

Motivation

Why electrochemical CO₂ Reduction on Gas Diffusion Electrodes (GDEs)?

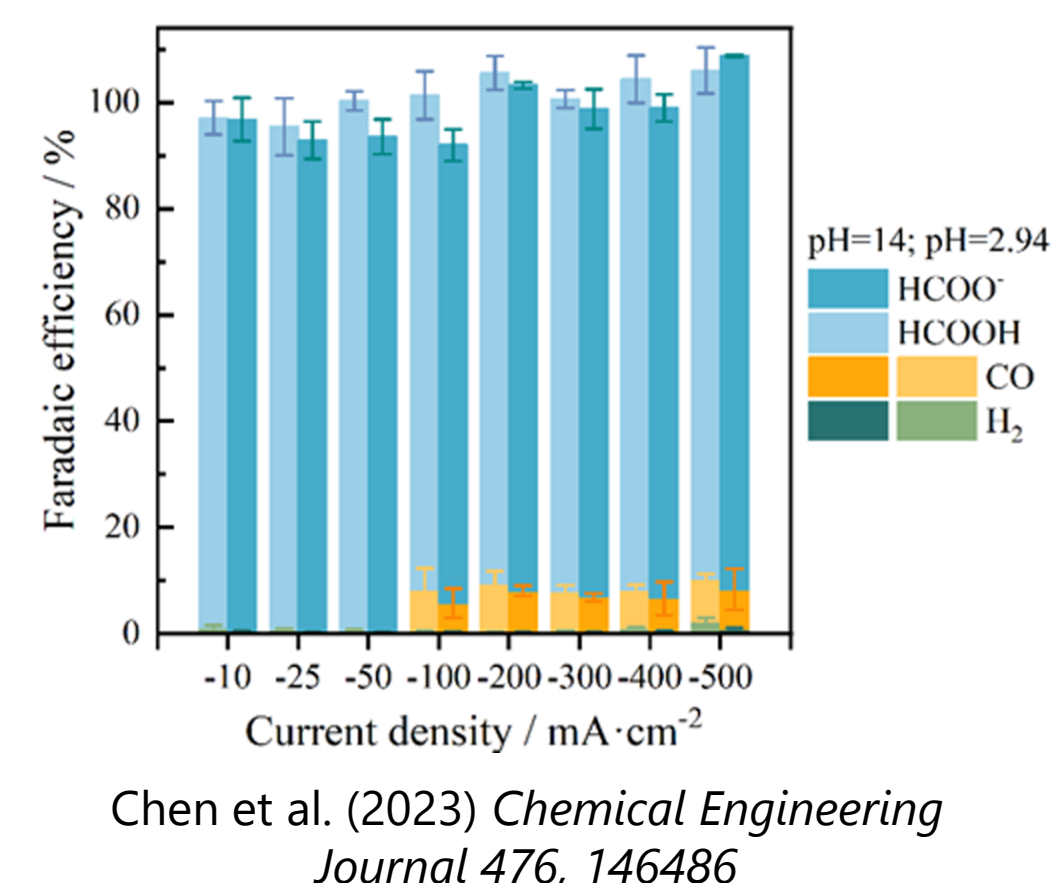
- **Sustainable pathway:** Employs renewable electricity to reduce CO₂, supporting greenhouse gas neutrality and climate targets.
- **Scalable technology:** Converts CO₂ from industrial point sources (waste incineration, cement, biogenic processes) into value-added products

- 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 CO₂eRR & single layer GDE limitation

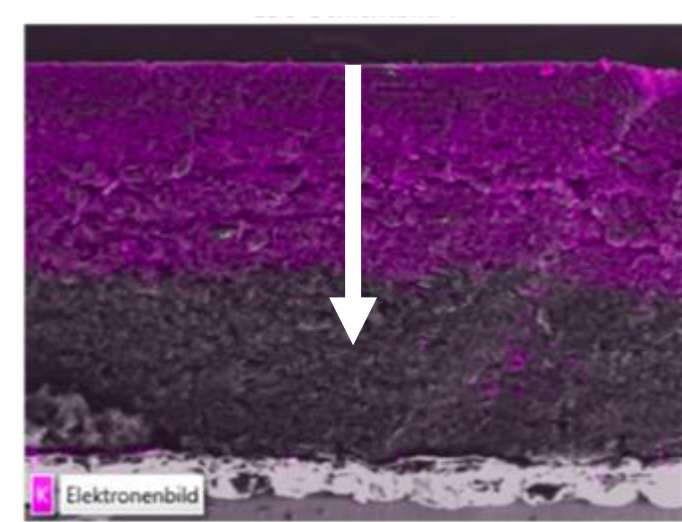
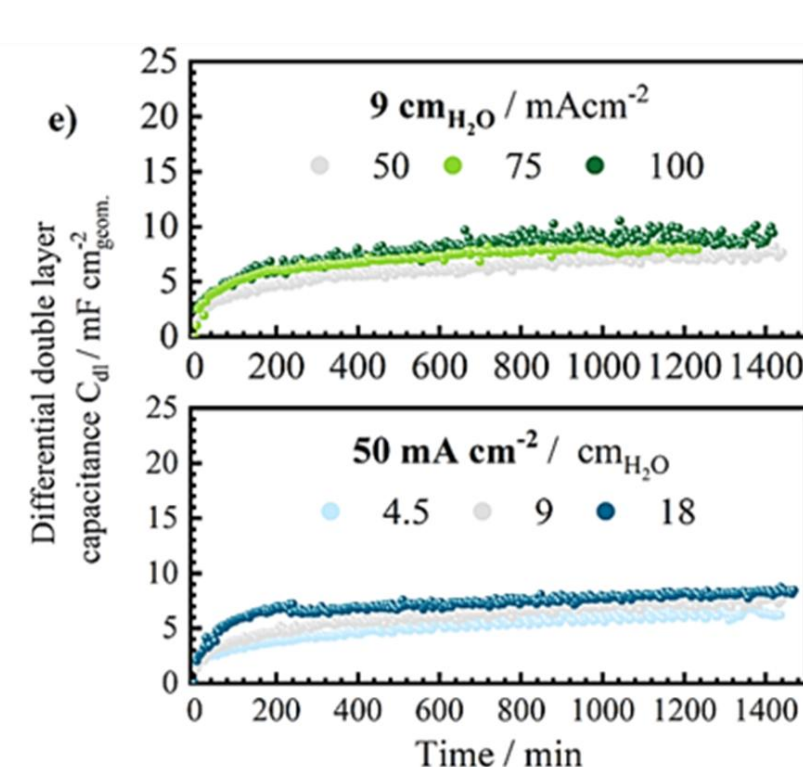
Electrochemical performance

- Comparable performance in bulk acidic and in alkaline conditions
- HCOOH production up to 500 mA/cm² with ~90% Faradaic efficiency.
- Local acidic pH in both cases similar due to product accumulation within GDE structure



Limitations of thick single-layer electrode design

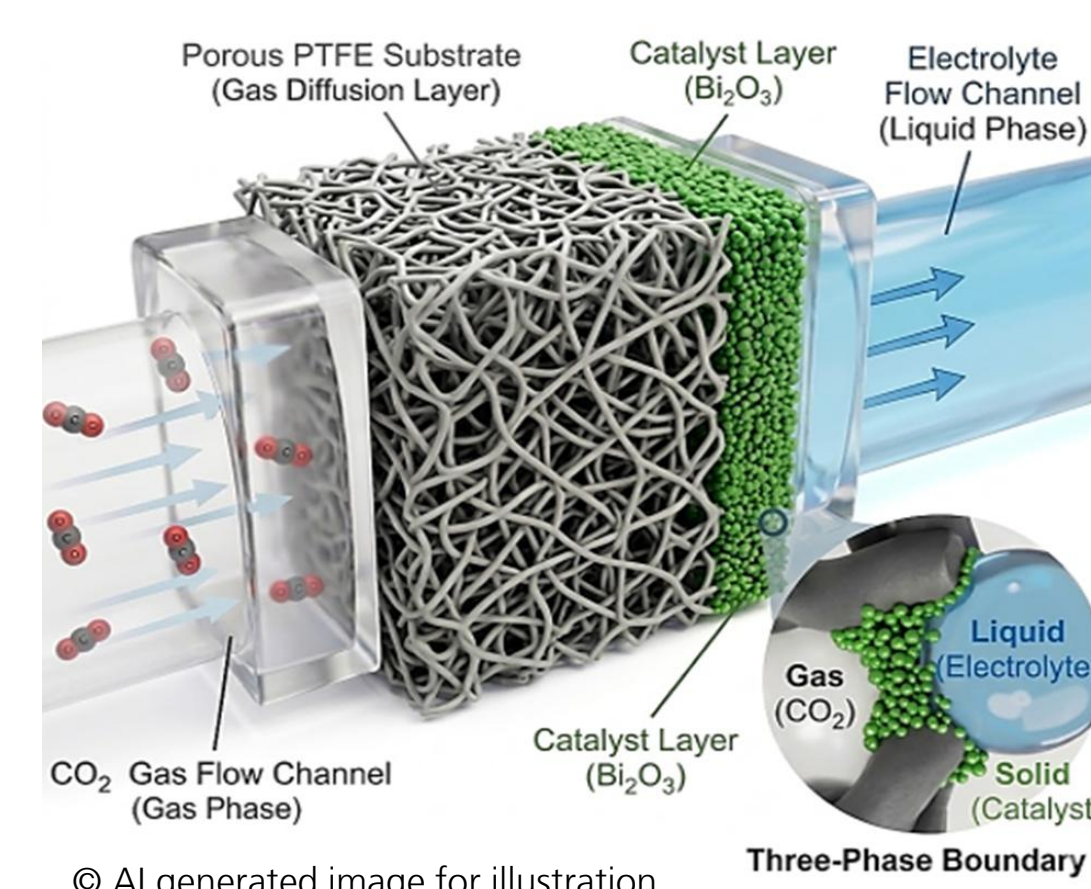
- Continuous electrolyte intrusion into the GDE caused by electrowetting during prolonged operation.
- Extended diffusion pathways which limit mass transport



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

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.

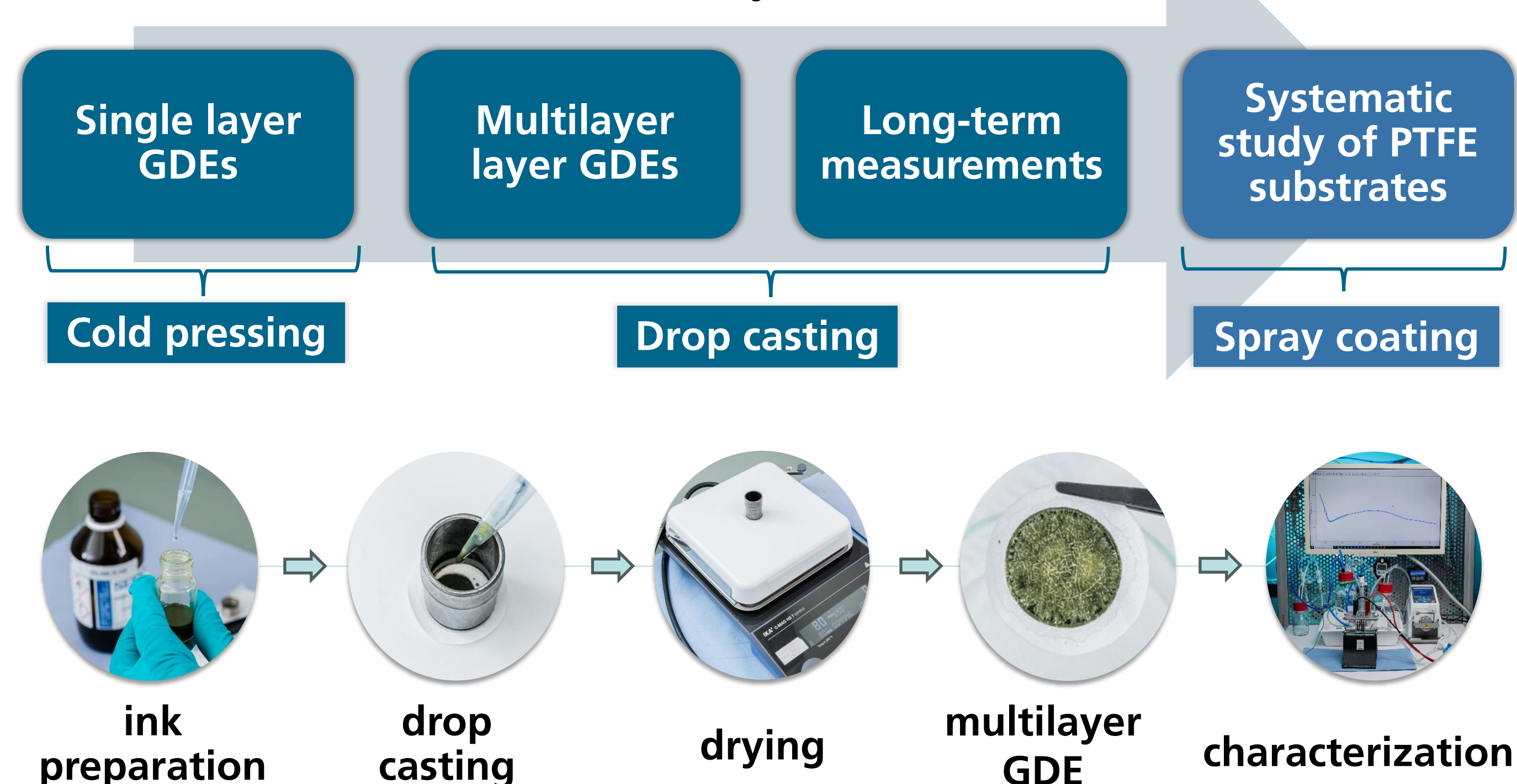


From single- to multi-layer GDE assembly (Multilayer approach)

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

Methodology

Transition to multilayer GDE



GDE characterization

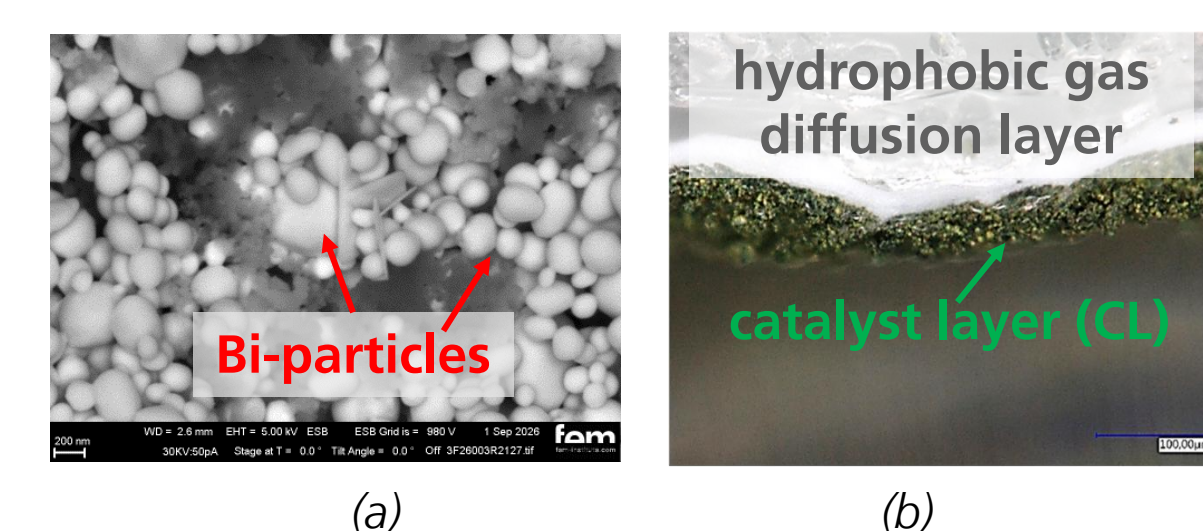
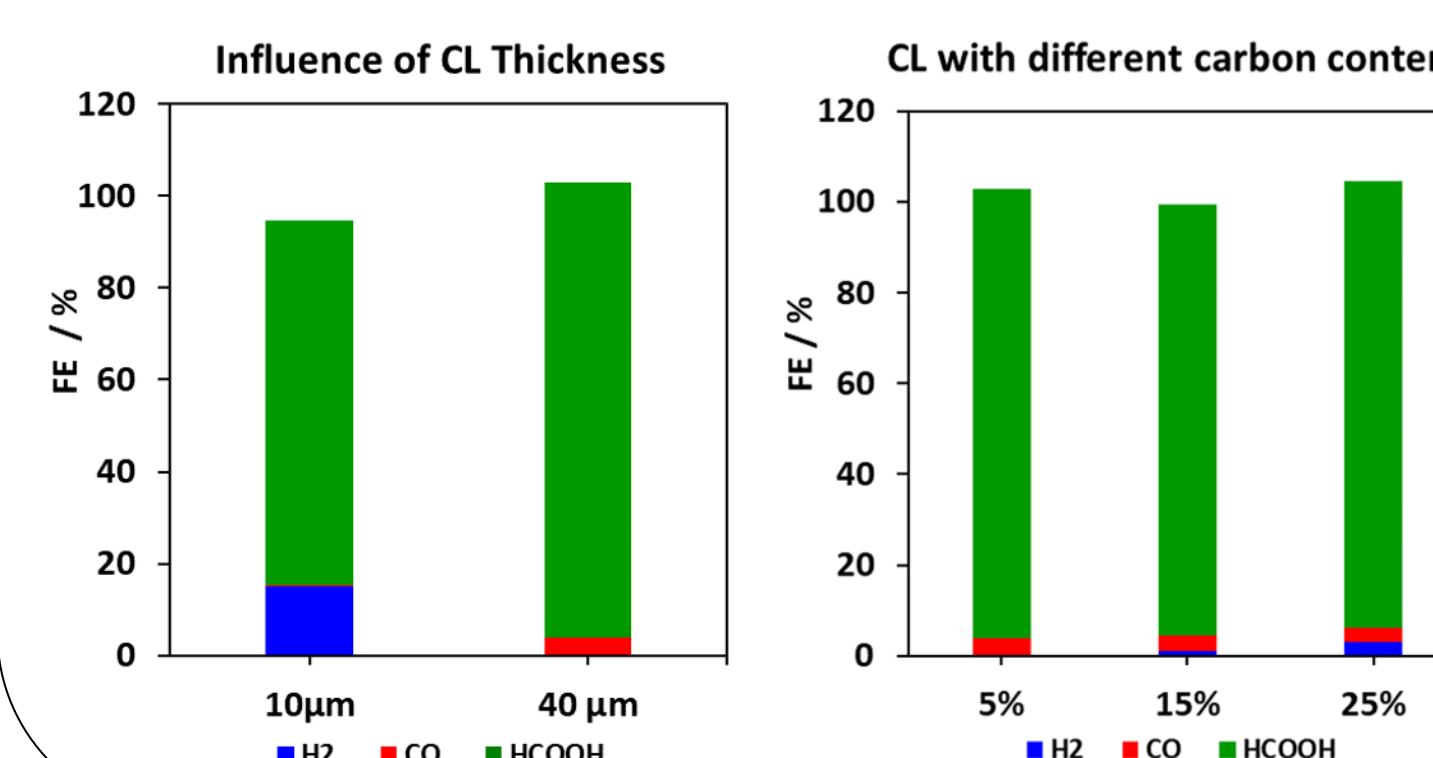
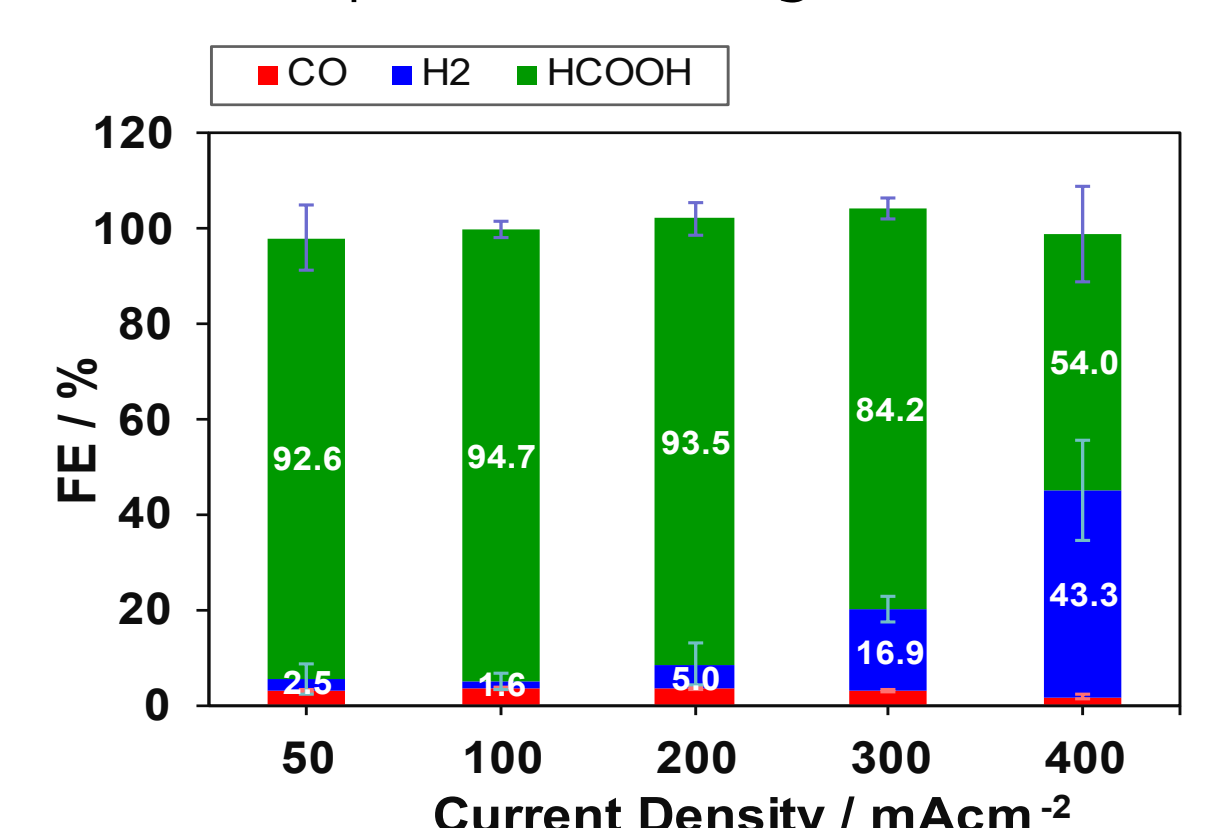


Figure: (a) top-down SEM image of catalyst layer, (b) cross-sectional image of GDE using optical microscope

Galvanostatic measurements at 200mAcm⁻²



Product distribution at different current densities of GDE with optimum configuration



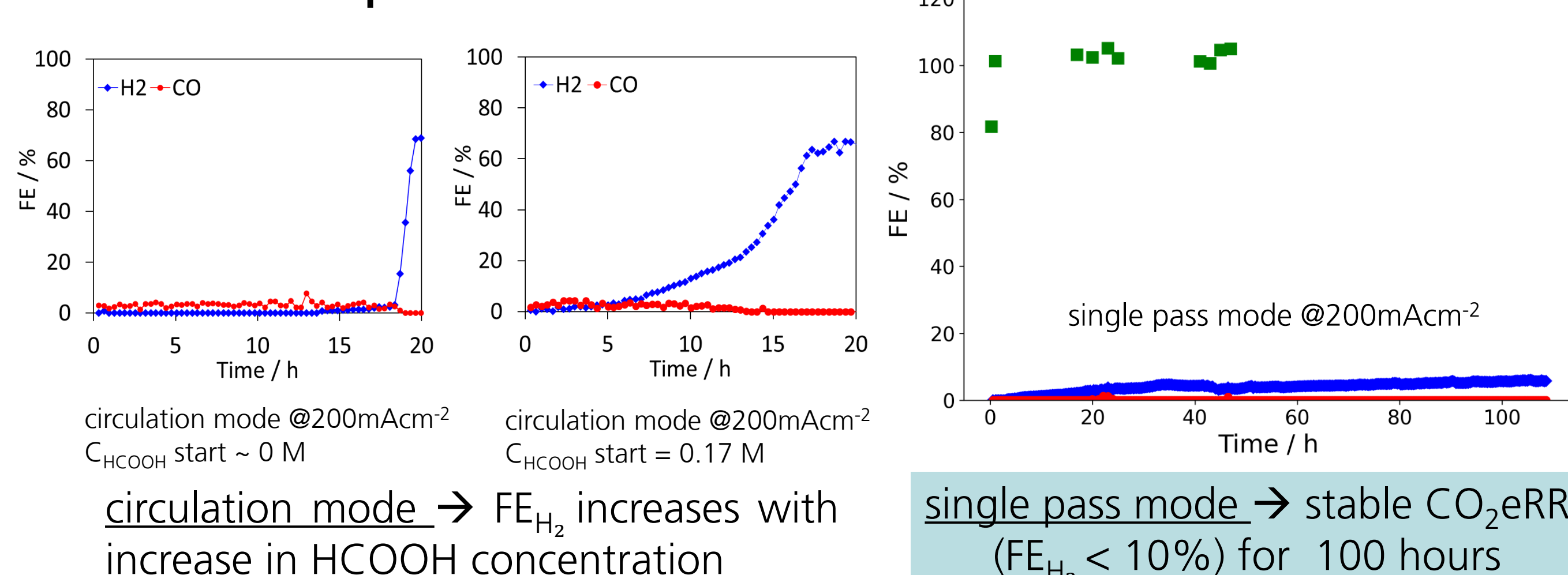
- Optimum configuration
 - thickness: 40μm (~5mgcm⁻²)
 - carbon content: 5 wt%
- ✓ **High HCOOH selectivity** up to current density of 200 mA cm⁻²

Long-term Measurements

Why PTFE membranes as GDL for CO₂eRR?

- commercial carbon-based GDL rapidly fails due to electrolyte flooding
- Hydrophobic polymer membrane prevents liquid breakthrough

➤ Influence of product accumulation



Conclusion

- In the present work the transition from a conventional single-layer to a multilayer architecture have been accomplished and addressed the associated challenges.
- The PTFE membrane functions as a barrier that prevents electrolyte intrusion while permitting gas transport, whereas the thin CL defines the reaction zone.
- GDE characterization shows that product selectivity is governed by the physicochemical properties of the CL.
- Multilayer GDEs achieved compatible performance (FE_{HCOOH} > 90%) at an industrially relevant current density of **200 mA cm⁻²**.
- Further studies are required to understand and resolve the shift in product selectivity toward HER due to product accumulation.
- Single-pass operation demonstrated **stable GDE performance for 100 hours**.

Acknowledgements

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