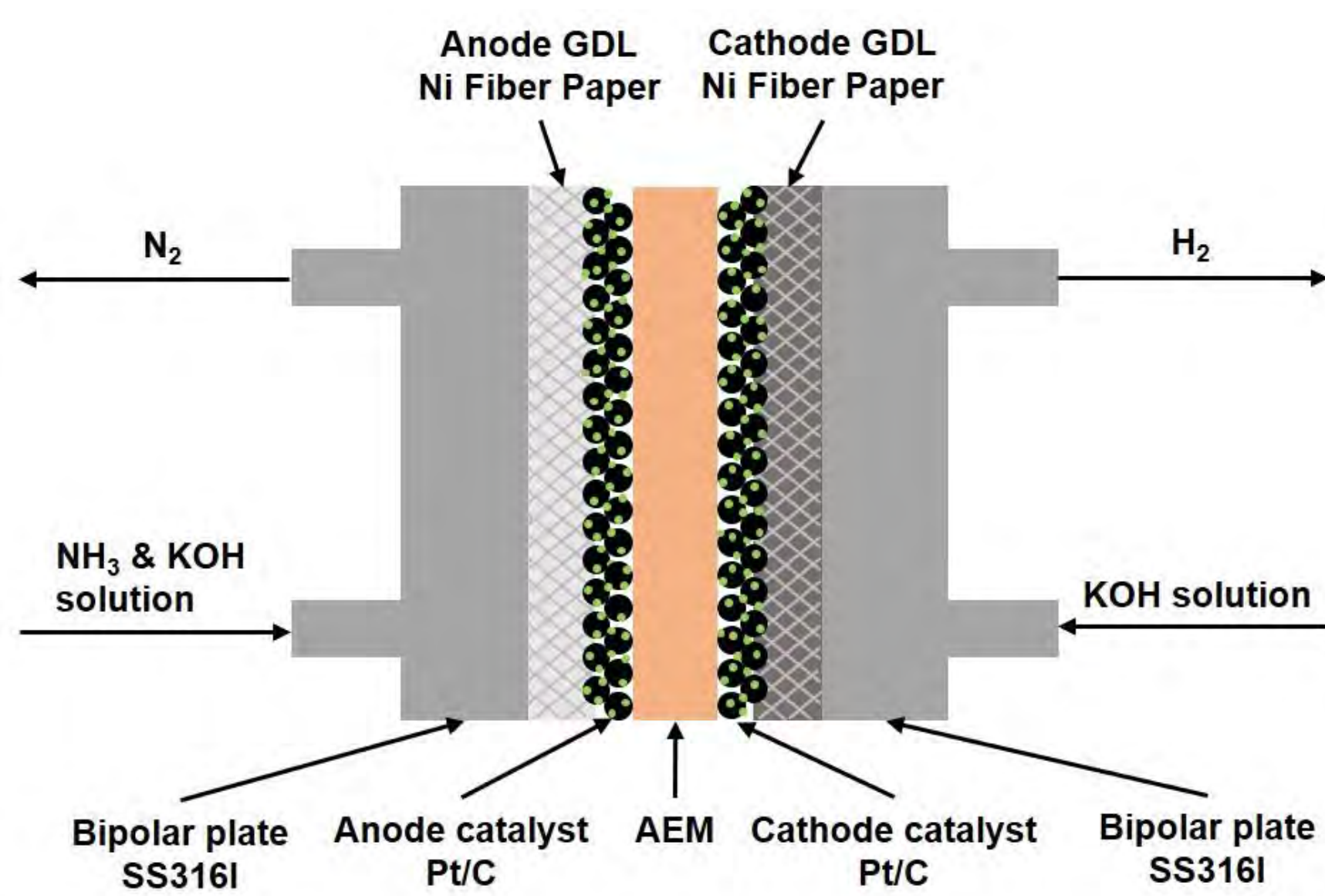
# Ammonia E-Cracking

Chencheng Dai<sup>1,2</sup>, Adrian C. Fisher<sup>1</sup> and Zhichuan J. Xu<sup>1,2</sup>

## Introduction

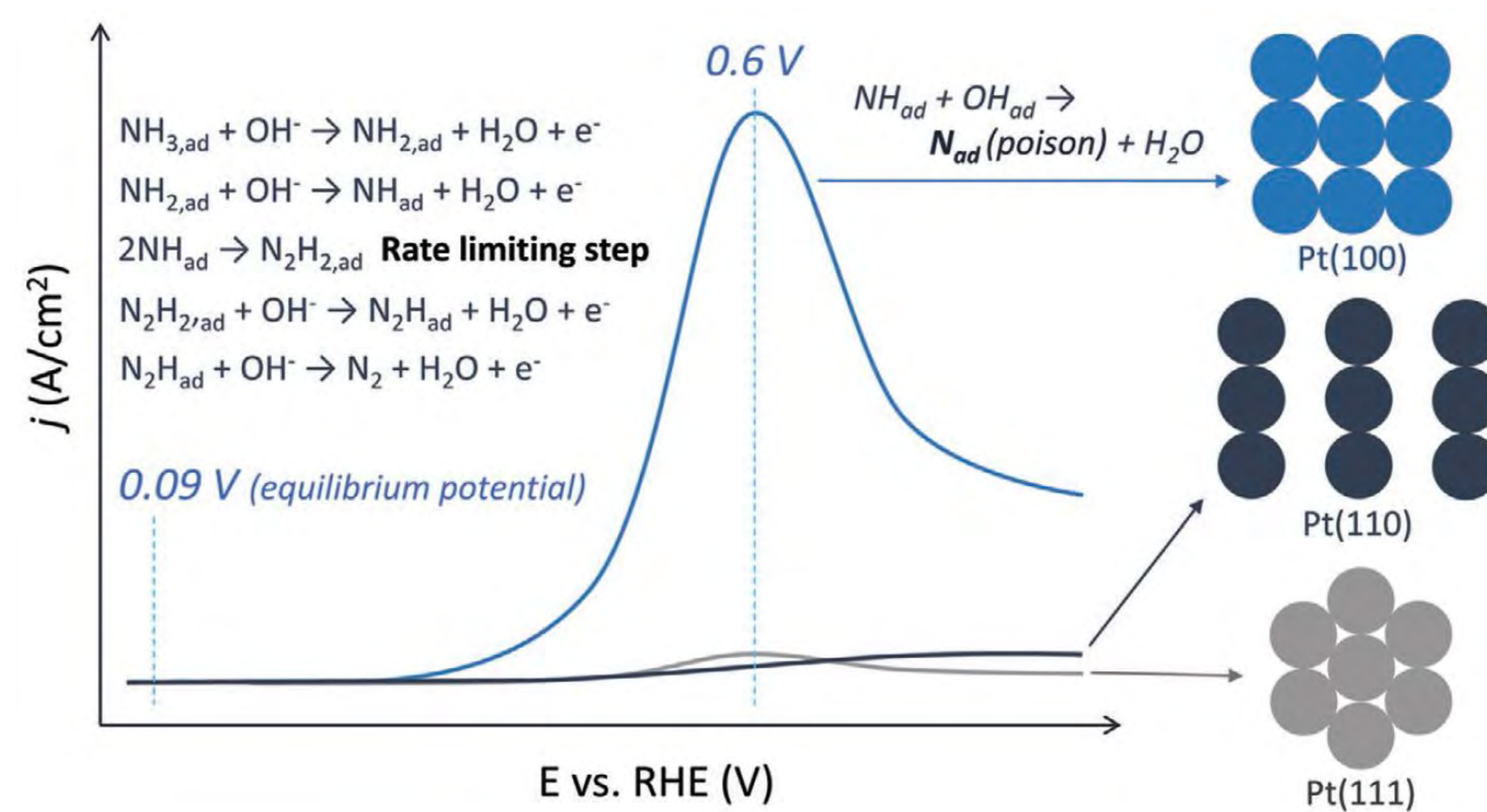
Ammonia is electrochemically cracked under low temperature and ambient pressure in an MEA electrolyzer, where nitrogen and hydrogen are generated at anode and cathode, respectively. The MEA configuration increase ammonia e-cracking activity, as well as produce hydrogen and nitrogen gases via different outlets. The stable industrial-level current density of 200 mA cm<sup>-2</sup> can be achieved with a low cell voltage of 0.67 V.

## MEA Electrolyzer



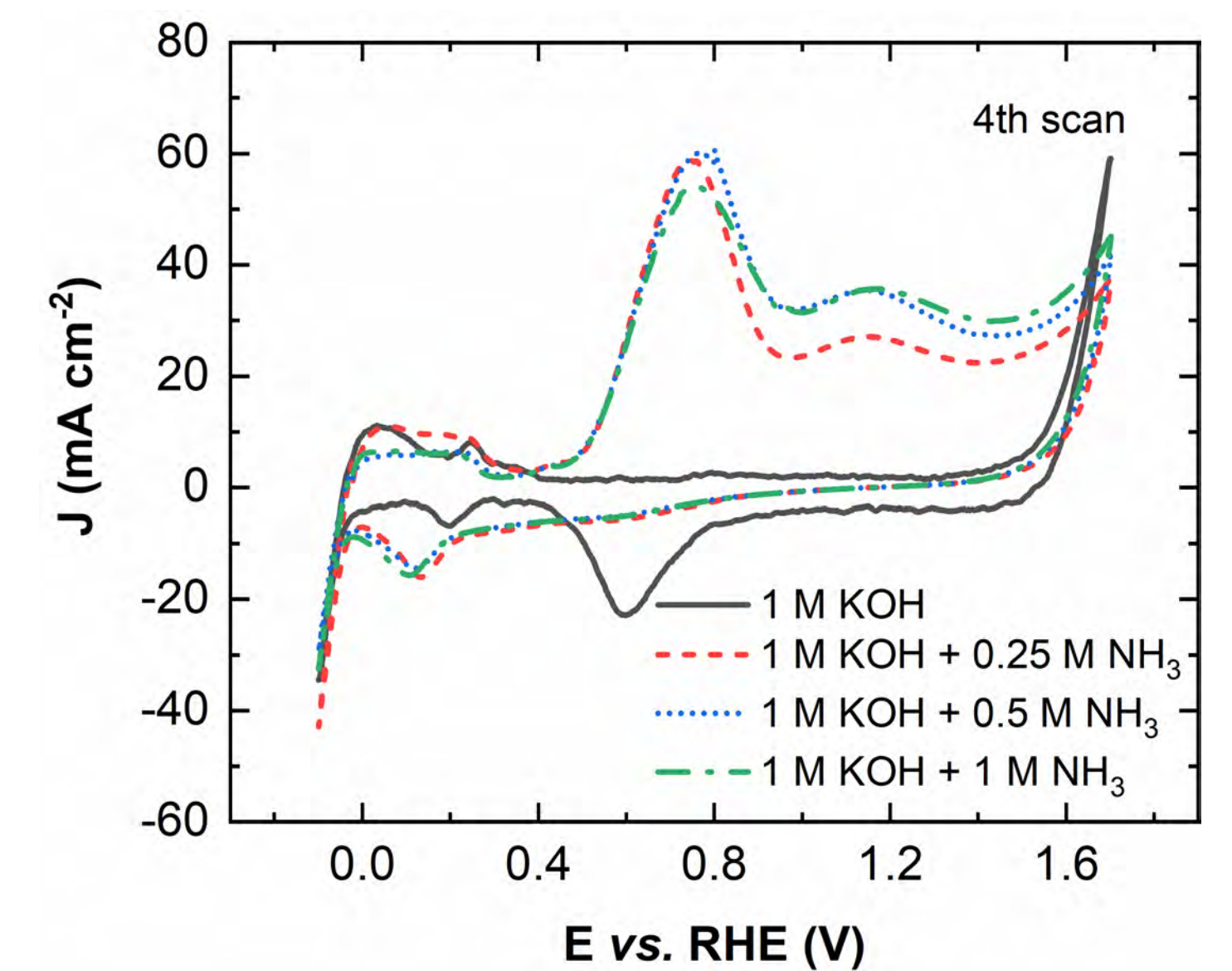
Cross-sectional illustration of MEA electrolyzer  
 Anode:  $2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-$   
 Cathode:  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 Overall:  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

## Electrochemical AOR Catalyst Poisoning



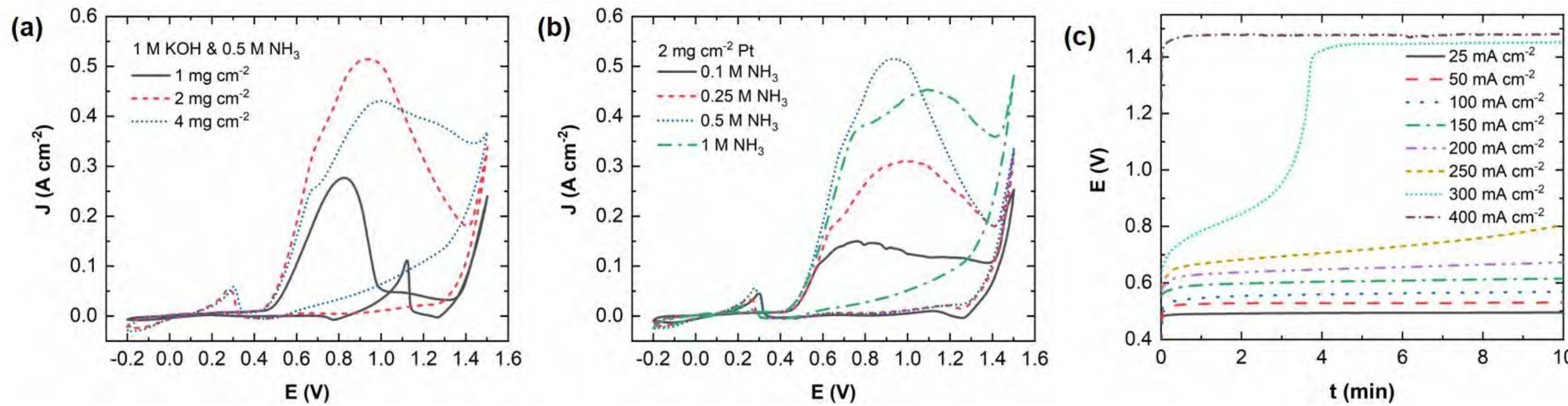
The catalyst poisoning at higher potentials hinders the obtain of higher current densities.  $\text{N}_{\text{ad}}$  forms when the potential is more positive than the peak potential, which can eventually poison the Pt catalyst.

## AOR on Pt in an H-cell



AOR catalyzed by Pt/C on glassy carbon electrode in an H-cell with various ammonia concentrations at room temperature and pressure

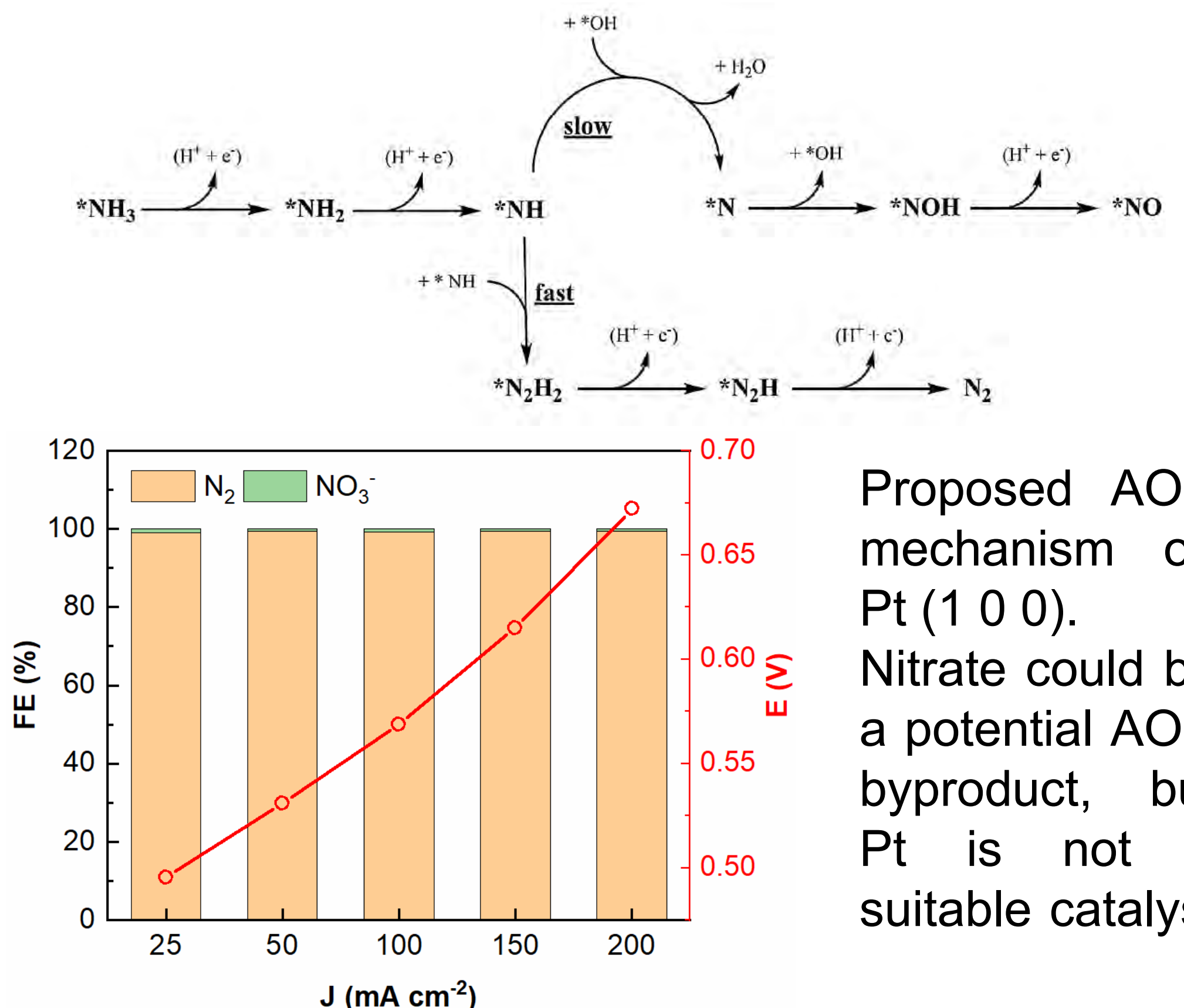
## AOR on Pt in an MEA Electrolyzer



AOR catalyzed by Pt/C in an MEA electrolyzer with various ammonia concentrations, catalyst loadings and applied current densities at 80 °C and ambient temperature.

- The comparison of various Pt loading shows the 2 mg cm<sup>-2</sup> is the best loading;
- The comparison of various ammonia concentration suggest the 0.5 M is the optimal concentration.
- A stable cell voltage of 0.67 V can be achieved at the current density of 200 mA cm<sup>-2</sup>.

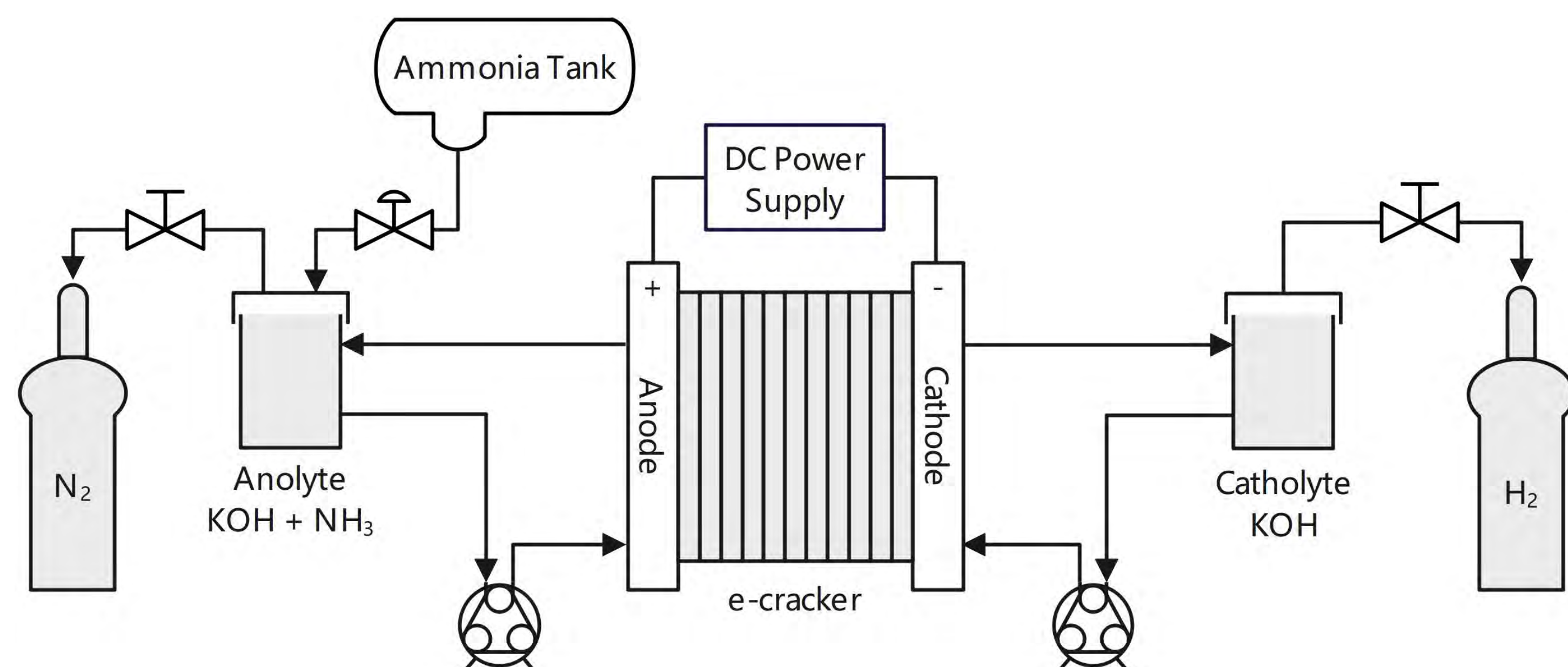
## AOR Byproducts



Proposed AOR mechanism on Pt (1 0 0). Nitrate could be a potential AOR byproduct, but Pt is not a suitable catalyst.

## AOR Electrolyzer Stack

- A variable number of MEA electrolyzers can be stacked to achieve a large scope of the hydrogen production rate, suitable for on-demand and on-site hydrogen production.



## Green Hydrogen Production

Reactant	Reactions	$E^0$ (V vs. RHE)	$U_{EC}$ @ 0.2 A cm <sup>-2</sup> (V)	$W_e$ @0.2 A cm <sup>-2</sup> (kWh / kg H <sub>2</sub> )	Electricity cost (SGD / kg H <sub>2</sub> )*
H <sub>2</sub> O	$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$	1.23	1.6Q	42.9	11.8
NH <sub>3</sub>	$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$	0.06	0.67	18.0	4.9

\*Cost is calculated based on the electricity price in Singapore (27.43 cents per kWh)

## Conclusions

- The electrochemical ammonia cracking to produce hydrogen can be conducted at a low cell voltage at low temperature and ambient pressure.
- The anodic product nitrogen and the cathodic product hydrogen are separated by the MEA. So, the product gases separation/purification processes can be simplified.

## References

- Singapore Patent Application # 10202301326Y
- Adv. Mater. 2019, 31, 1805173.
- J. Catal. 2018, 359, 82.
- Electrochim. Acta 2011, 56, 8085.

"This research project is funded by the National Research Foundation (NRF) Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme."

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# Electrochemical carbon dioxide reduction

Mikhail K. Kovalev<sup>1</sup>, Hangjuan Ren, Simon Rihm, Magda Barecka, Sheng Yuan, Alexei Lapkin<sup>2</sup>, Joel W. Ager<sup>3</sup>

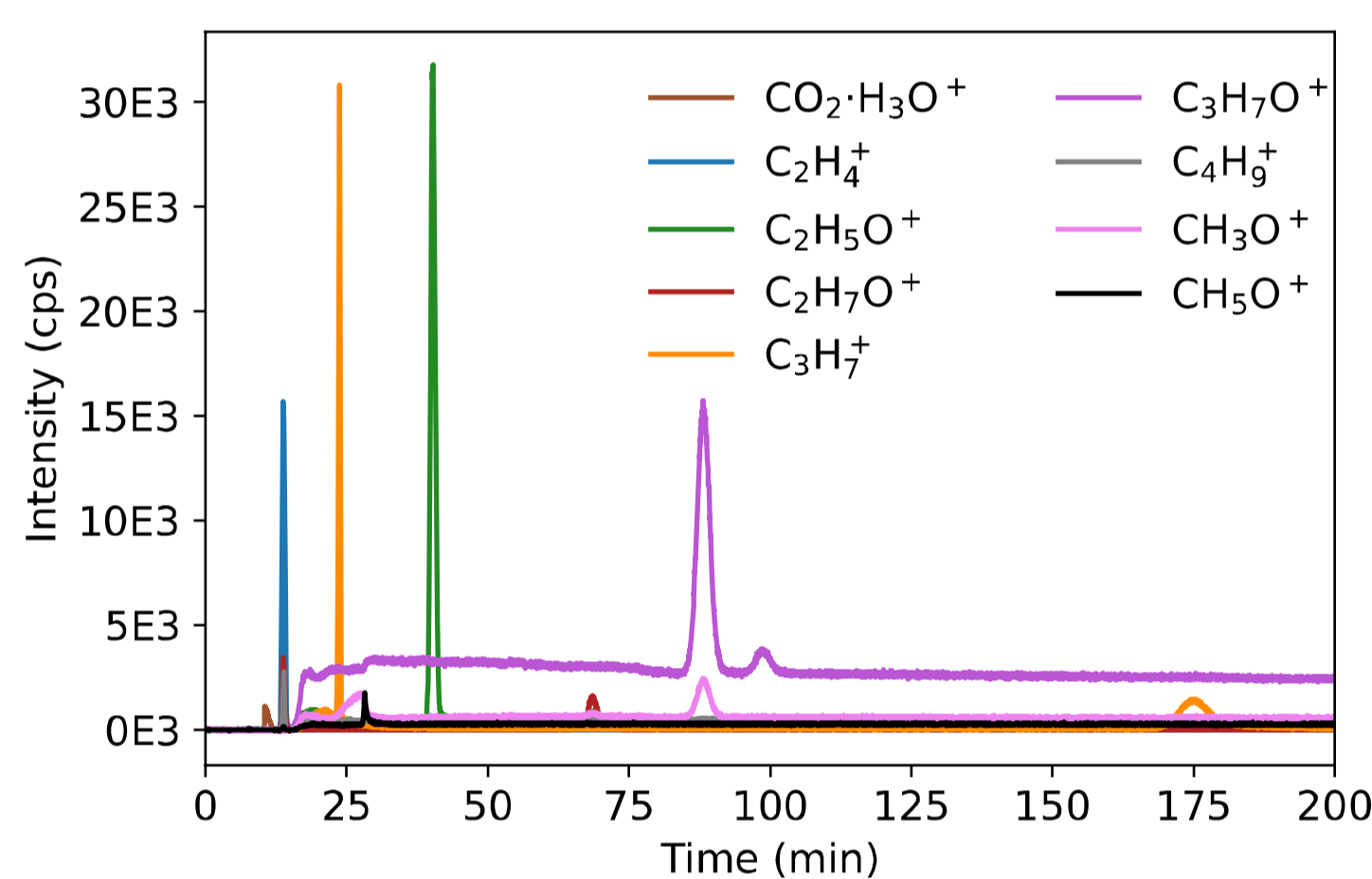
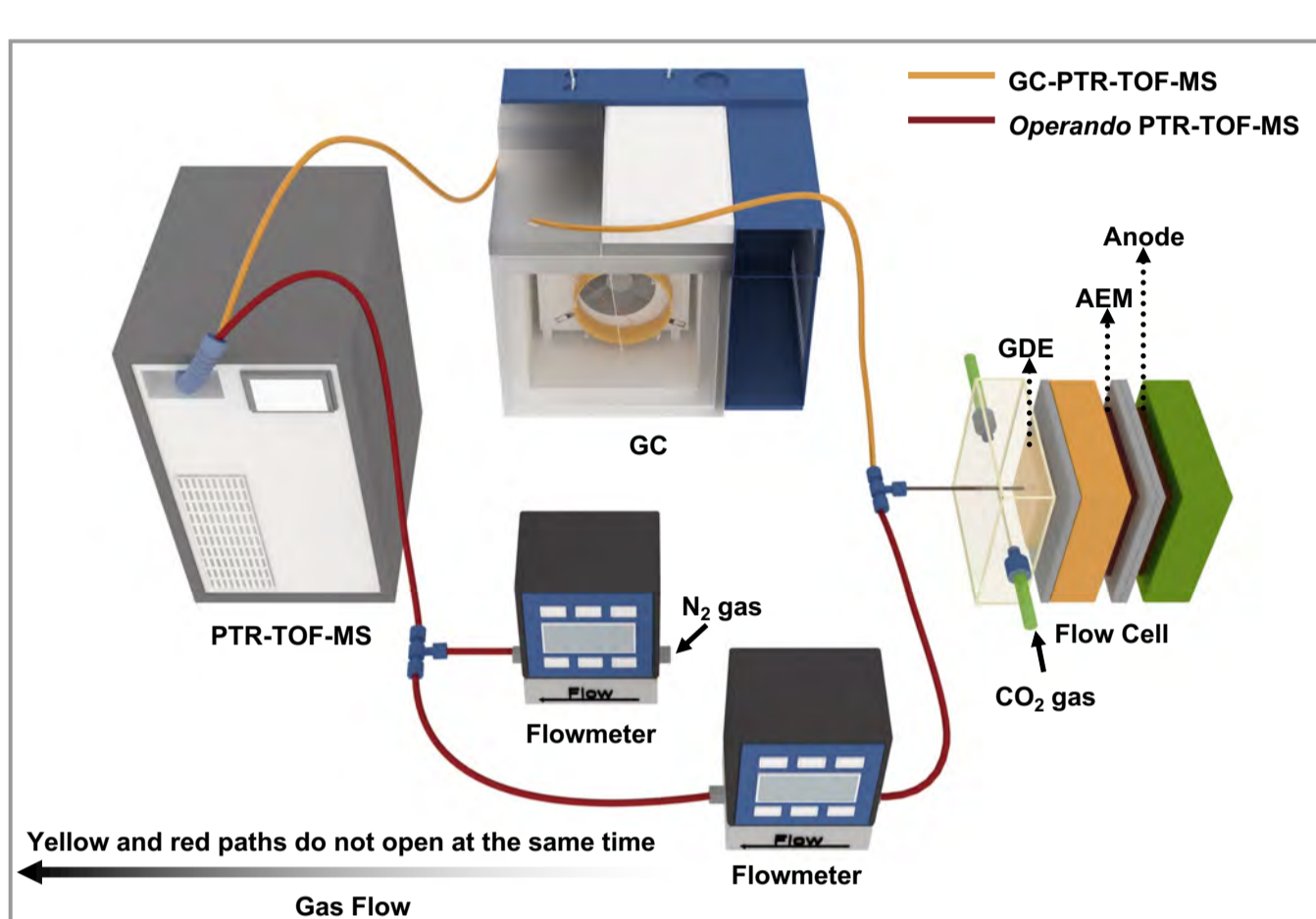
## Introduction

The project, driven by the urgent need to tackle CO<sub>2</sub> over-emission, has focused on utilizing renewable energy sources for converting carbon dioxide into valuable chemical products. The study has unveiled critical electro-catalytic mechanisms for CO<sub>2</sub> conversion and explored potential industrial applications for this process. The resulting table-top electrochemical plant equipped with large electrodes capable of operating currents up to 100 A. This groundbreaking initiative aims to play a pivotal role in mitigating climate change and promoting sustainable practices.

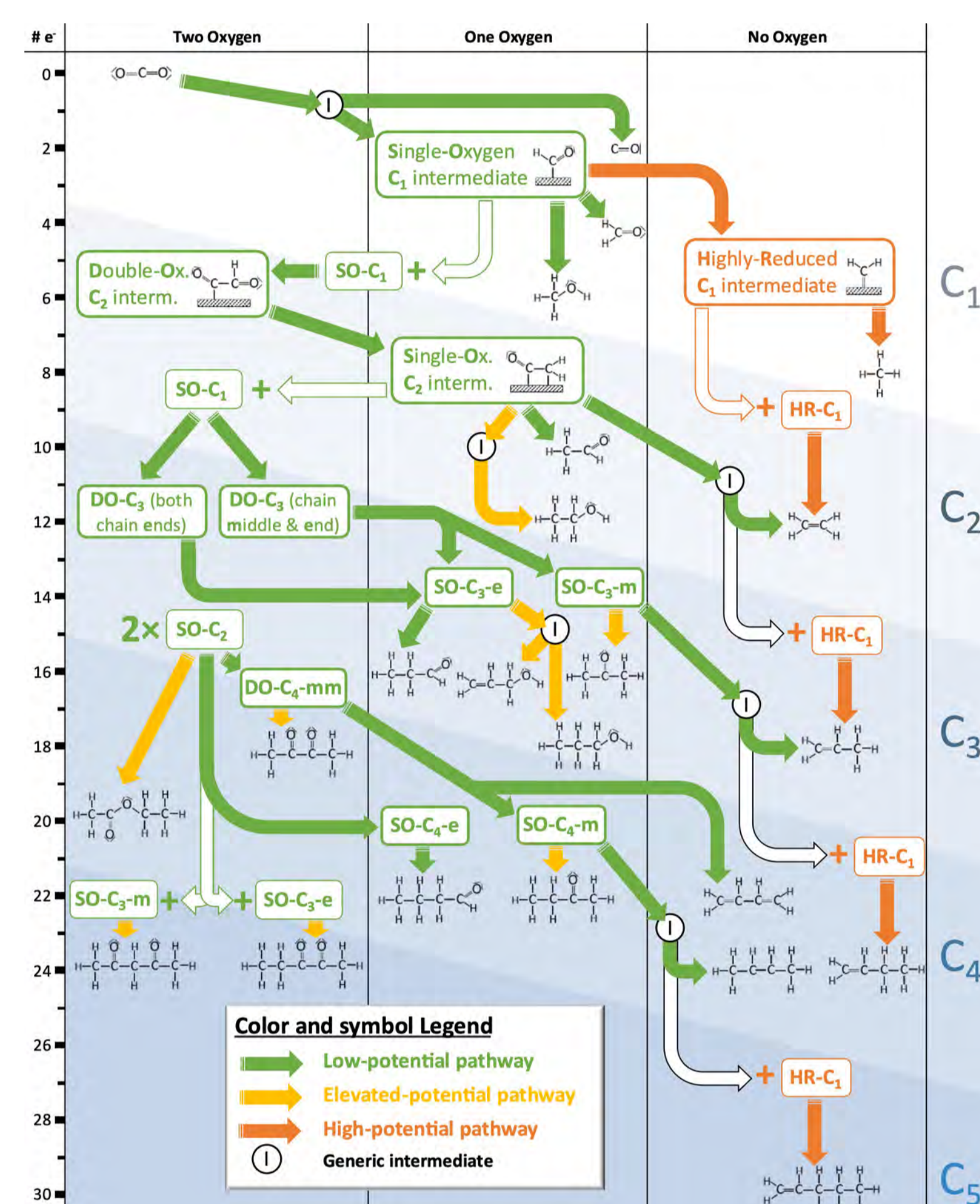
## Small scale electrode setup for fundamental studies

### Small-scale setup scheme for reaction studies:

- Gas diffusion electrode (GDE) size 1 x 1 cm<sup>2</sup>
- Operates with or without coupled gas chromatograph
- GC-MS results example below

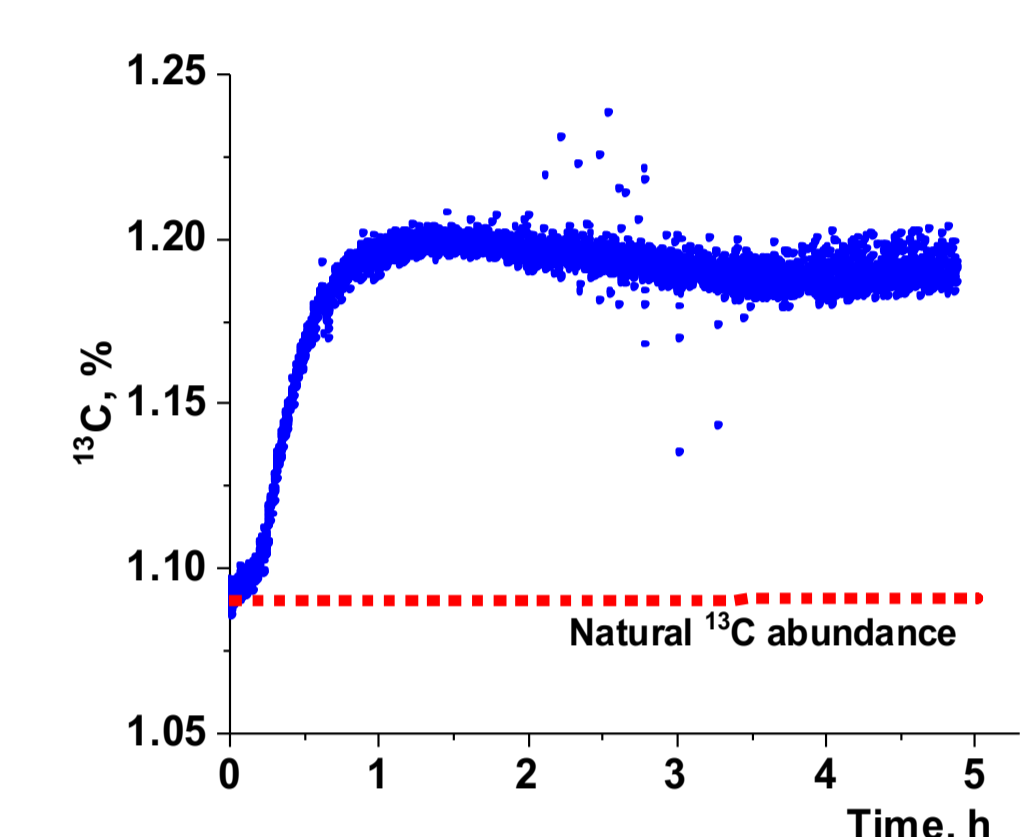


### Proposed mechanism of CO<sub>2</sub> electroreduction on copper-based GDE. The scheme divided by the number of C-atoms that have been detected by GC-MS analysis



### Isotope 13C distribution in electroreduction products and unreacted CO<sub>2</sub>

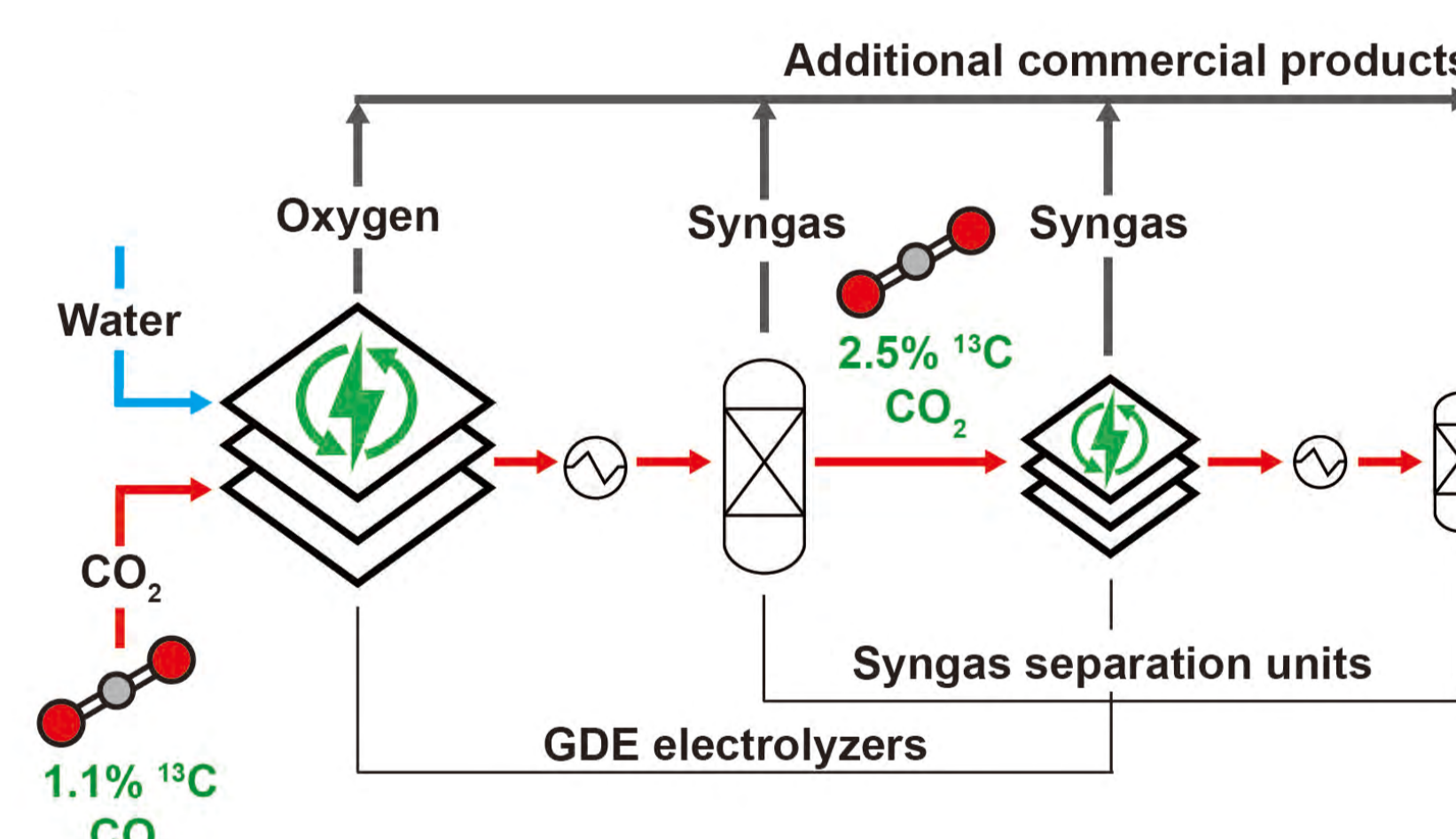
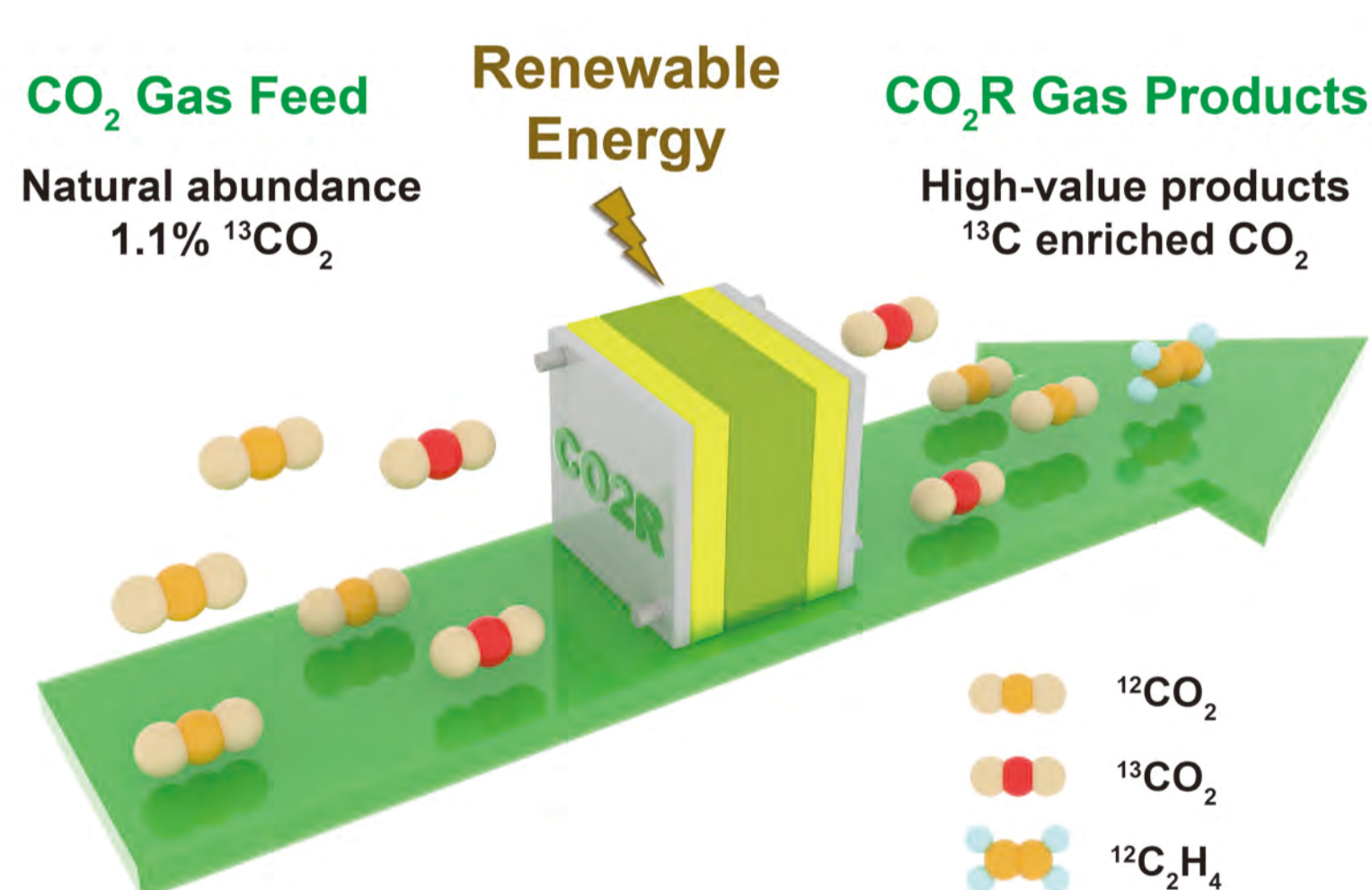
	$\delta^{13}\text{C}$ (‰)
CO <sub>2</sub>	+138.3±75.7
C <sub>2</sub> H <sub>5</sub> OH	-59.4±23.3
C <sub>2</sub> H <sub>4</sub>	-75.1±36.2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-81.2±11.7
CH <sub>3</sub> CH <sub>2</sub> CHO	-81.4±5.2
C <sub>3</sub> H <sub>6</sub>	-108.7±13.8
CH <sub>3</sub> COCH <sub>3</sub>	-118.3±36.1
CH <sub>3</sub> CHO	-130.3±7.8



### Summary:

- GC-PTR-TOF-MS analysis identified over 20 distinct products –confirming 10 previously unknown ones, including multiple C5 species
- Operando PTR-TOF-MS shown 12C/13C isotope fractionation ( $\delta^{13}\text{C}$ ) to be highly negative in reaction products and highly positive for unreacted CO<sub>2</sub>
- 13C isotope can be enriched even more under specific conditions as it remains in unreacted CO<sub>2</sub>

## Possible applications

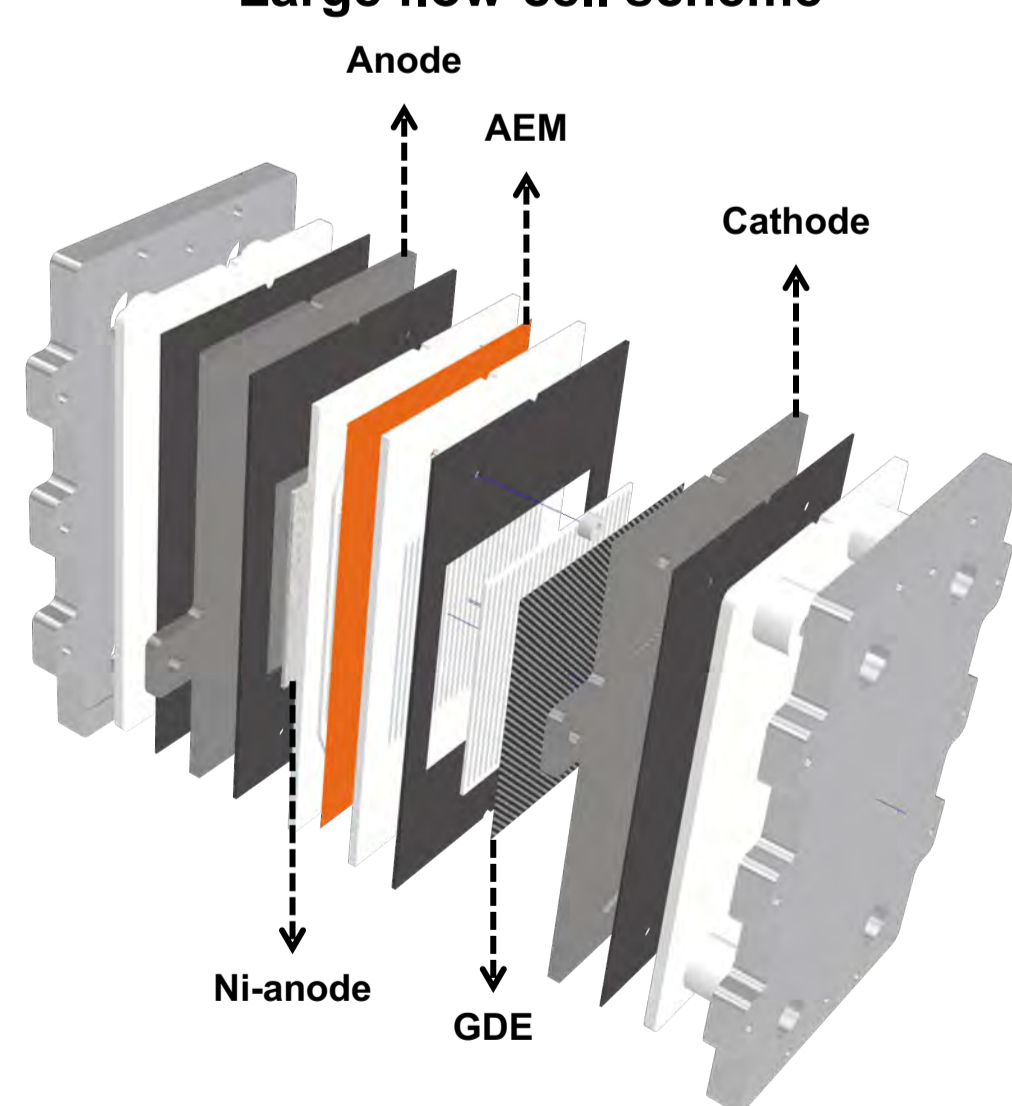


### Possible applications:

- Production of carbon monoxide that can be used in syngas with silver-based electrodes
- Production of high-value multi-carbon products such as ethylene, ethanol, propylene or propanol with copper-based electrodes
- Recirculation of unreacted CO<sub>2</sub> opens possibility to continuously enrich 13C to commercially viable concentrations

## Tabletop reactor for large scale electrodes - 10x10 cm<sup>2</sup>

### Large flow-cell scheme



### Large-electrode table-top reactor



### eCO<sub>2</sub>EP team



## References

Ren, H., Kovalev, M., Weng, Z. et al. *Nat. Catal.* 5, 1169–1179 (2022).  
 Rihm, S., Kovalev, M., et al. *Environ. Sci.*, 16, 1697-1710 (2023)  
 Barecka et al., *iScience*, (in-press)

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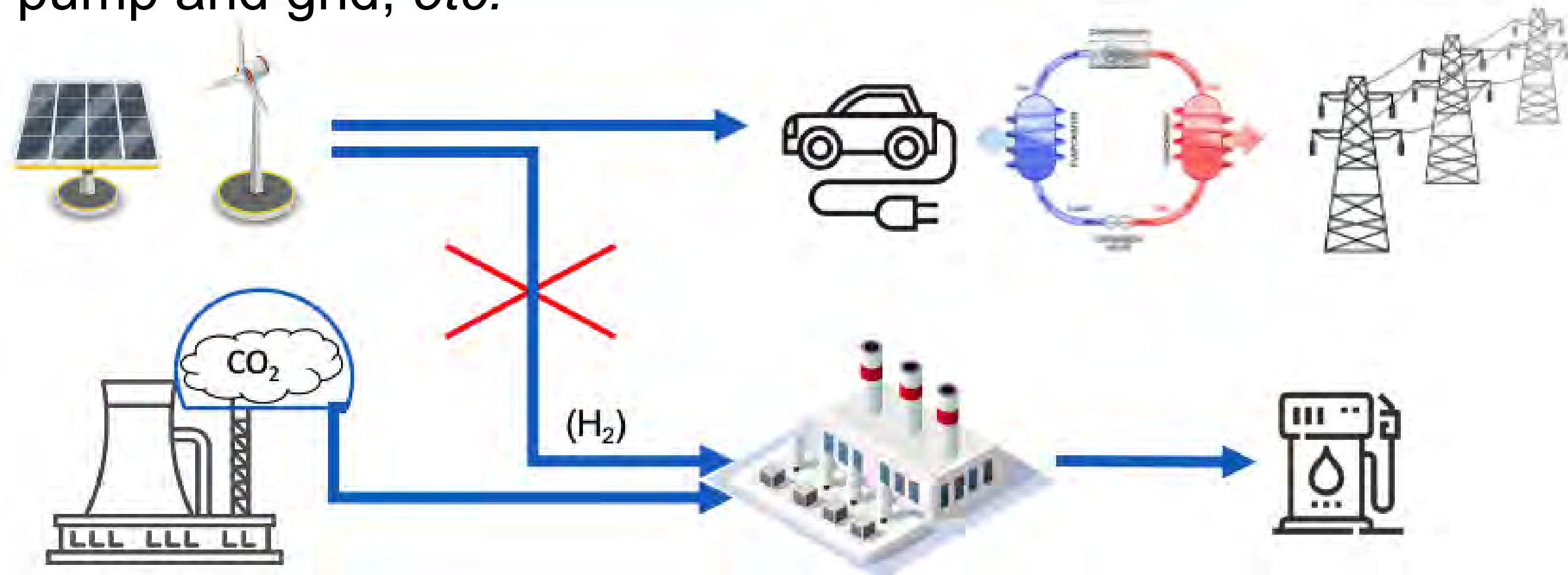
# Empowering Low-Carbon Future: Unveiling the Vital Role of Energy in Carbon Capture and Utilization

Zhimian Hao<sup>1</sup>, Alexei Lapkin<sup>1,2</sup>

## Introduction

Net zero promotes the energy transition from fossil fuels to renewables. Carbon capture and utilization (CCU) presents an intermediate solution, as CCU is believed to be effective in decarbonizing fossil-based industries. However, numerous CCU studies incorporate renewables,<sup>1</sup> and such a 'reverse transition' may underestimate the full potential of CCU. Herein, this work evaluates a 'worst-case' scenario of CCU, by excluding renewables.

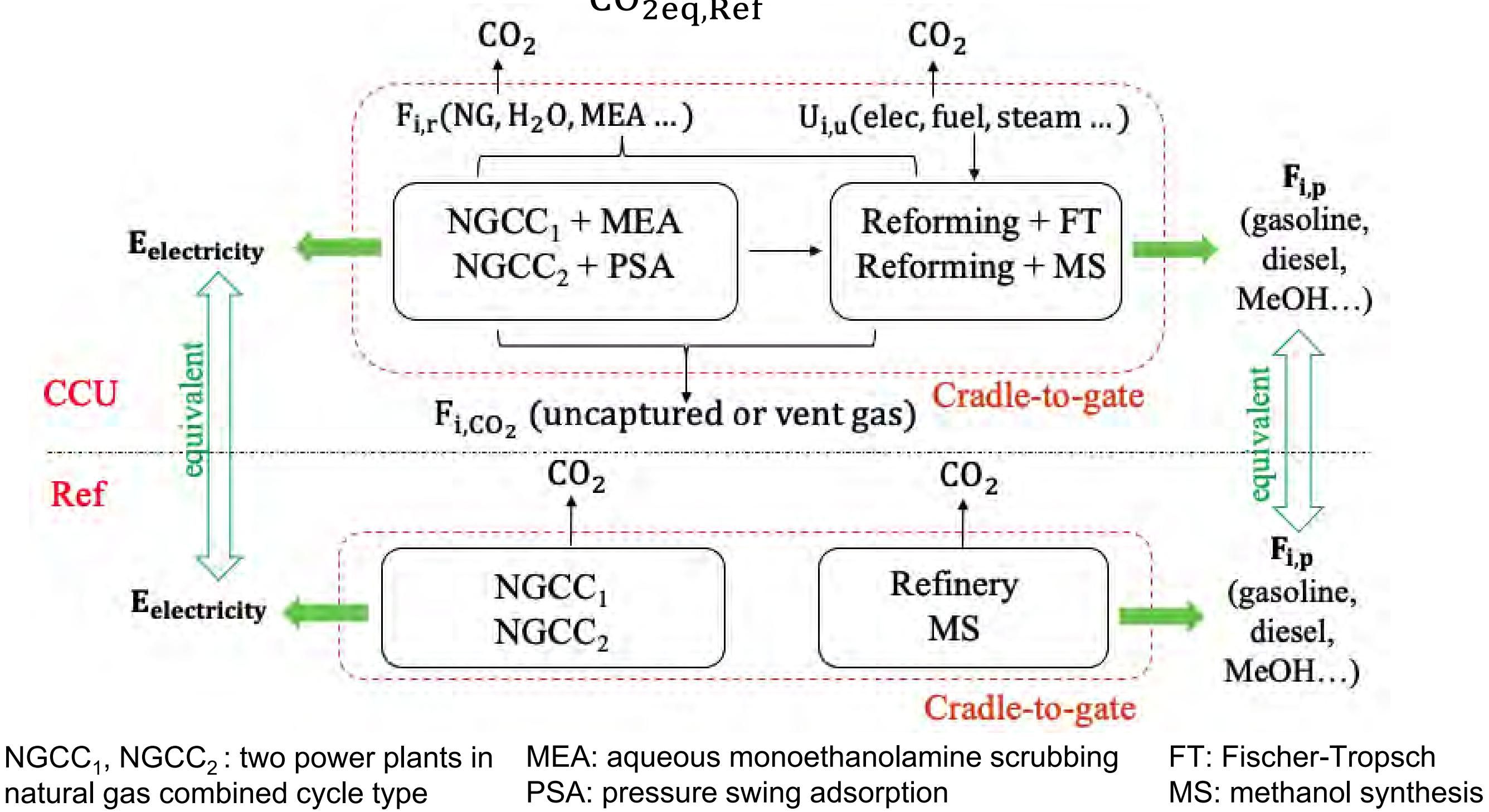
- ❖ We build a hypothetical industrial park, where power plants are integrated with carbon capture and utilization (CCU), to produce power and fuels.<sup>2</sup>
- ❖ No renewables are considered for CCU, as the decarbonization efficiency is higher by utilizing renewables in electric cars, heat pump and grid, *etc.*<sup>3</sup>



### ❖ Evaluation: system boundary

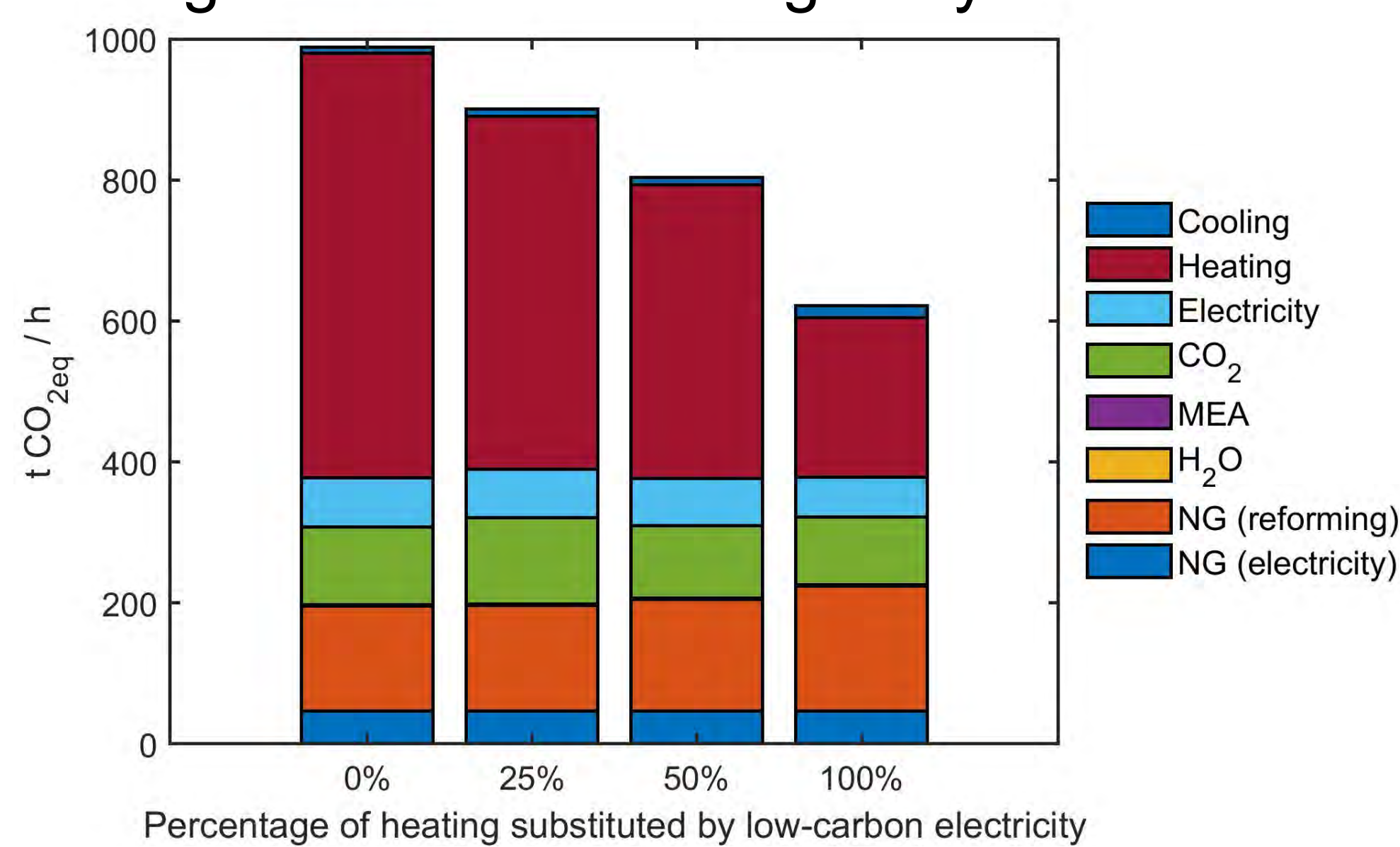
- Greenhouse gas (GHG) emissions are measured by the cradle-to-gate system boundary.
- GHG emissions are also evaluated in a reference system (produce equivalent power & fuels, but no CCU included)

$$\text{GHG reduction} = \frac{\text{CO}_{2\text{eq,Ref}} - \text{CO}_{2\text{eq,CCU}}}{\text{CO}_{2\text{eq,Ref}}} \times 100\%$$

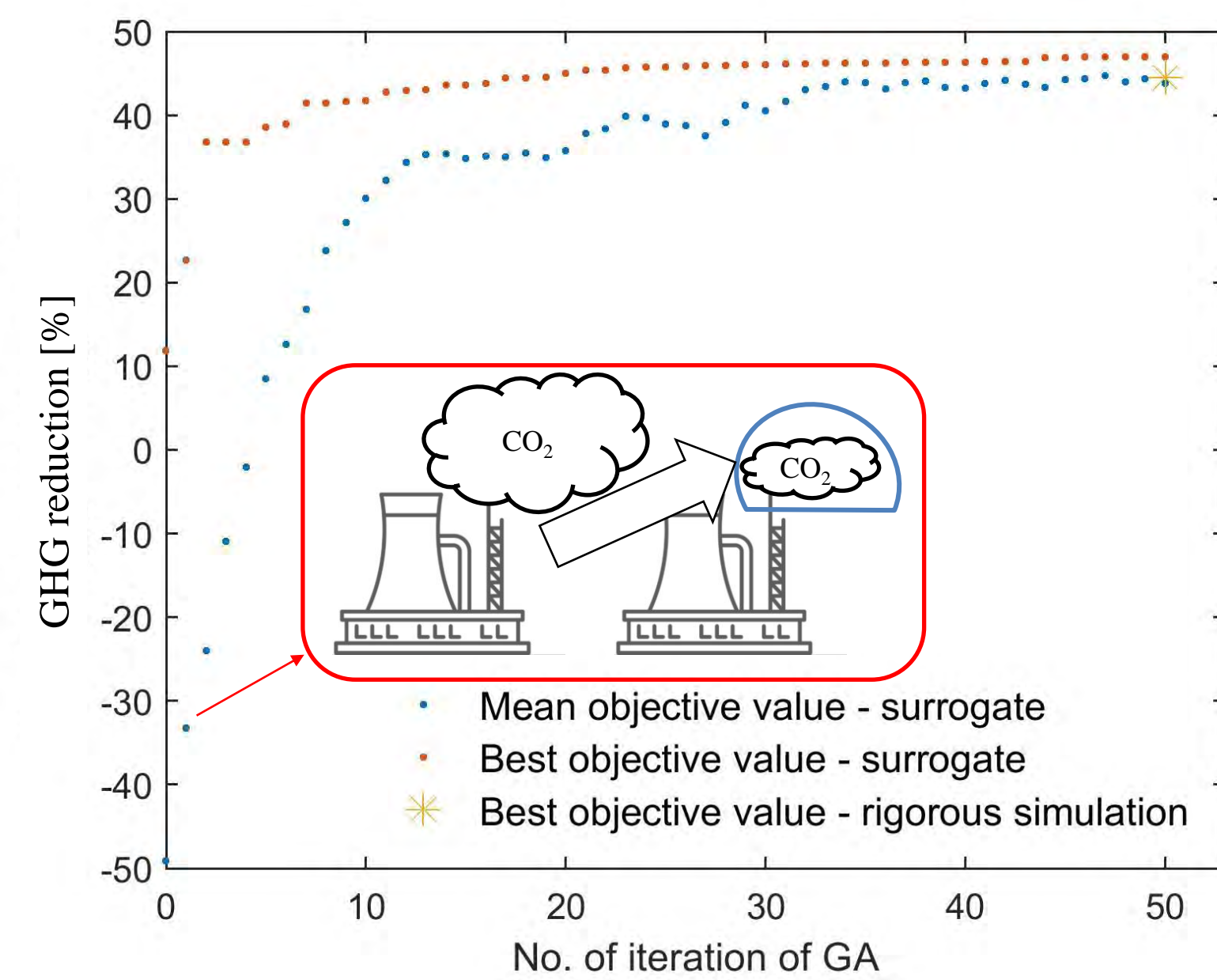


### ❖ Hotspot analysis: breakdown of GHG emissions

- Heating is the biggest source for GHG emissions.
- Heating electrification can greatly reduce GHG emissions.

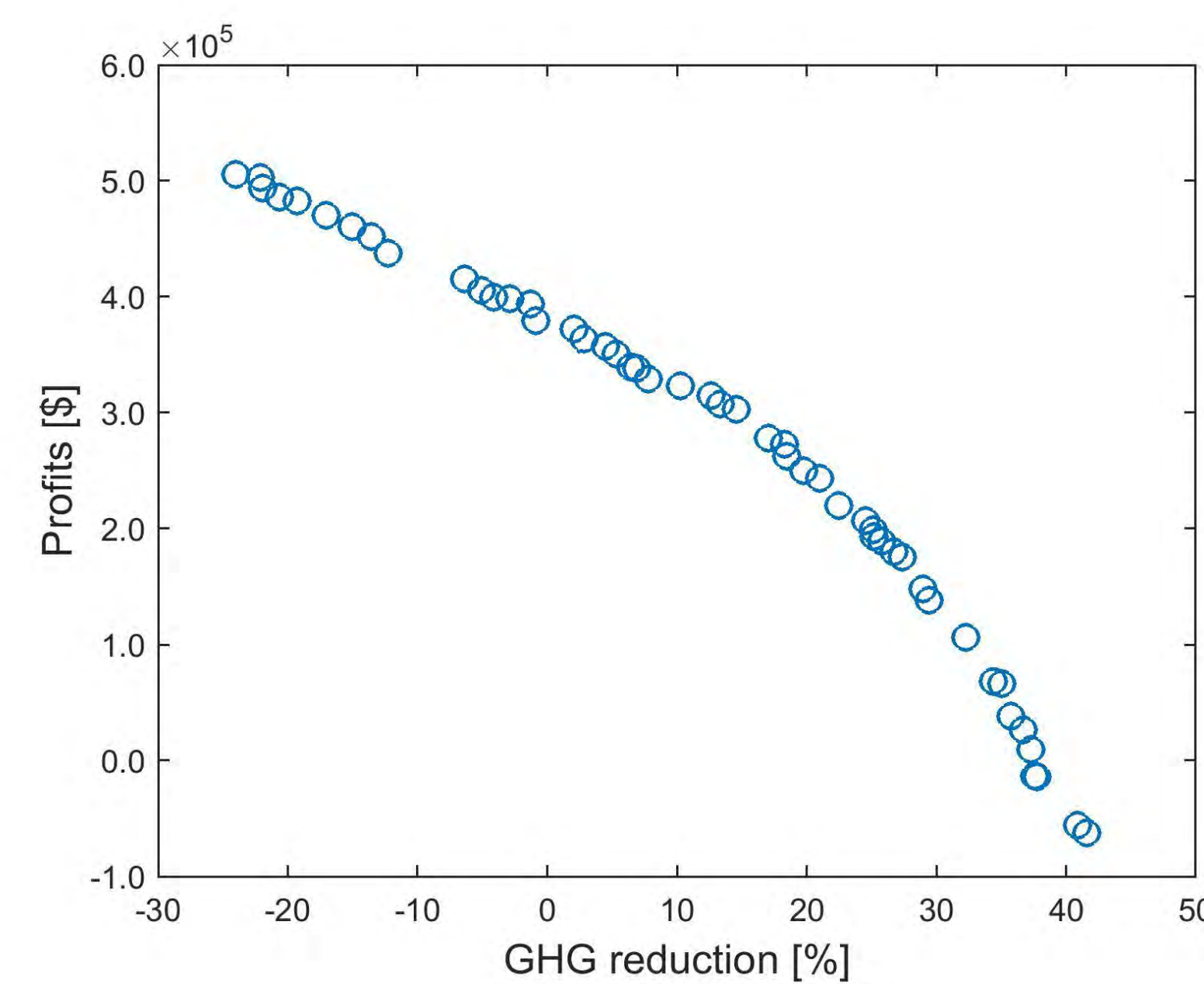


### ❖ Single-objective optimization regarding GHG reduction

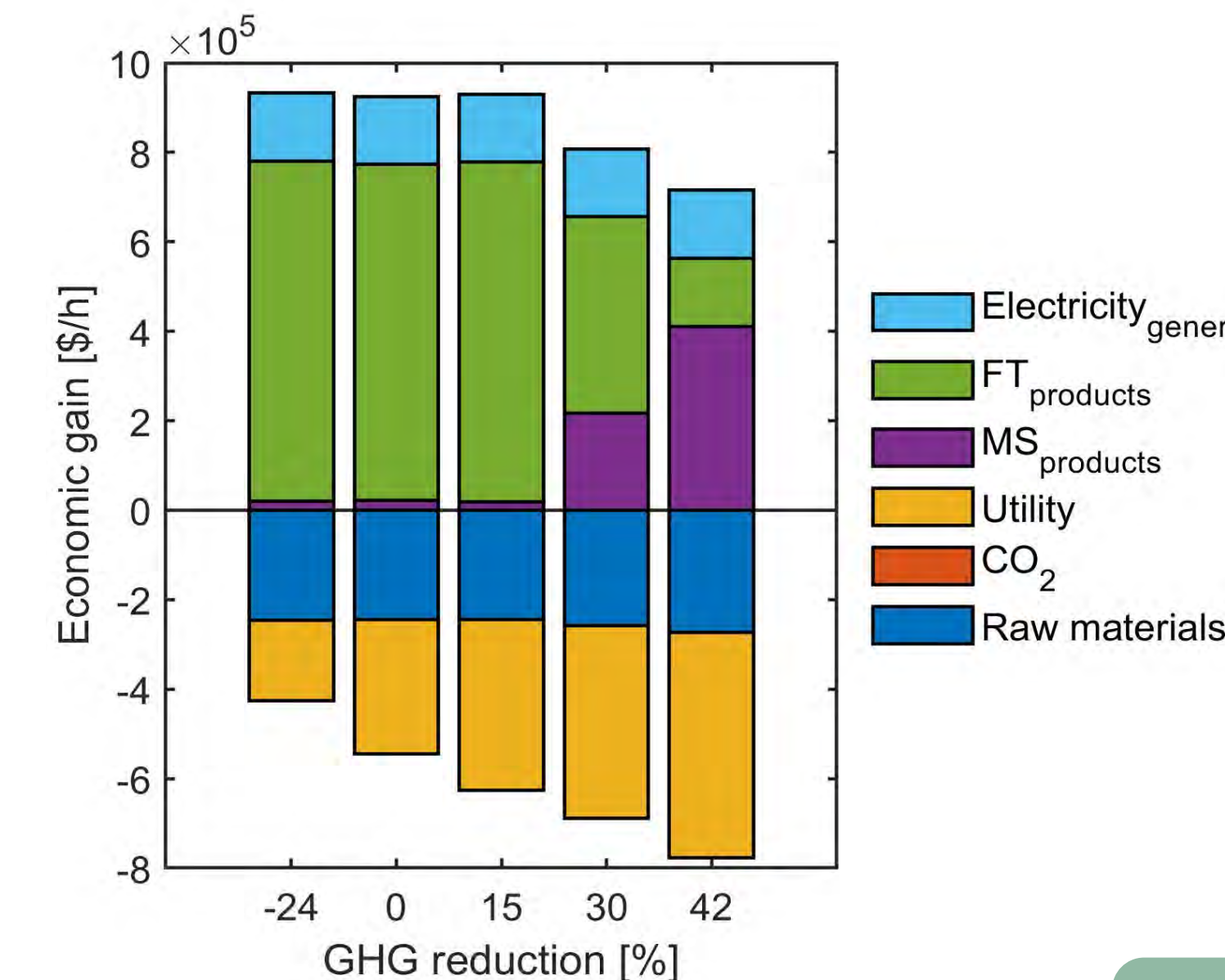


- max (GHG reduction)  $\theta$
- $\theta$ : 29 operating conditions
- Without optimization, CCU can potentially cause more GHG emissions
- Optimization reduces GHG emissions by 45 %
- ~ 8.26 min

### ❖ Multi-objective optimization of GHG reduction vs. profit



- max (GHG reduction, profit)  $\theta$
- $\theta$ : 29 operating conditions
- Non-dominated sorting genetic algorithm-II is used to approximate the Pareto front.
- Trade-off trend between two objectives.



- Select several Pareto points.
- The reduction of GHG emissions requires the transition to the low-carbon fuels and high-cost of utility (low-carbon electricity).

## Take-home messages

- "Low-carbon" process systems, *e.g.*, CCU, may potentially cause more GHG emissions, due to the high energy demand.
- System boundary: this work highlights the importance of considering the entire energy system and energy source when evaluating the environmental impacts of CCU.
- Specifically, regarding CCU based on thermal-chemical processes, heating can be a significant contributor to GHG emissions.
- Fuel products: CCU-to-methanol exhibits greater carbon efficiency than CCU-to-gasoline/diesel via Fischer-Tropsch (FT).
- Digitalization enables the efficient evaluation of multi-process systems.<sup>2,4</sup>
- Multi-objective optimization can better balance competing criteria.

## References

1. Rego de Vasconcelos, B., Lavoie J.-M., *Front. Chem.*, 2019, 7.
2. Hao, Z., Barecka, M., Lapkin, A. A., *Energy Environ. Sci.* 2022, 15, 2139-2153
3. Kätelhön, A., *et al.*, *PNAS*, 2019, 116, 11187-11194.
4. Hao, Z., Zhang C., Lapkin, A. A., *AIChE J.*, 2022, e17616.

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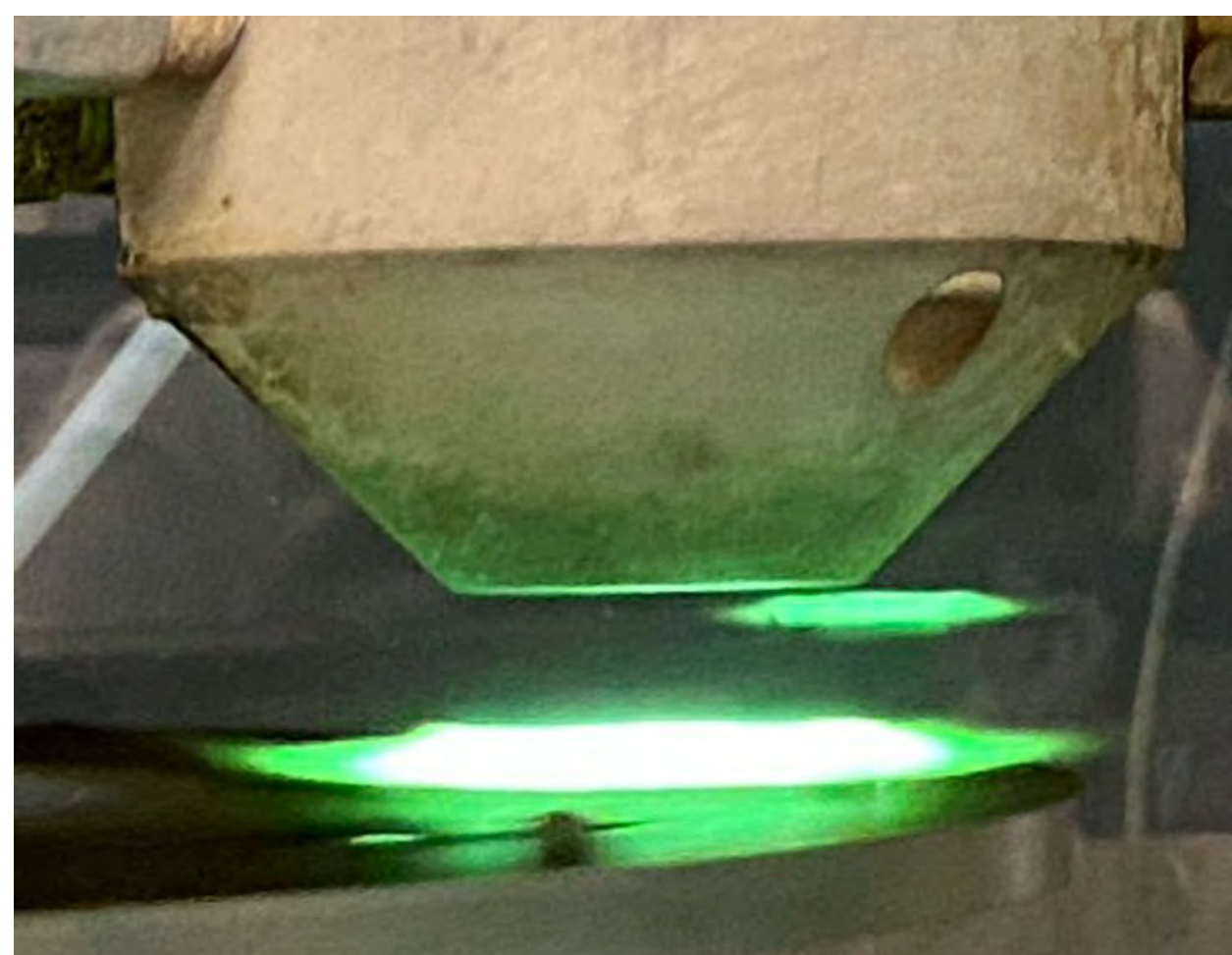
# Flame Aerosol Synthesized Copper Based Oxide Catalyst for Electrochemical Reduction of Carbon Dioxide

Guanyu Liu,<sup>1,2,3</sup> Yuan Sheng,<sup>1,2,4</sup> Markus Kraft,<sup>2,5</sup> Alexei A. Lapkin,<sup>2,5</sup> Joel W. Ager,<sup>6,7</sup> Rong Xu<sup>1,2,\*</sup>

## Introduction

Flame aerosol synthesis is scalable and enables direct deposition of flame-synthesized catalyst onto the substrate without the need for post-treatment such as purification or preparation of ink which is commonly used in traditional catalyst preparation for electrochemical reduction of carbon dioxide.

## Flame Aerosol Synthesis (FAS)



- Advantages of FAS in electrode preparations:
- Ink-free technique
  - Direct deposition onto substrate
  - Highly scalable and industrial relevant
  - Properties of the catalyst can be easily tuned by adjusting flame conditions

Figure 1: Flame deposition of copper oxide onto carbon paper substrate

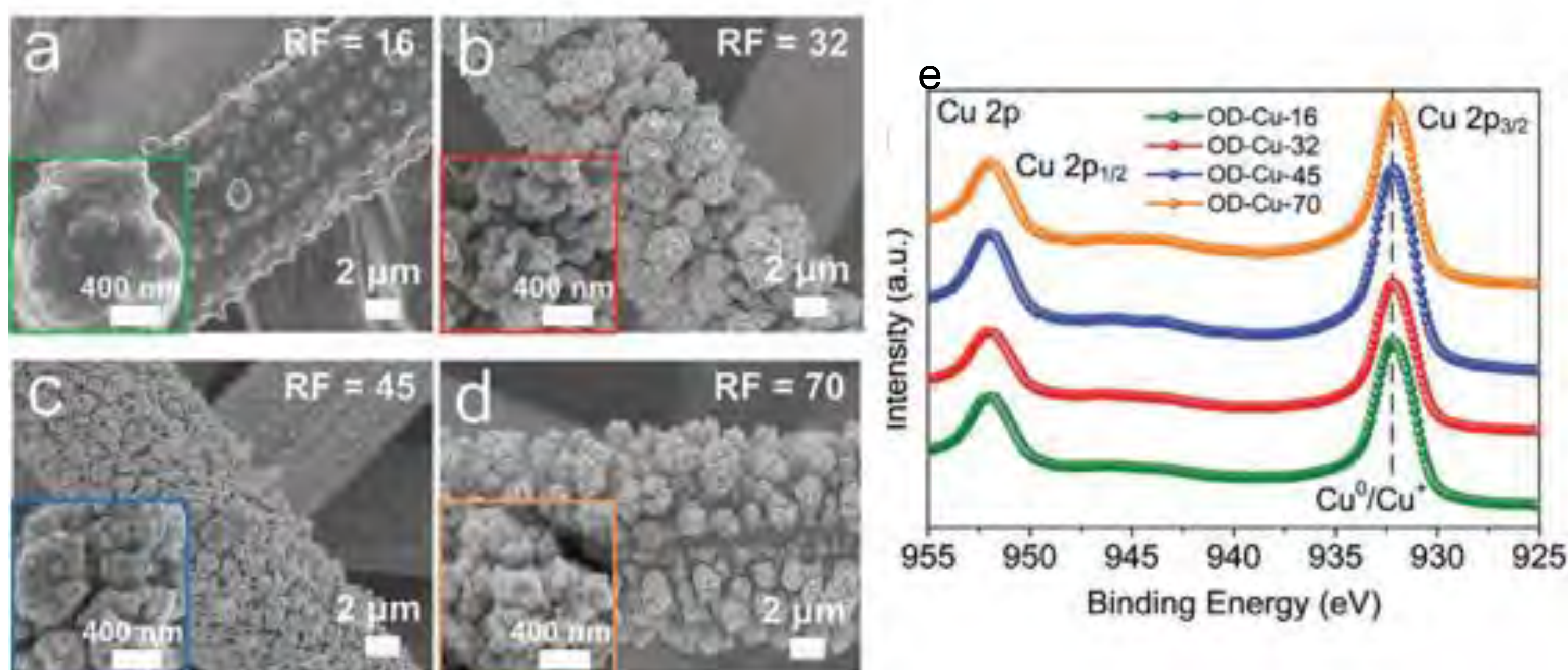


Figure 2: SEM images of oxide derived (OD) copper electrodes with different roughness factor (RF): a) OD-Cu-16 with RF of 16, b) OD-Cu-32 with an RF of 32, c) OD-Cu-45 with an RF of 45, d) OD-Cu-70 with an RF of 70, e) XPS spectra of the Cu 2p. These OD-Cu electrodes were obtained upon CO<sub>2</sub>RR in CO<sub>2</sub>-saturated 0.1M KHCO<sub>3</sub> electrolyte at -1.1V vs RHE for 60mins.

## CO<sub>2</sub>RR Performance

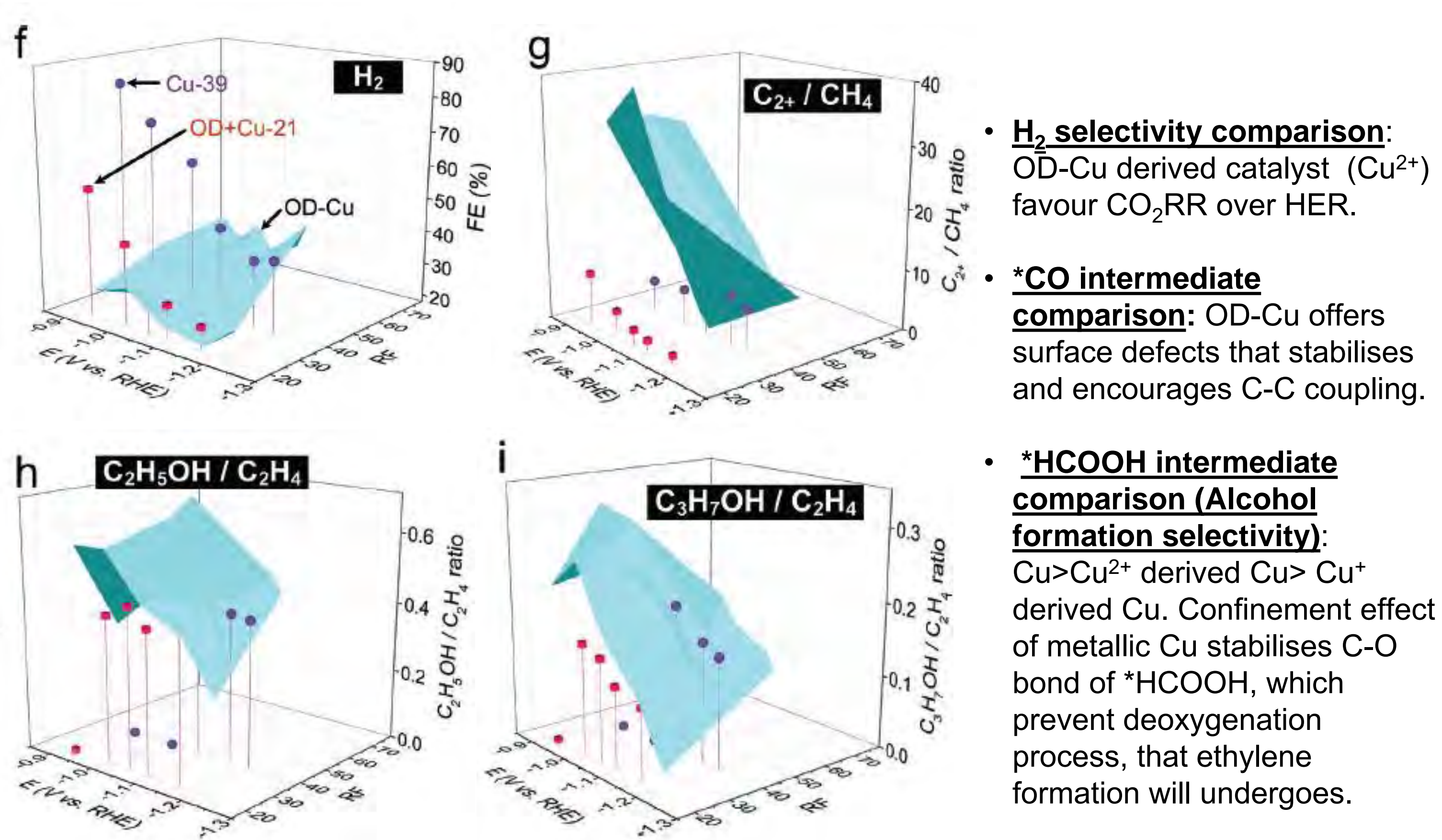


Figure 3: Comparison of CO<sub>2</sub>RR performance between metallic Cu and OD-Cu f) FE of H<sub>2</sub>, g) C<sub>2</sub>/methane ratio, h) ethanol/ethylene ratio and i) n-propanol/ethylene ratio as a function of applied potentials and RF over Cu-39 (violet sphere), OD+Cu-21 (pink cube) and OD-Cu (i.e. OD-Cu-16, OD-Cu-32, OD-Cu-45 and OD-Cu-70). Cyan surface corresponds to OD-Cu with various RF.

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<sup>3</sup>School of Materials Science and Engineering, Tongji University, Shanghai 201804, China.

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<sup>5</sup>Department of Chemical Engineering and Biotechnology, University of Cambridge, West Cambridge Site, Philippa Fawcett Drive, Cambridge CB3 0AS, UK

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<sup>7</sup>Berkeley Educational Alliance for Research in Singapore (BEARS), CREATE Tower, 1 Create Way, Singapore 138602, Singapore

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## Computational studies

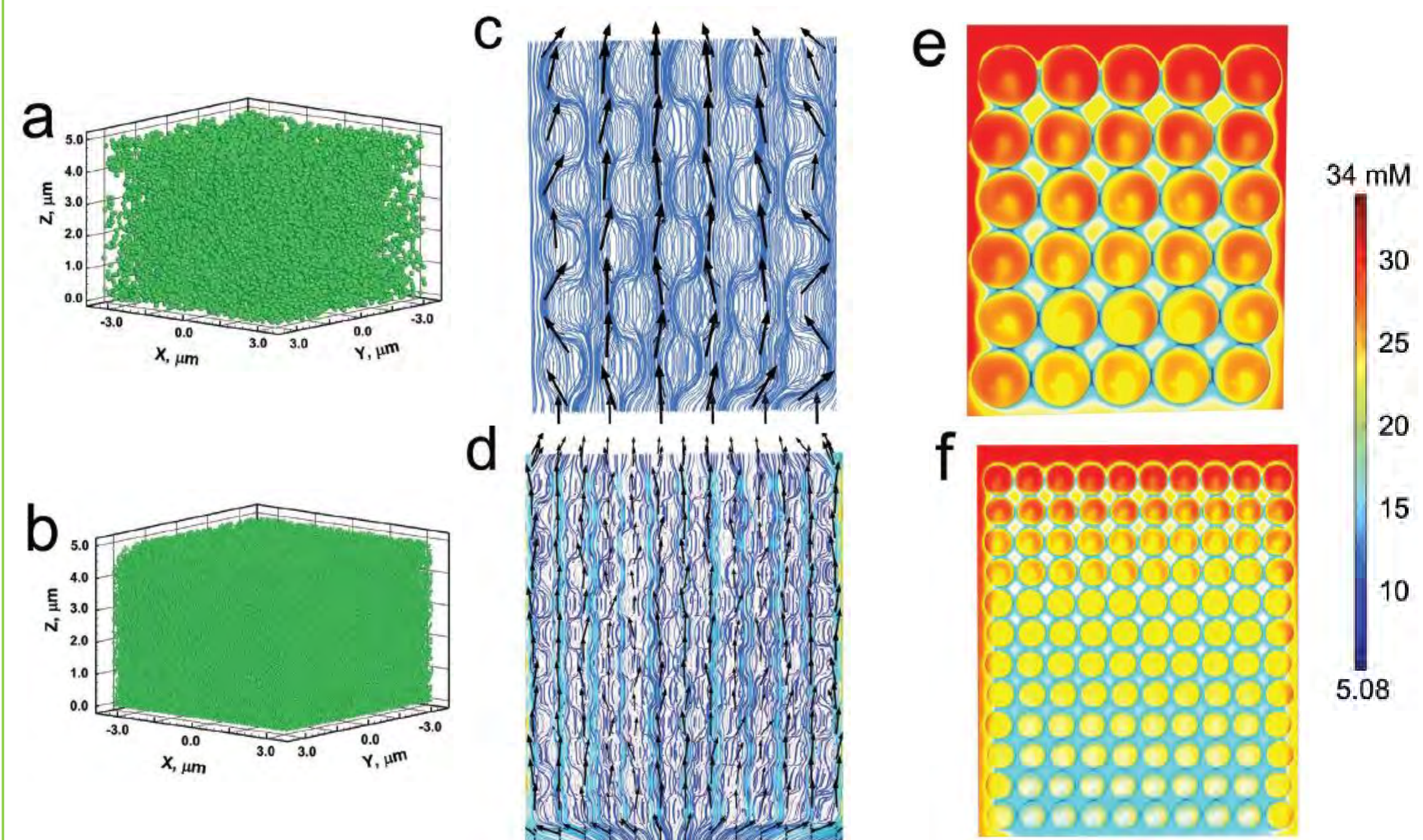


Figure 4: Gas diffusion/transport behaviour in porous Cu electrodes. Surface models of Cu electrodes with a) low surface area and b) high surface area. Simulated flow streamlines and velocity vectors inside porous Cu electrodes with c) low surface area, d) high surface area. Calculated CO<sub>2</sub> concentration distribution in mM for Cu electrodes with e) low surface area and f) high surface area.

## Scale up CO<sub>2</sub> Electrochemical Flow Cell

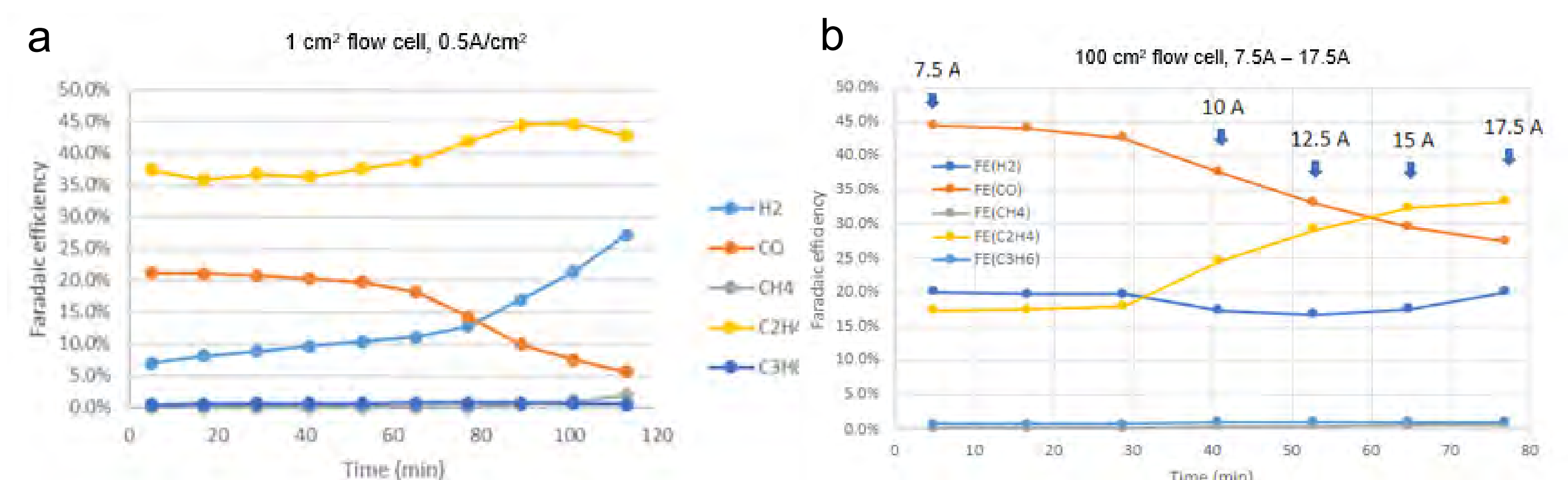


Figure 5: CO<sub>2</sub>RR performance in flow cell configurations a) 1cm<sup>2</sup> flow cell at operating current of 0.5A, b) 100 cm<sup>2</sup> flow cell at operating current of 7.5A to 17.5A.

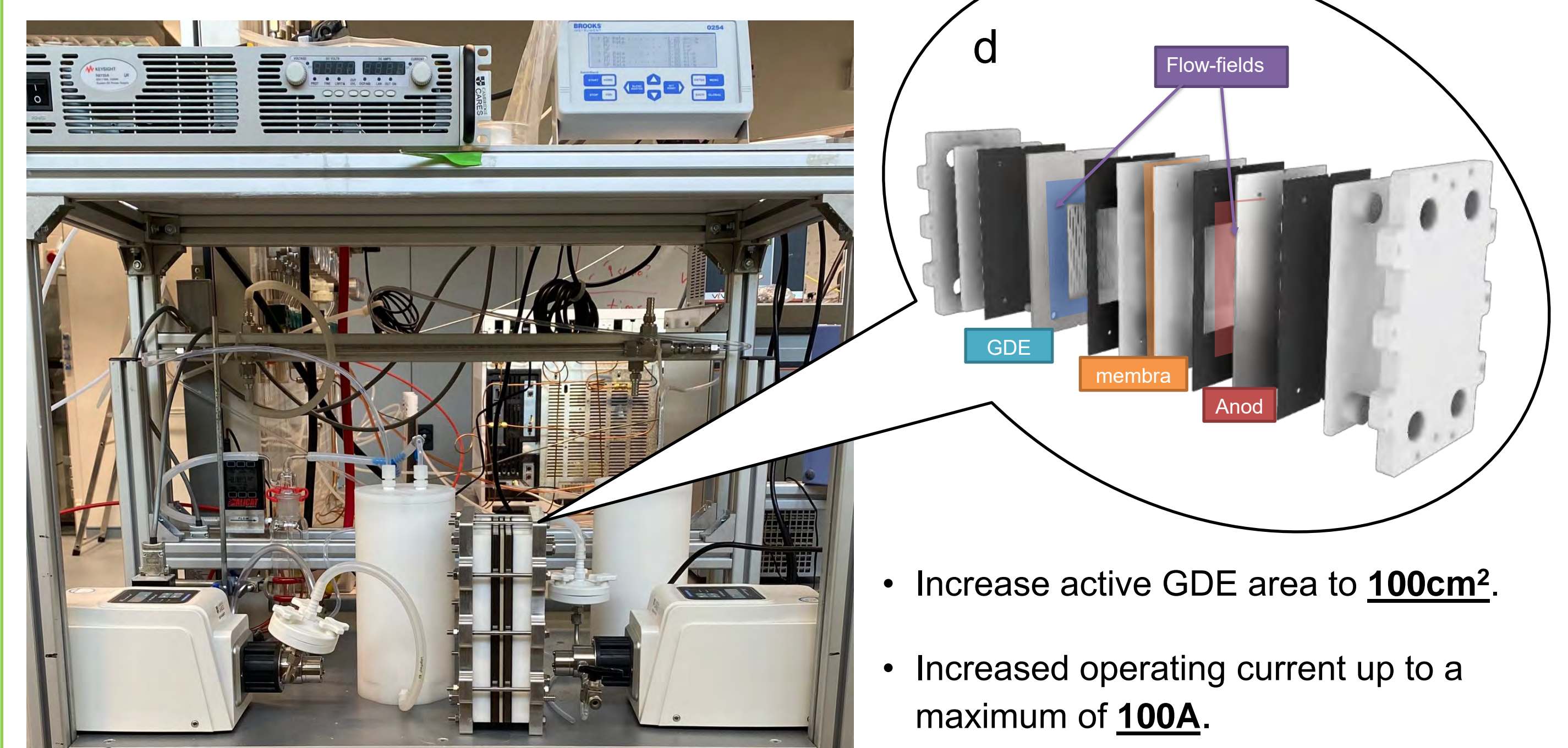


Figure 6: c) Electrochemical set-up for 100cm<sup>2</sup> flow cell configuration, d) structural design of the 100cm<sup>2</sup> flow cell.

## Future works

- Increasing **stability** of electrocatalyst using different catalyst design
- Electrode design with a different substrate with post-treatment.
- Improves the **performance** of electrocatalyst
- Introduction of co-catalyst or multi-layer catalyst design.

## References

Liu, G.; Adesina, P.; Nasiri, N.; Wang, H.; Sheng, Y.; Wu, S.; Kraft, M.; Lapkin, A. A.; Ager, J. W.; Xu, R. *Adv Funct Materials* **2022**, *32* (36)

\*Contact: rxu@ntu.edu.sg

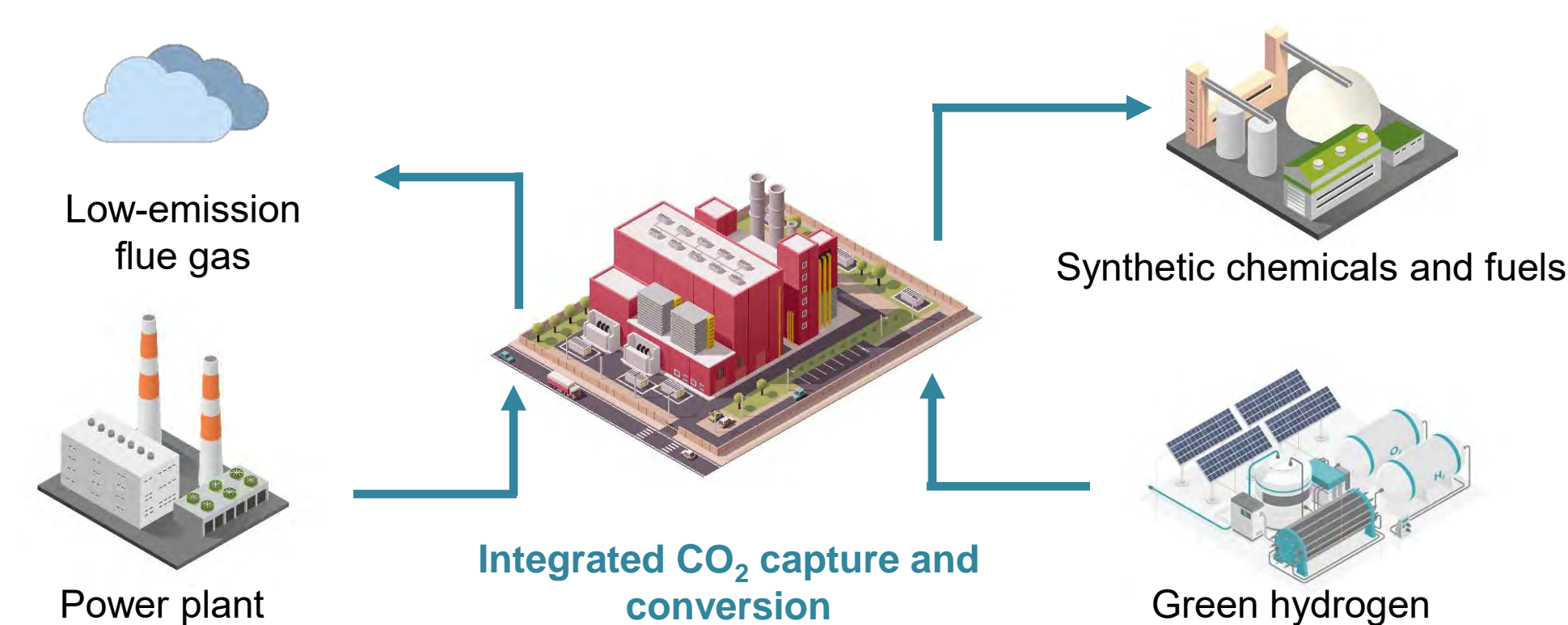
# In situ CO<sub>2</sub> Capture and Catalytic Hydrogenation at Ni/Alkaline Earth Metal Carbonate Interfaces

Xianyue Wu<sup>a,b,c</sup>, Ribooga Chang<sup>d</sup>, Ocean Cheung<sup>d</sup>, Wen Liu<sup>a,b,c,\*</sup>

## Introduction

Integrated CO<sub>2</sub> capture and utilization (ICCU) scheme facilitates the direct hydrogenation of captured CO<sub>2</sub> to fuels and chemicals (e.g., methane) without the energy-intensive step of sorbent regeneration, thereby achieving process intensification.

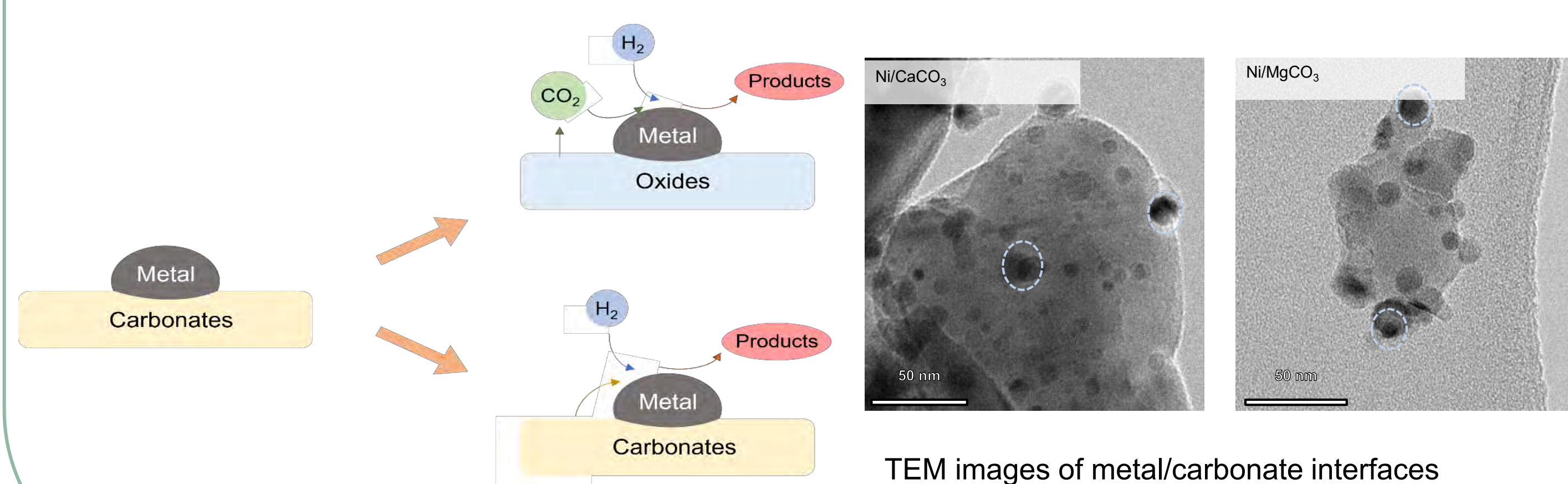
The key to the commercial deployment of ICCU is the development of dual functional materials (DFMs). First, one needs to fundamentally understand the interplay between the two functionalities.



## Methodology

The synergy between CO<sub>2</sub> sorbents and active sites for CO<sub>2</sub> hydrogenation is investigated by synthesizing model metal-carbonate interfaces.

Depending on the alkalinity of the oxides/stability of the carbonates, reaction could take distinctly different pathways.

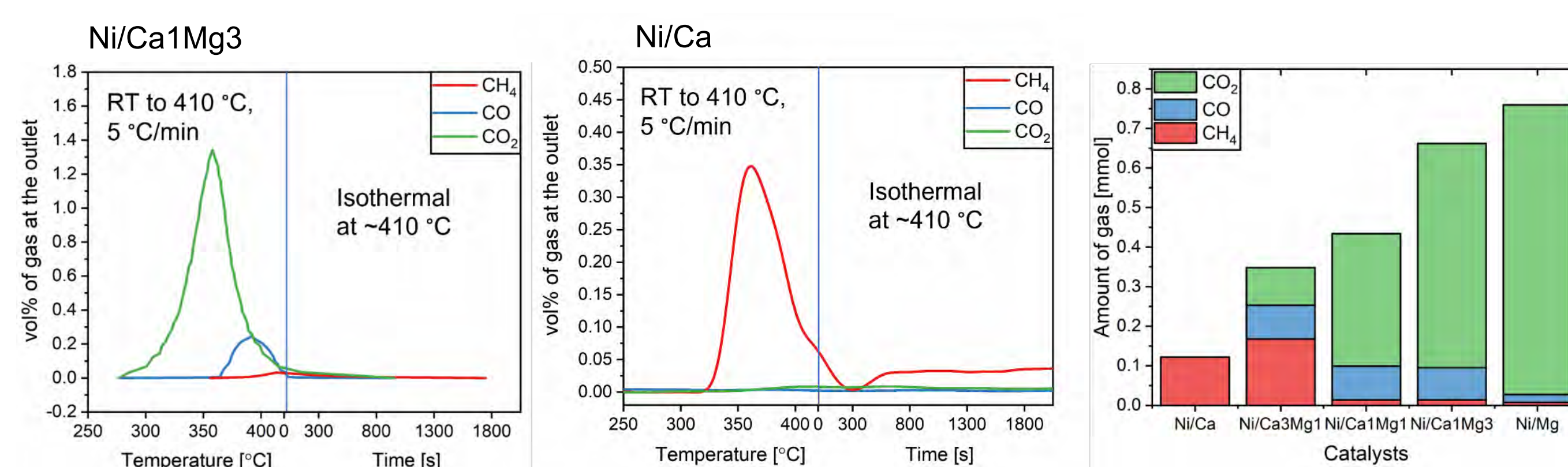


TEM images of metal/carbonate interfaces

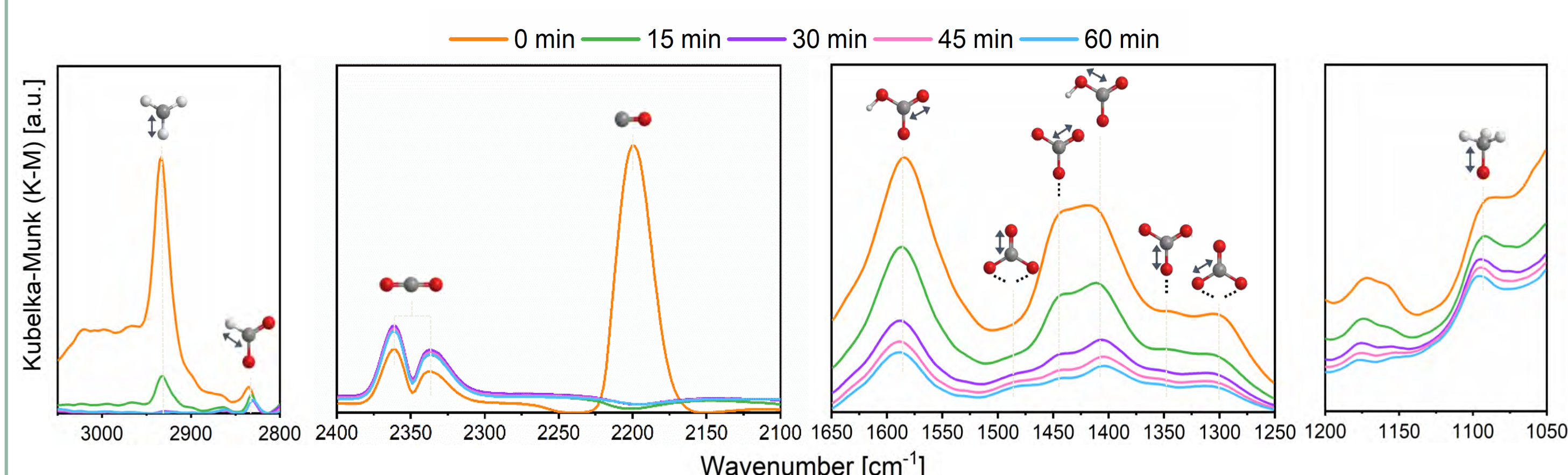
## Ni/MgCO<sub>3</sub> vs Ni/CaCO<sub>3</sub>

Ni/MgCO<sub>3</sub> favors the production of CO via the hydrogenation of re-adsorbed CO<sub>2</sub> released by MgCO<sub>3</sub> decomposition.

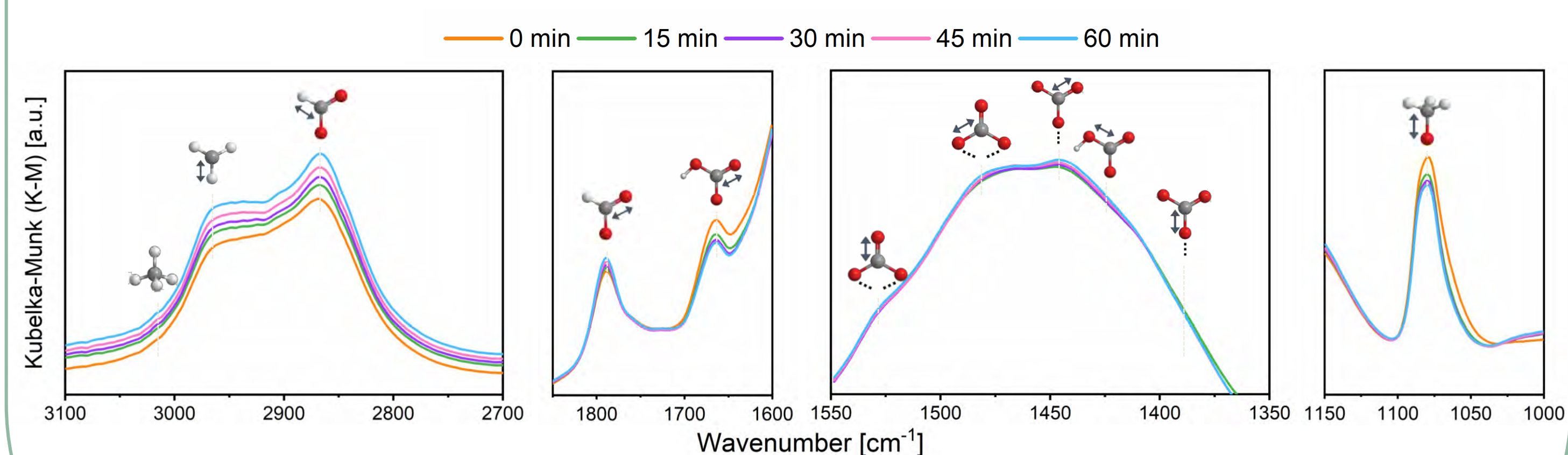
Ni/CaCO<sub>3</sub> favors the production of methane via the direct hydrogenation of carbonates.



In situ DRIFTS measurements (direct hydrogenation at 400 °C) on Ni/MgCO<sub>3</sub> reveal the decomposition of MgCO<sub>3</sub> accompanied by the formation of CO.

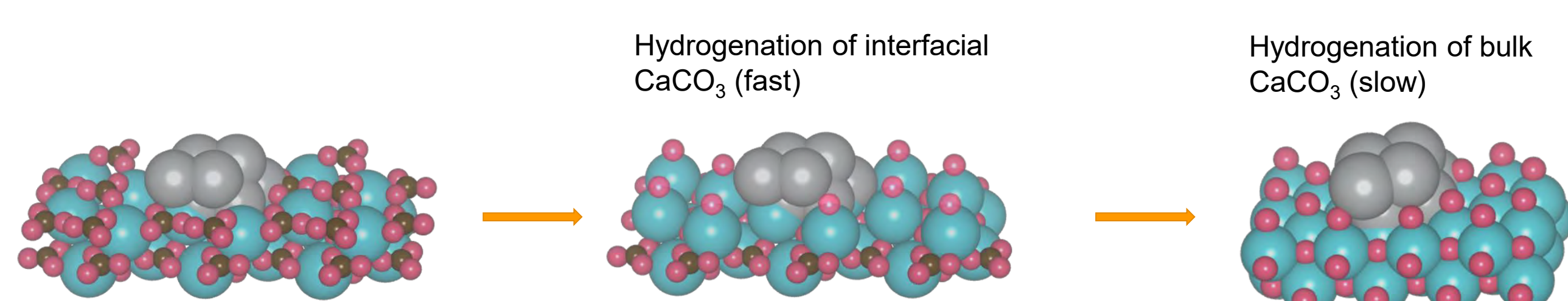
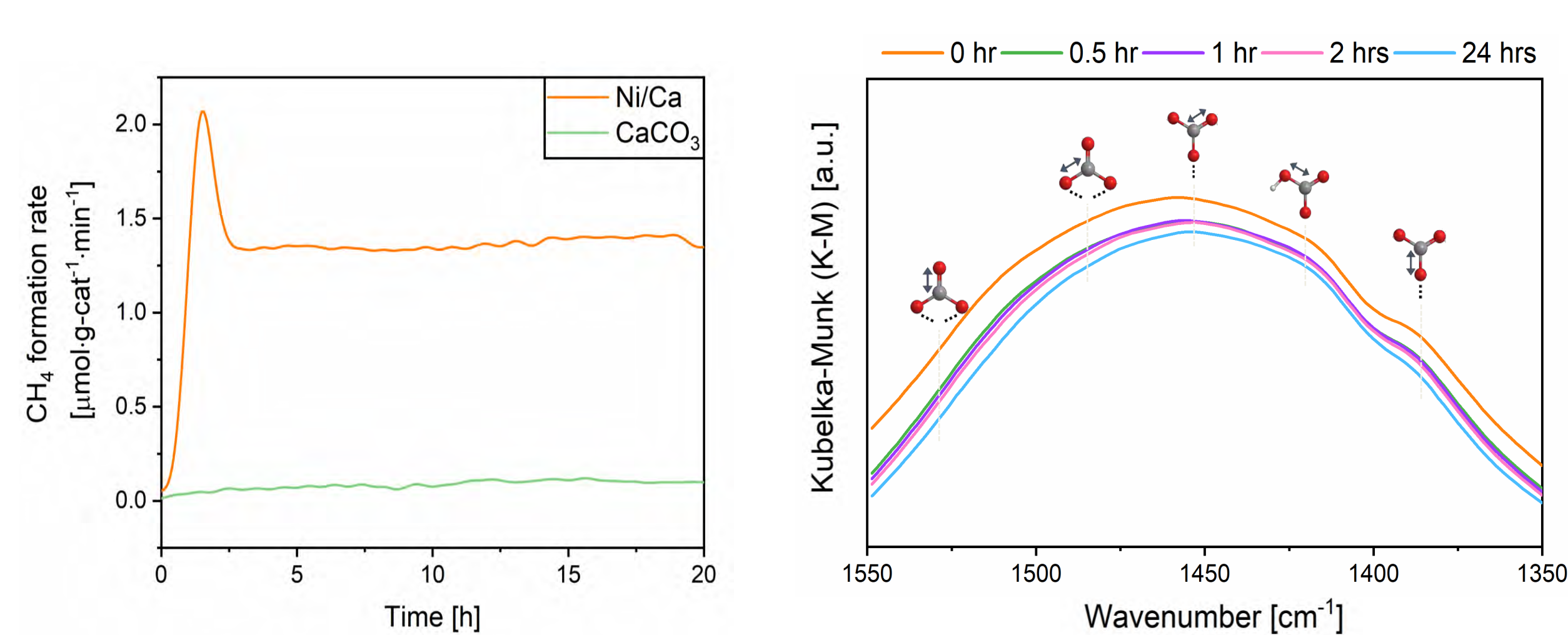


On Ni/CaCO<sub>3</sub>, stable CaCO<sub>3</sub> is slowly converted to HCOO\*, H<sub>3</sub>CO\* and eventually CH<sub>4</sub>, i.e. CO<sub>2</sub> methanation via the formate pathway.



## Kinetics of hydrogenation

The direct methanation of CaCO<sub>3</sub>, catalyzed by Ni, consists of a fast stage (hydrogenation of surface carbonate) and a slow stage (hydrogenation of bulk carbonate).



## References

- Journal of CO<sub>2</sub> Utilization*, Volume 58, 2022, 101922.  
*Catalysts*, 2017, Volume 7, Issue 3, 88  
*Applied Catalysis B: Environmental*, Volume 310, 2022, 121294, ISSN 0926-3373  
*Applied Catalysis B: Environmental*, Volume 338, 5 December 2023, 123053 (this work)

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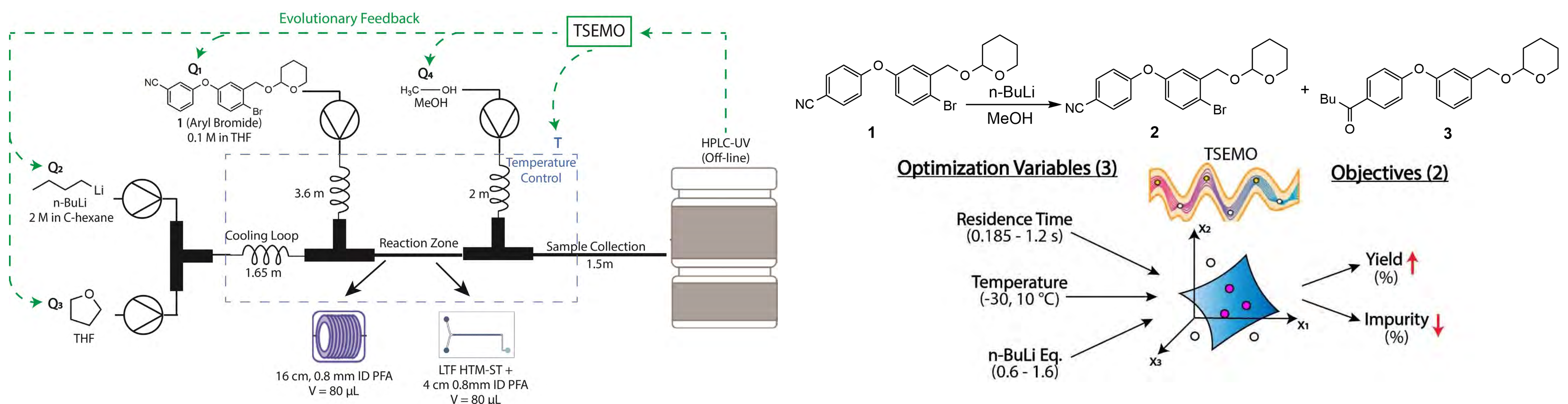
# A Machine Learning-Enabled Process Optimization of Ultra-Fast Flow Chemistry with Multiple Reaction Metrics

[Dogancan Karan<sup>1</sup>, Paul McDaid<sup>2</sup>, Alexei A. Lapkin<sup>1,3</sup>]

## Introduction

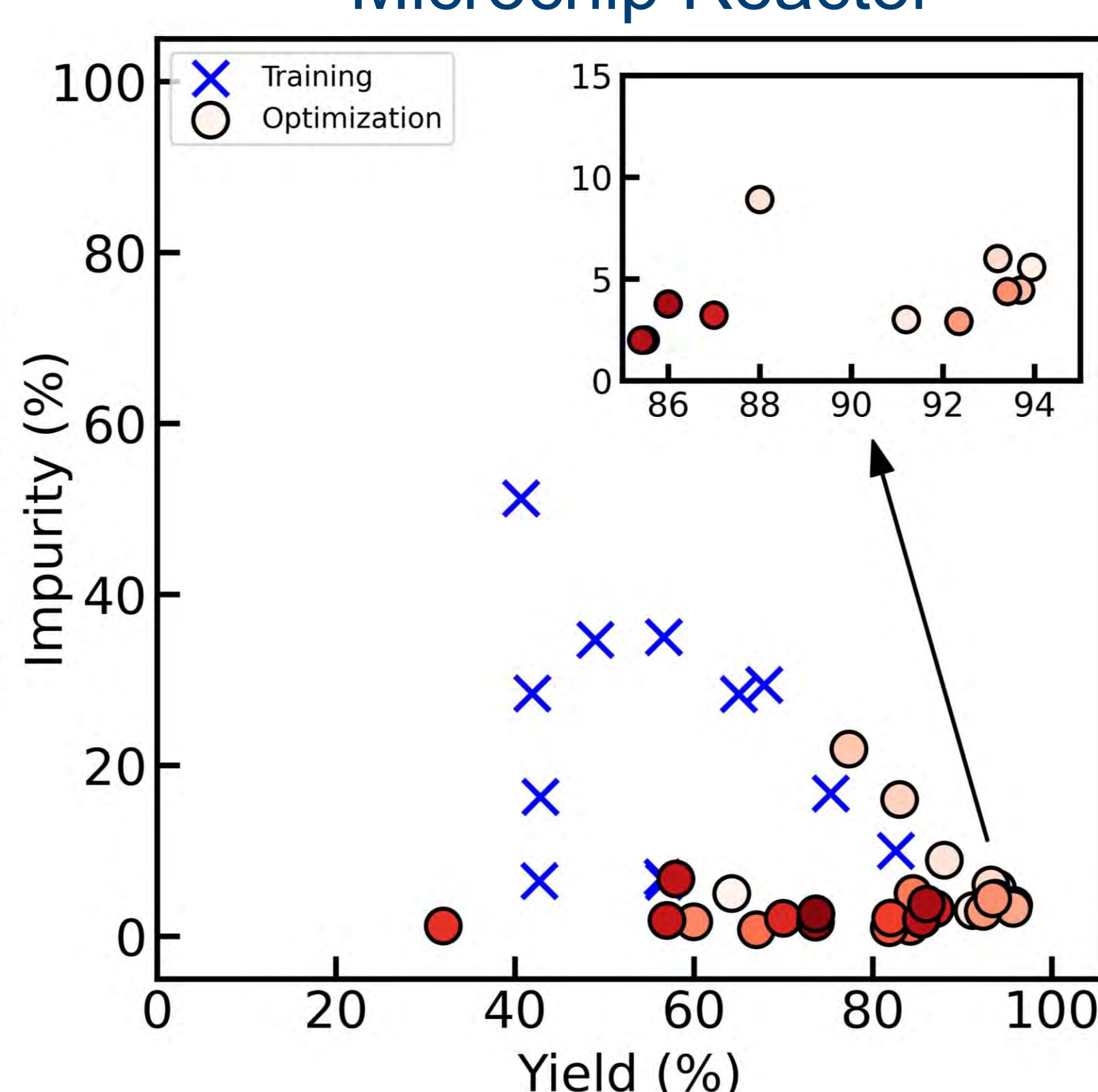
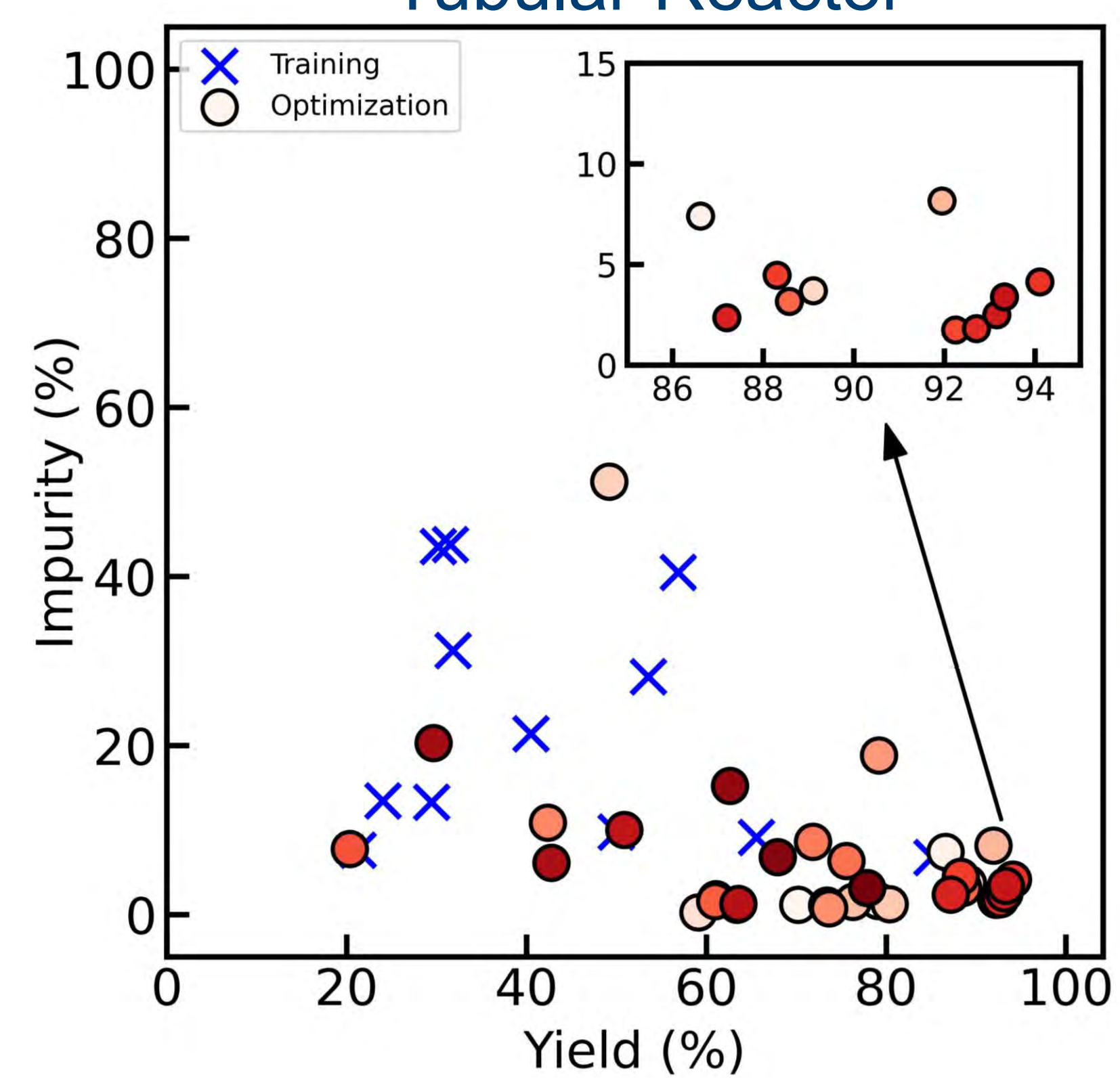
Discovering the optimum process parameters of lithium-halogen exchange reactions represents a highly challenging problem. Herein, we demonstrate the development of a machine learning workflow coupled with a flow chemistry platform to build process knowledge of an extremely fast and difficult to control chemistry with multiple conflicting objectives. The workflow revealed rich information about the reaction studied compared conventional approaches.

- A multi-objective optimization problem is solved via TSEMO where yield (2) is maximized, impurity (3) is minimized. Three continuous variables were optimized



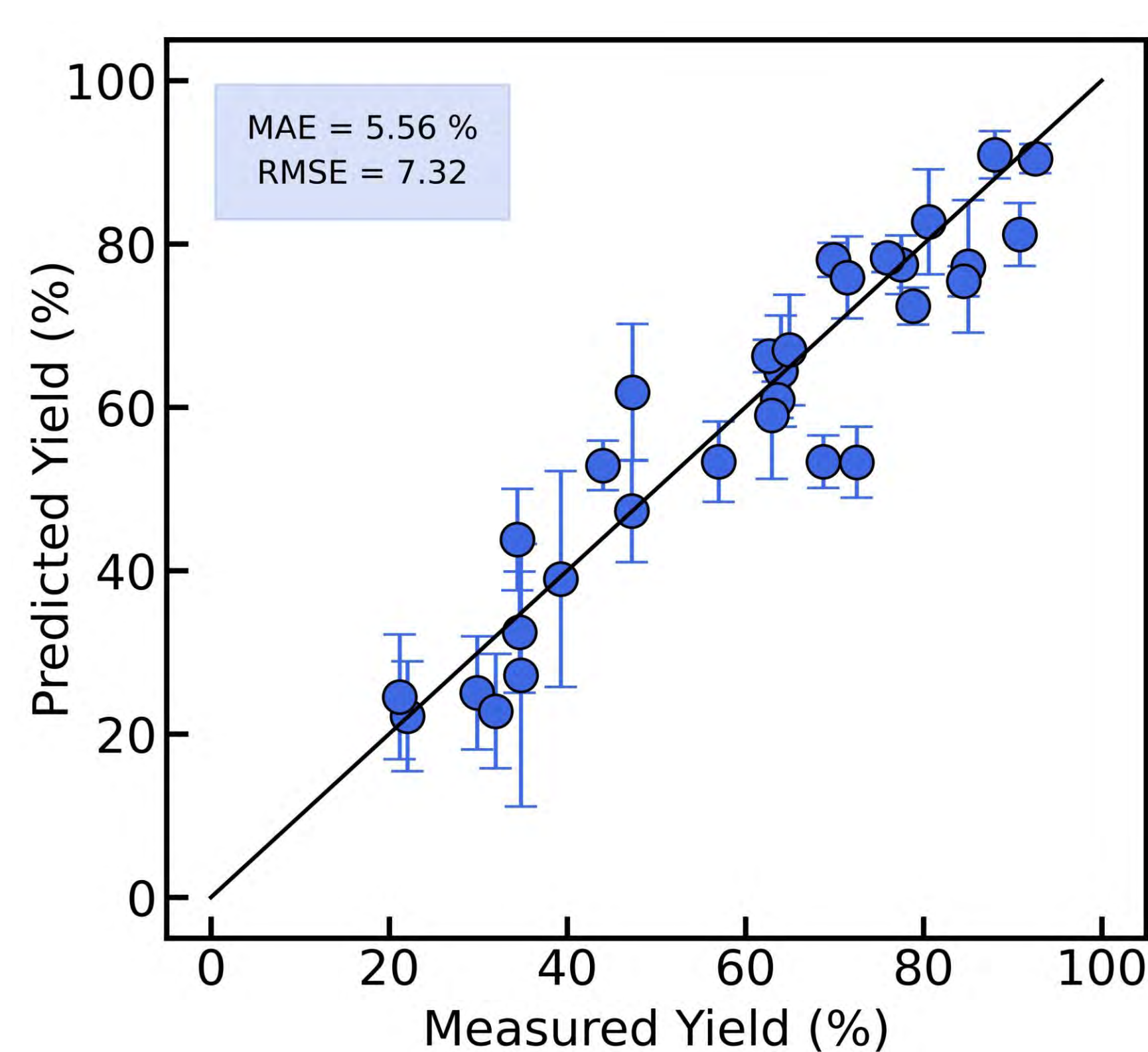
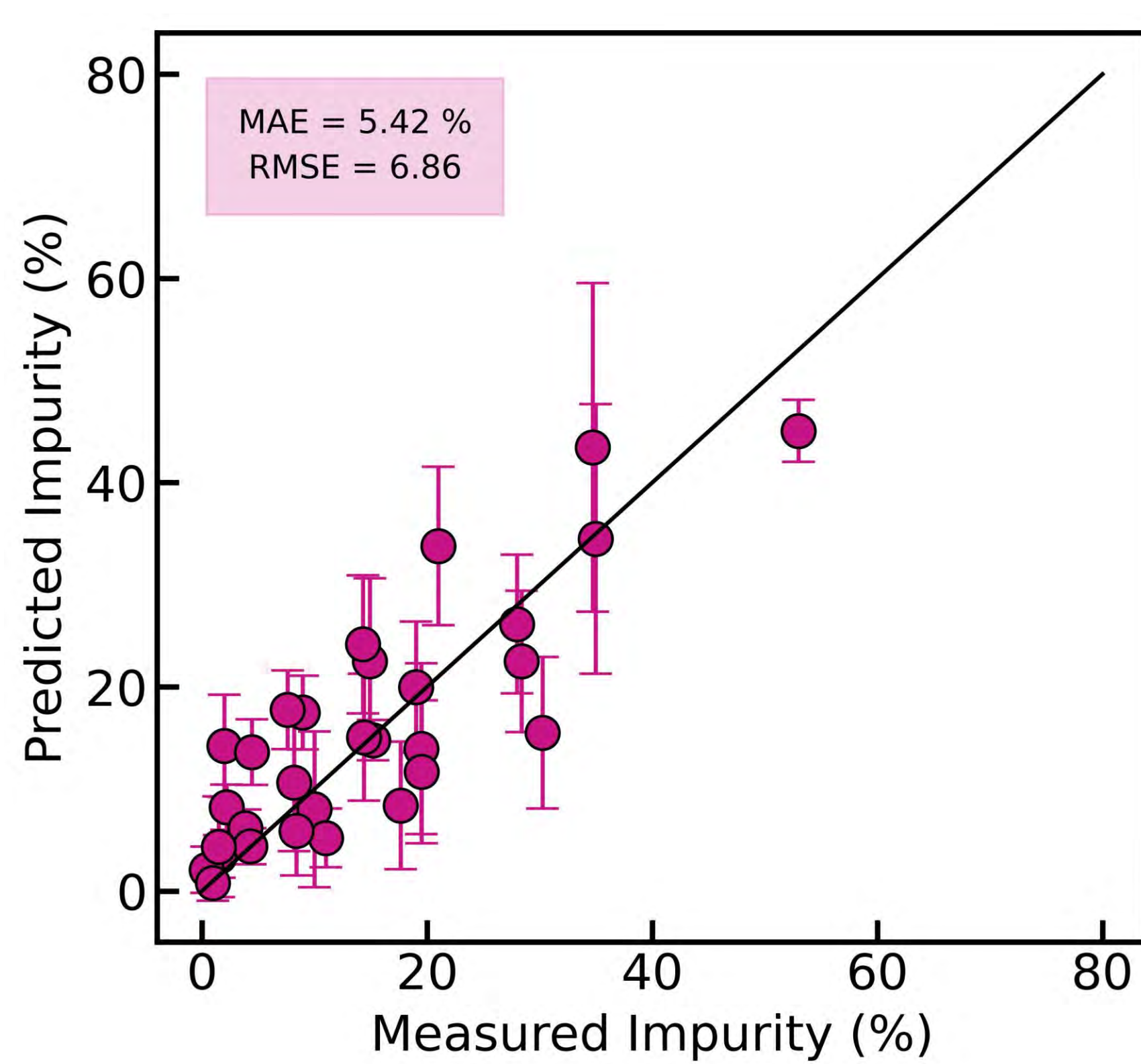
### Tubular Reactor

### Microchip Reactor



- Two different reactor configuration is tested
- TSEMO identifies the Pareto front in less than 50 experiments.
- Complete trade-off between two objectives can be identified.

☐ Mixing-controlled-process in tubular reactor, kinetically-controlled process in chip reactor



- Gaussian Process (GP) surrogate models trained within TSEMO are used to predict the outcome of unseen experiments.
- 30 conditions are predicted from the ML model trained during optimization.

☐ Accurate predictions of unseen conditions

☐ Provides additional interpretability and process knowledge.

- ✓ Robust and data efficient method to obtain process knowledge
- ✓ First demonstration of multi-objective optimization of ultra-fast chemistry

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## References

[1] Jeraal, Mohammed I. et. al. *Chemistry-Methods* 1.1 (2021): 71-77.

<sup>1</sup> Cambridge Centre for Advanced Research and Education in Singapore, CARES Ltd.

<sup>2</sup> Pfizer Private Limited, Co. Cork, Ireland

<sup>3</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge

"This research was a member-specific project with Pfizer as part of the Pharmaceutical Innovation Programme Singapore (PIPS)"

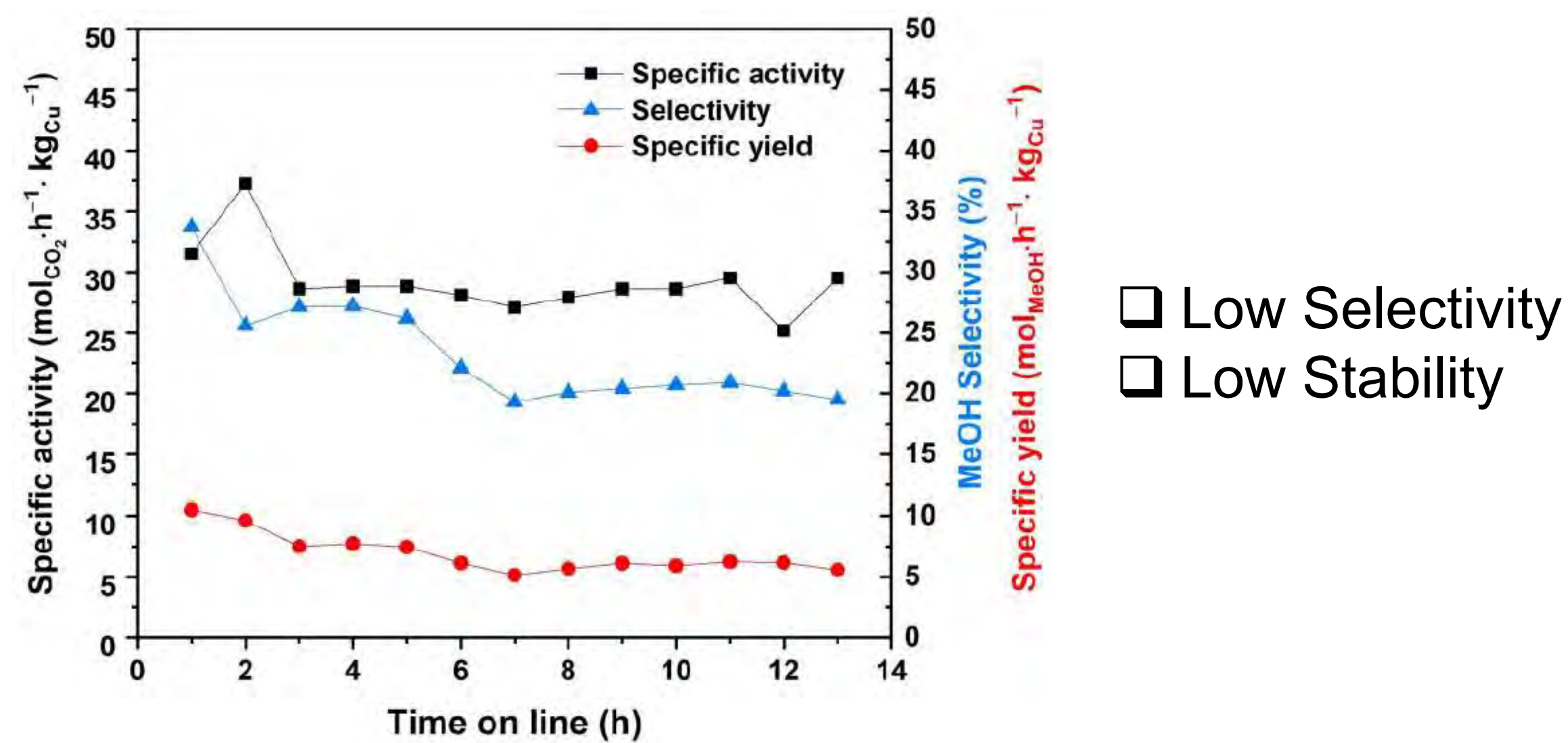
# CO<sub>2</sub> Hydrogenation to Methanol

Yu Shao<sup>1,2</sup>, Wen Liu<sup>1,2</sup>, Tej Choksi<sup>1,2</sup>, Ning Yan<sup>1,3</sup>, Hua Chun Zeng<sup>1,3</sup>, Alexei Lapkin<sup>1,4</sup>, Laura Torrente<sup>1,4</sup>

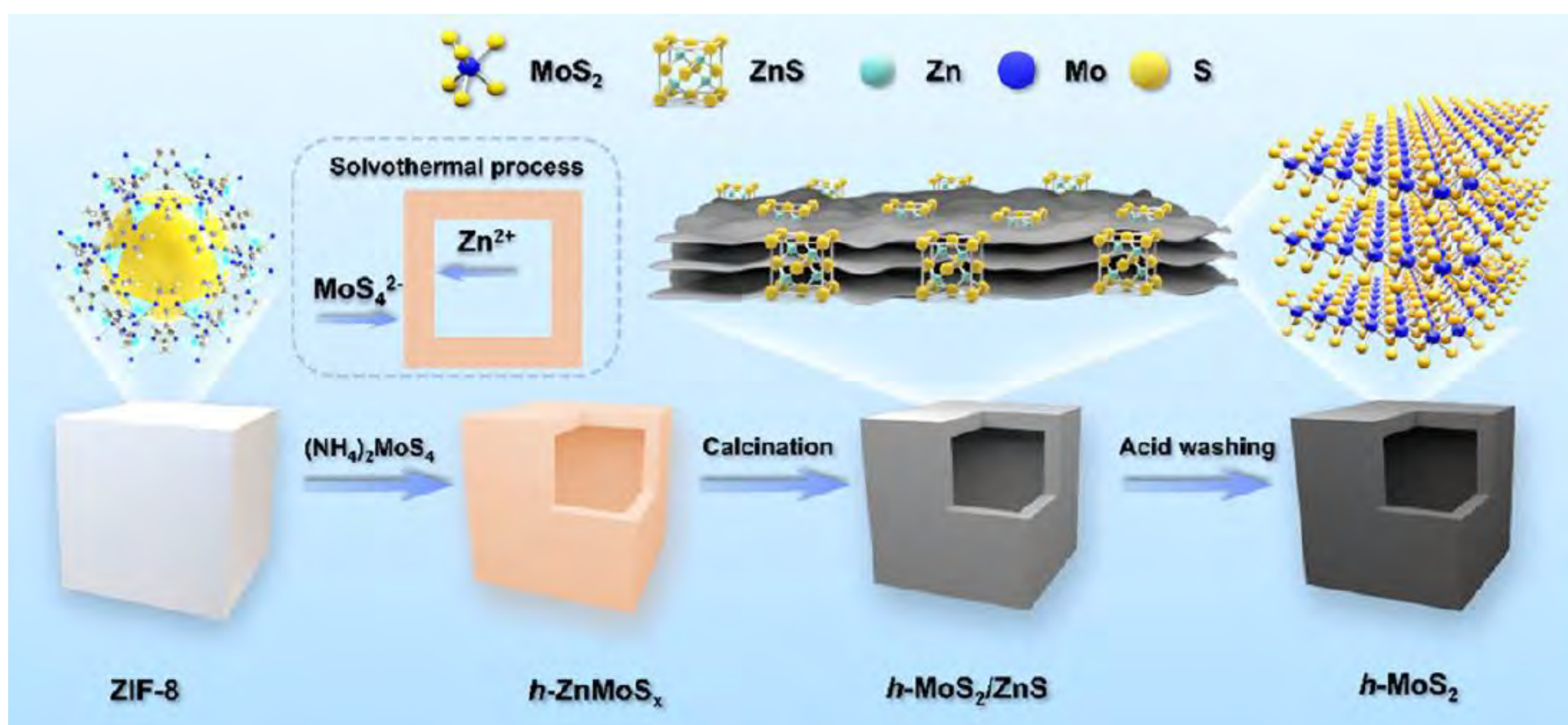
## Introduction

Researchers from NTU, NUS, and Cambridge have developed several high-performance, noble-metal-free catalysts and validated them for the hydrogenation of CO<sub>2</sub> to methanol (MeOH), a key gateway chemical for achieving carbon circularity for the chemical industry. These catalysts successfully overcome process challenges such as low MeOH selectivity and poor performance stability faced by conventional catalysts.

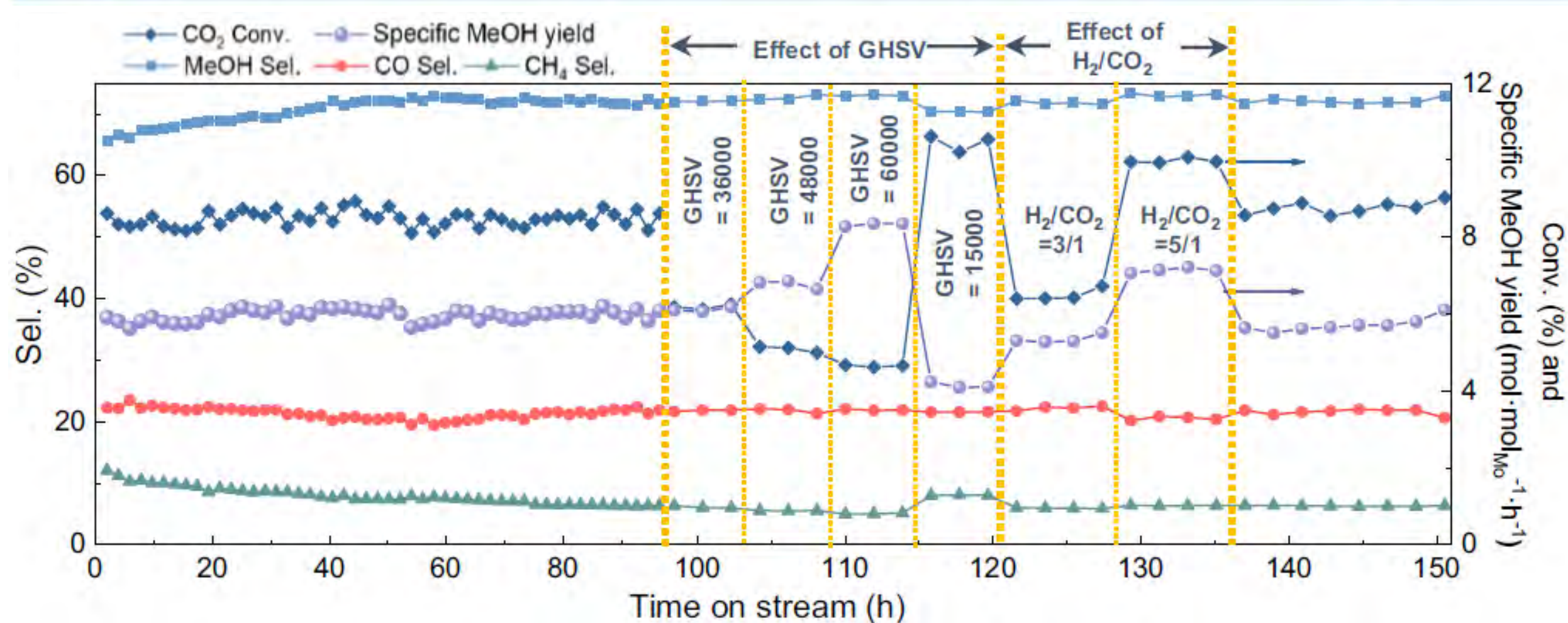
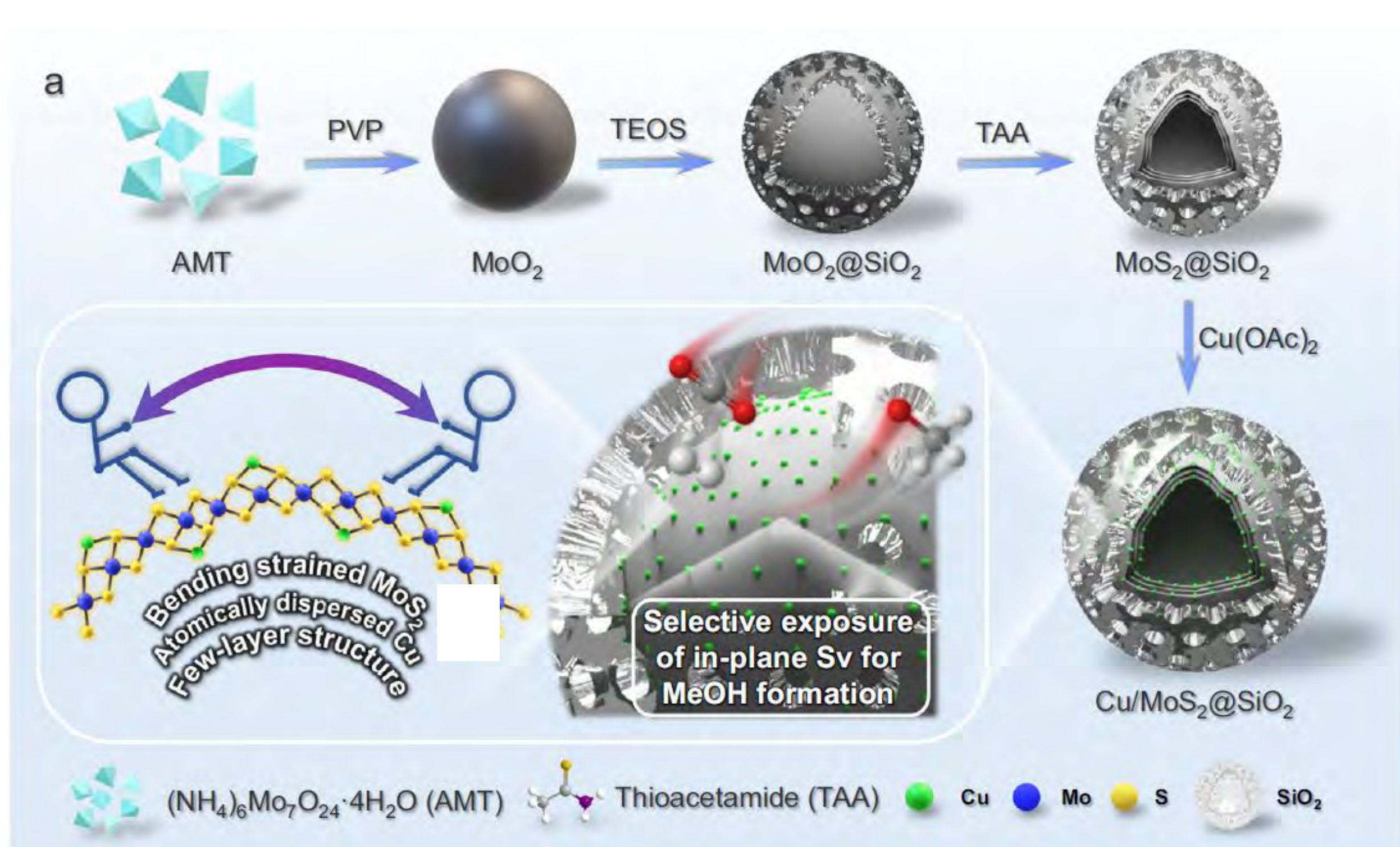
### Commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst



### MoS<sub>2</sub> Nanosheets with S-Vacancies



### Boxlike Assemblages of MoS<sub>2</sub> Nanosheets with Edge Blockage

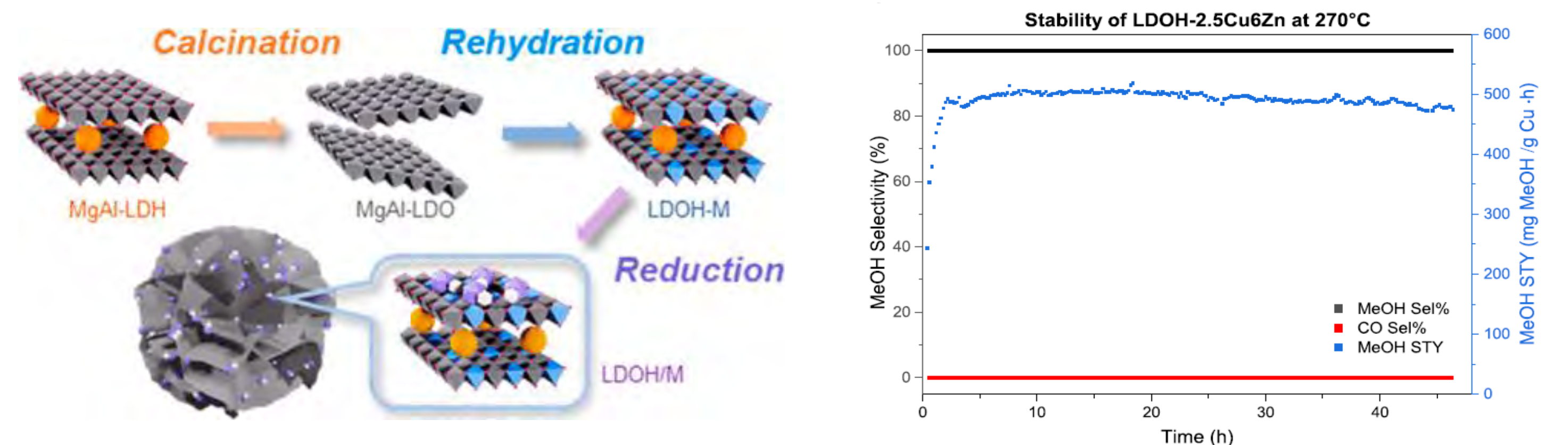


### mSiO<sub>2</sub>-Encapsulated MoS<sub>2</sub> Catalysts with Fullerene-Like Structure and Atomic Copper (Cu/MoS<sub>2</sub>@SiO<sub>2</sub>).

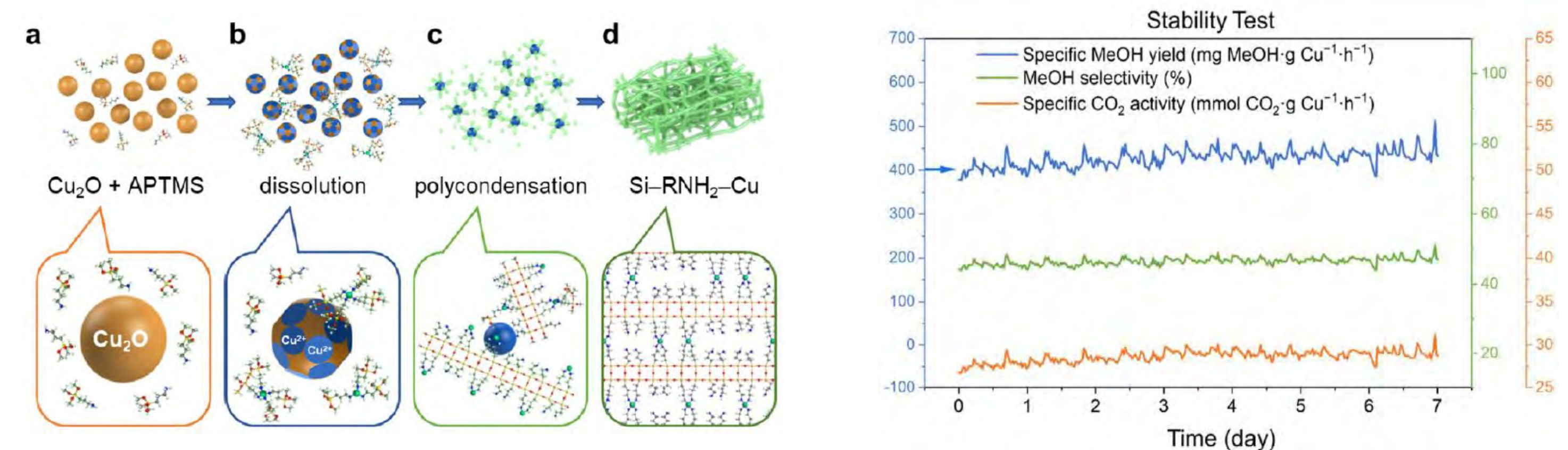
## References

Adv. Funct. Mater. 2021, 31, 2102896. Ind. Eng. Chem. Res. 2023, 62, 1877-1890.  
 ACS Catal. 2022, 12, 9872-9886. J. Mater. Chem. A 2023, 11, 2698-2710.  
 Nat. Commun. 2023, 14, 5872.  
 ACS Appl. Energy Mater. 2023, 6, 782-794.  
 ACS Catal. 2022, 12, 5750-5765.  
 Appl. Catal. B 2022, 306, 121098.

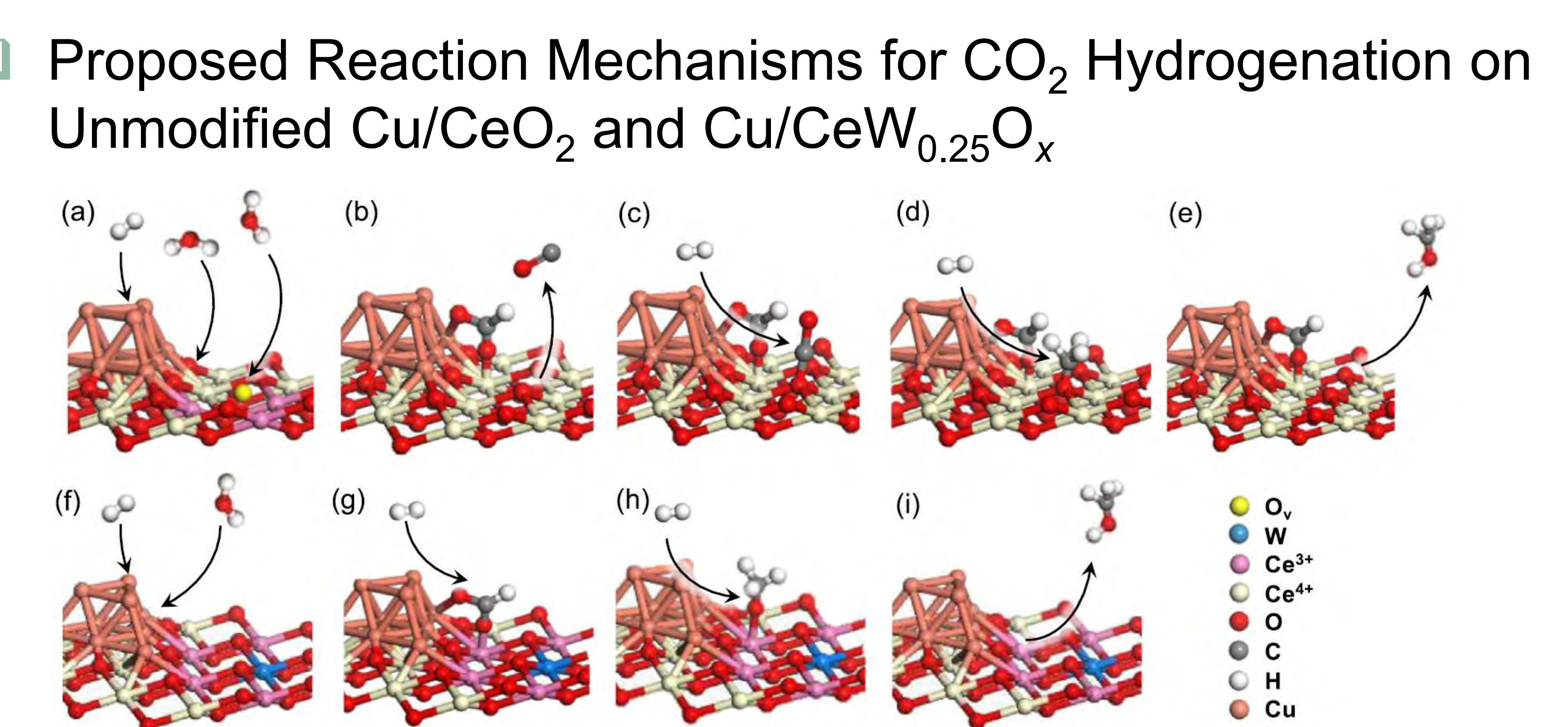
### New Synthetic Strategies for Conventional Cu-Zn Recipe



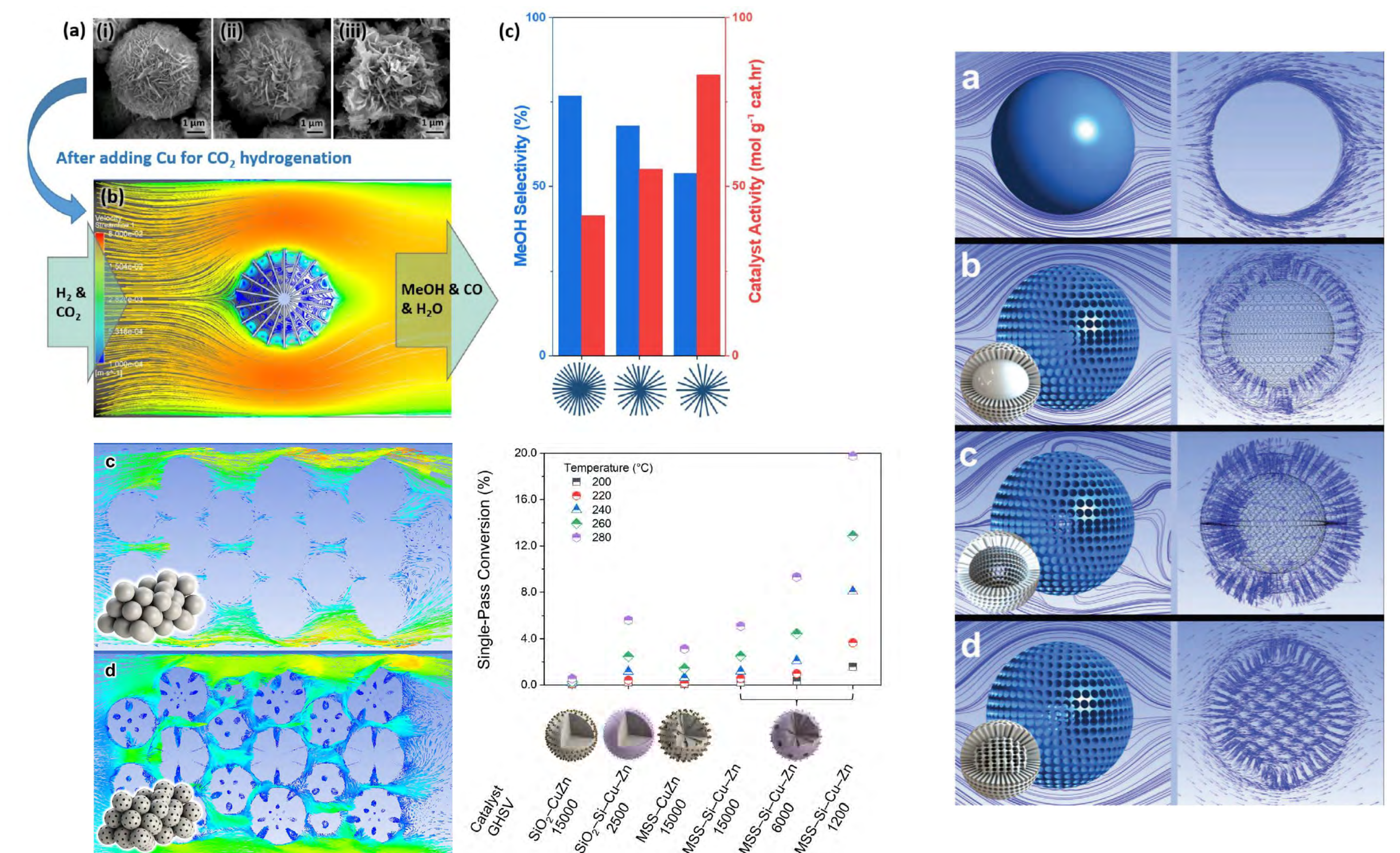
### Memory Effect of Hydrotalcite



### Proposed Reaction Mechanisms for CO<sub>2</sub> Hydrogenation on Unmodified Cu/CeO<sub>2</sub> and Cu/CeW<sub>0.25</sub>O<sub>x</sub>



### Computational Fluid Dynamics (CFD) Studies



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<sup>2</sup> School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore

<sup>3</sup> Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

<sup>4</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge, United Kingdom

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