# German Aerospace Center

# Deutsches Zentrum für Luft- und Raumfahrt, DLR

Institute of Engineering Thermodynamics Department of Electrochemical Energy Technology

# Multilayer GDEs for long-term stable acidic CO<sub>2</sub> reduction to formic acid

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### Motivation

Why electrochemical CO<sub>2</sub> Reduction on Gas Diffusion Electrodes (GDEs)?

- Sustainable pathway: Employs renewable electricity to reduce CO<sub>2</sub>, supporting greenhouse gas neutrality and climate targets.
- Scalable technology: Converts CO<sub>2</sub> from industrial point sources (waste incineration, cement, biogenic processes) into value-added products such as CO, ethylene, and formic acid.
- Acidic electrolysis to formic acid is preferred over alkaline conditions due to significant advantages for down-stream processing; no requirement for protonation of formate and less carbonate accumulation.
- Current densities and FE already in the range but long-term stability and achievable formic acid concentrations are still far from the industrial requirements for economically competitive formic acid production.

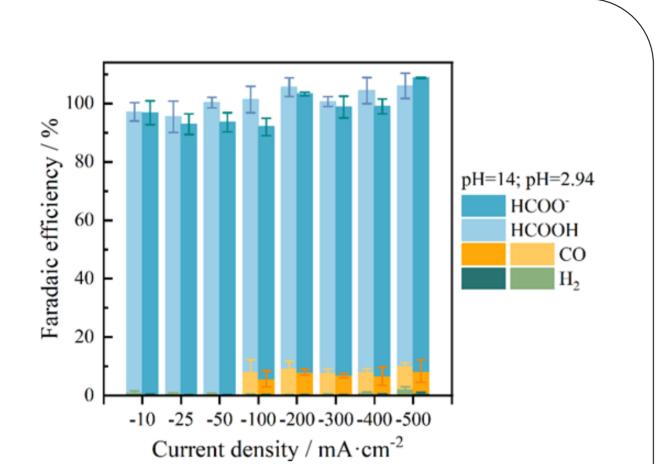
### **Acidic CO2RR**

#### **Electrochemical performance**

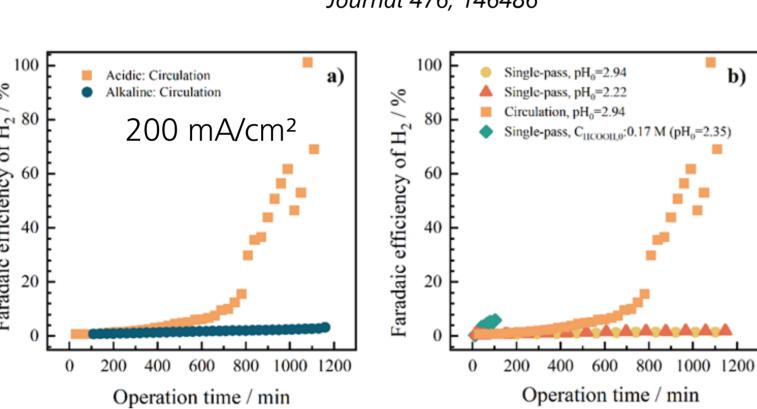
- We showed comparable performance in bulk acidic and in alkaline conditions
- HCOOH production up to 500 mA/cm<sup>2</sup> with ~90% Faradaic efficiency.
- Local pH in both cases similar due accumulation within product GDE structure

#### **Long-term stability**

- In circulating flow performance breaks down in acidic conditions caused by HCOOH accumulation
- In single-pass mode stable behavior up to 20h demonstrated
- Very low HCOOH concentration achievable in single-pass mode



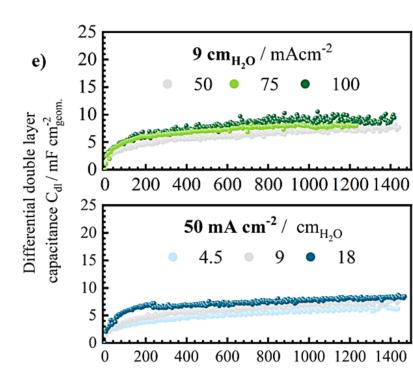
Chen et al. (2023) Chemical Engineering Journal 476, 146486



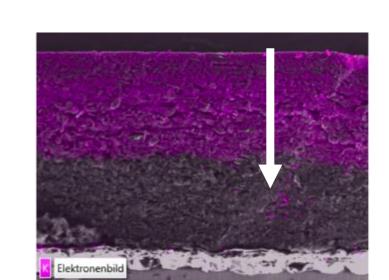
### Electrode Design

#### Limitations of thick single-layer electrode design

- Continuous electrolyte intrusion into the GDE caused by electrowetting during prolonged operation.
- Extended diffusion pathways which limit mass transport

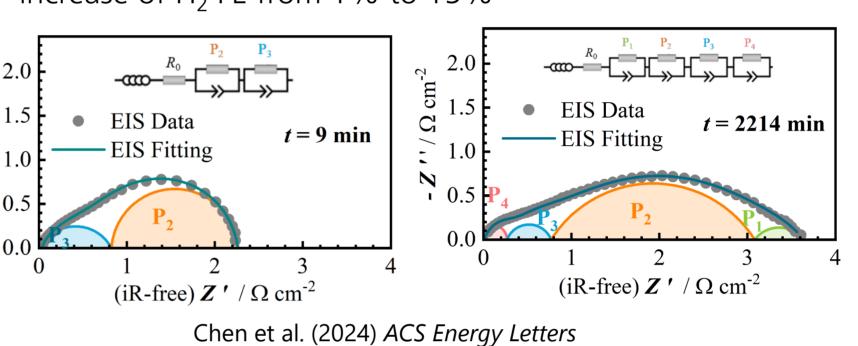


Time / min



Double layer capacitance via EIS SEM/EDX on cross-section shows electrolyte penetration

#### 100 mA/cm<sup>2</sup>, 12°C to accelerate degradation, increase of H<sub>2</sub> FE from 1% to 15%



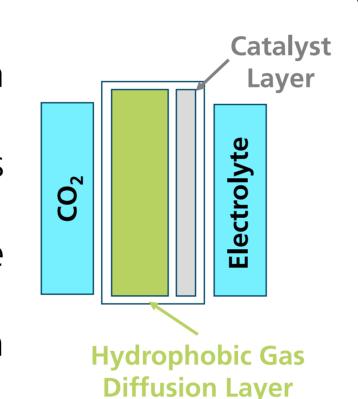
9, 6096-6103.

### **Degradation study**

- Long-term degradation governed by carbonate precipitation in GDE
- Systematic study via EIS and DRT
- Shorter diffusion path into bulk electrolyte desired

## Multilayer design with hydrophobic polymer backing

- Commercial carbon-based GDLs unsuitable for long-term stability due to too low hydrophobicity and electro-wetting.
- Porous polymer membranes could serve as effective GDLs due to their **high hydrophobicity**.
- PTFE membranes resist flooding and prevent electrolyte intrusion caused by electrowetting.
- Expected durability under prolonged operation in comparison with commercial GDLs.

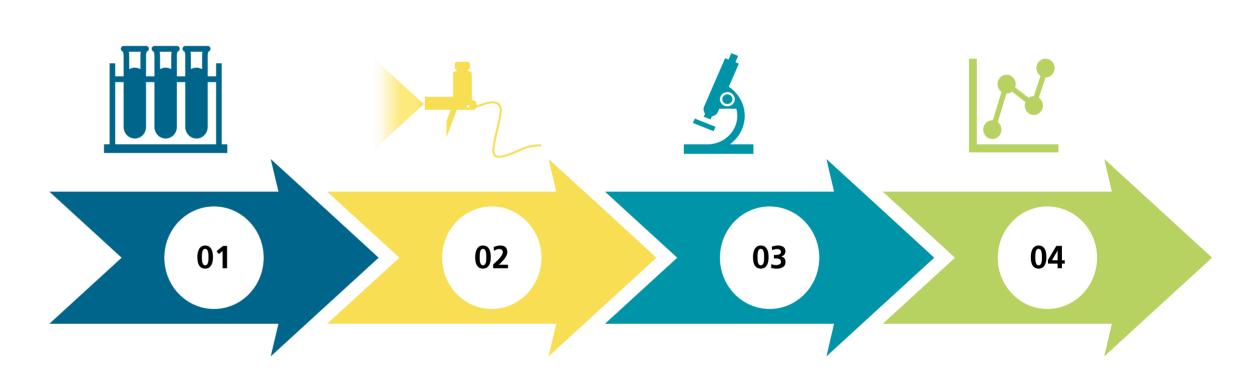




### From single- to multi-layer GDE assembly (Multilayer approach)

- Highly hydrophobic gas diffusion layer (GDL): Prevents electrolyte intrusion and enhances gas transport.
- Thin catalyst layer: Minimizes product accumulation and improves reaction efficiency.

## **Approach and Methods**



#### Air Brushing Ink Preparation

- Catalyst: Bi-coated acetylene black
- Uniform thickness Parameters: Flow
- Binder: Fumion FAA-3 rate and volume
- Method: Ultrasonic of catalyst ink Dispersion

### **Physical** Characterization

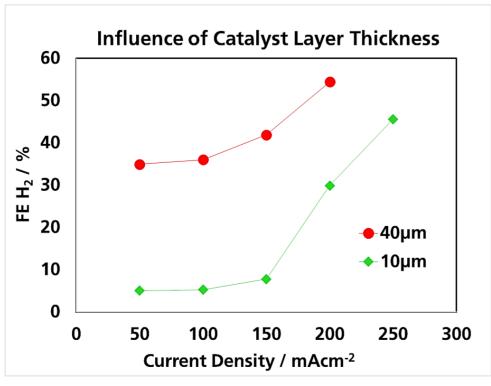
- Thickness
- measurement
- Catalyst loading SEM/EDX

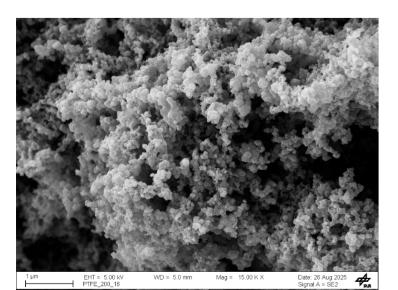
### **Electrochemical** Characterization

- Multistep-
- Chronopotentiometry
- Range: 0 250 mA/cm2
- Step size: 20 minutes

### **Preliminary Results**

Material Characteristics			
GDE	Binder:Catalyst Ratio	Catalyst Loading / mgcm <sup>-2</sup>	Coating Thickness / µm
GDE_A	1:4	0.703	40.28
GDE_B	1:4	0.281	9.28



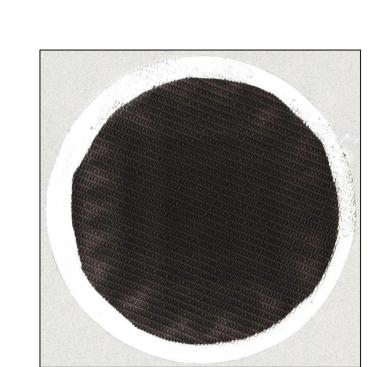


### **Performance Evaluation**

- Both electrodes show similar overall trends..
- Catalyst layer with 10µm thickness largely supresses HER up to 150 mA/cm<sup>2</sup>.
- Thicker layer (40µm) exhibit transport limitation and yield higher HER.

## Conclusion

- Successfully fabricated robust PTFE-based GDEs.
- Electrodes demonstrated catalytic activity with performance trends indicating that reduced catalyst layer thickness suppresses HER.
- Further systematic studies are required electrode structure-performance understand relationships.
- Optimizing contacting methods remains a key challenge.
- Long-term stability and benchmarking versus thick single layer GDEs currently under investigation.



> PTFE membrane electrode



### Acknowledgements

The IGF project Galmatrode II (01IF23102N) is funded by the Federal Ministry for Economic Affairs and Climate Protection.

We gratefully acknowledge the great cooperation with the partners: University of Stuttgart and fem (Forschungsinstitut Edelmetalle & Metallchemie).



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