The Effect of the Anion Exchange Membrane in the Electrochemical Production of Electrolyte-Free Formic Acid

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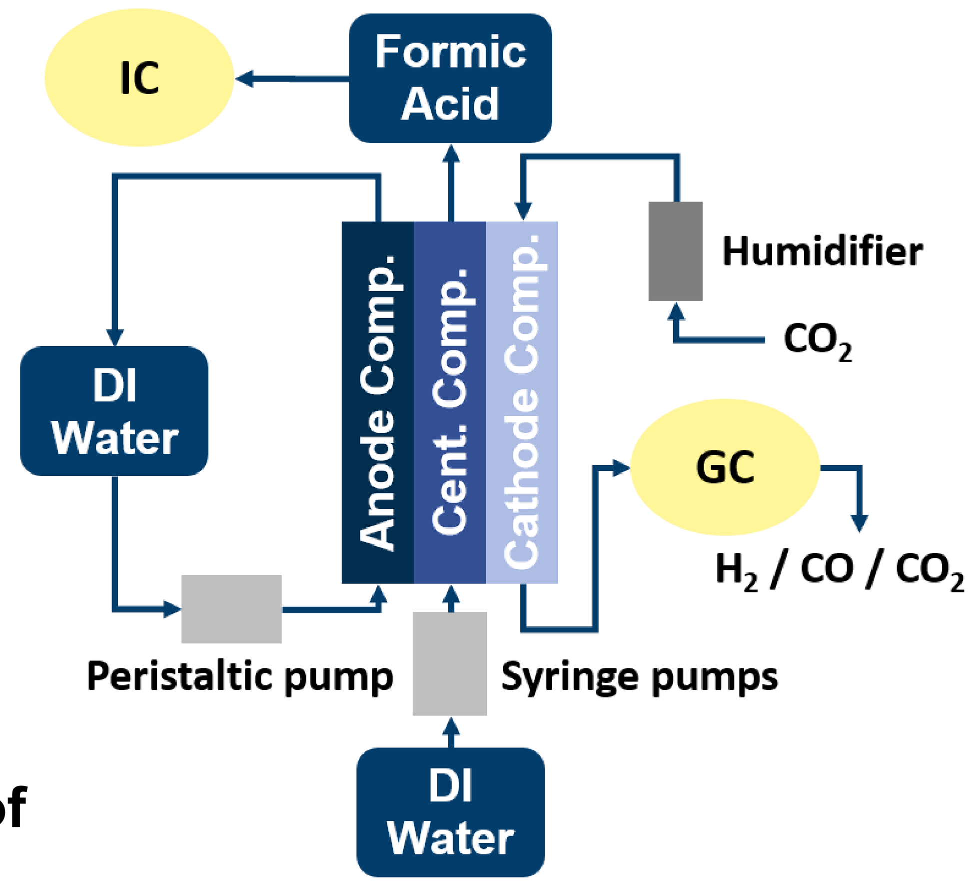
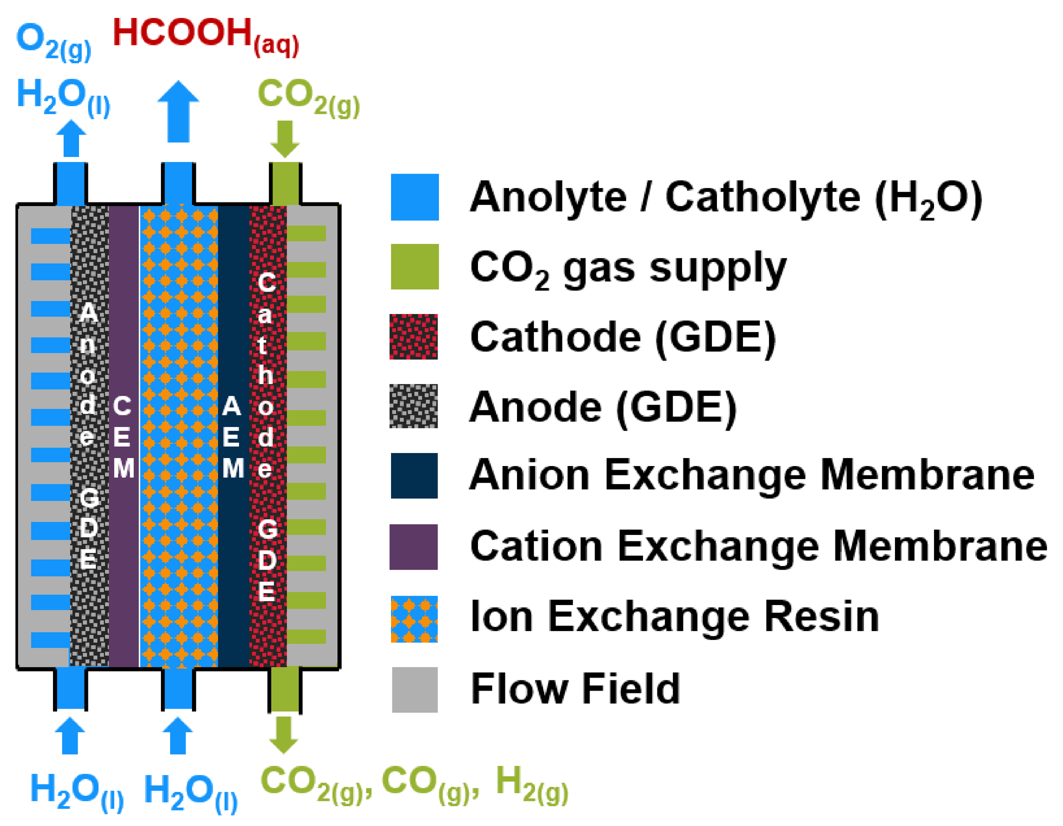
Introduction

The implementation of a closed carbon cycle by 'Power-to-X' (P2X) technologies is of great interest, aiming at a CO_2-neutral economy. Especially, formic acid is a relevant product of P2X processes, since it can be produced selectively and efficiently using earth-abundant catalysts. This study focuses on the investigation of a three-compartment flow cell designed to produce formic acid rather than formate. Herein, the electrolyzer performance using PiperION membranes of various thicknesses, ranging from 13 – 80 µm, is evaluated.[1–3]

Experimental Setup

- **Experimental Parameters:**
  - Active electrode area: 5 cm^2
  - Flow rate center compartment: 0.1 mL min^{-1}
  - CO_2 supply: 60 mL min^{-1} (λ = 8.0)
  - Flow rate anolyte: 3.0 mL min^{-1}
  - AEMs: PiperION (13, 22, 35, and 80 µm)
  - CEM: Nafion 324
  - GDEs: Custom-made GDEs
- **The ion exchange resin in the center compartment allows for the direct production of formic acid**





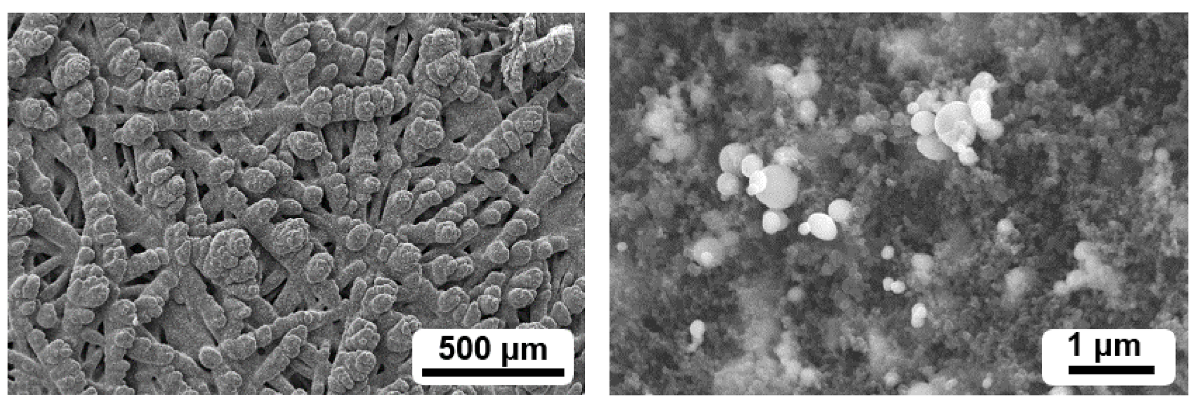
GDE Preparation

Ink preparation → Ultrasonication → Spray-coating

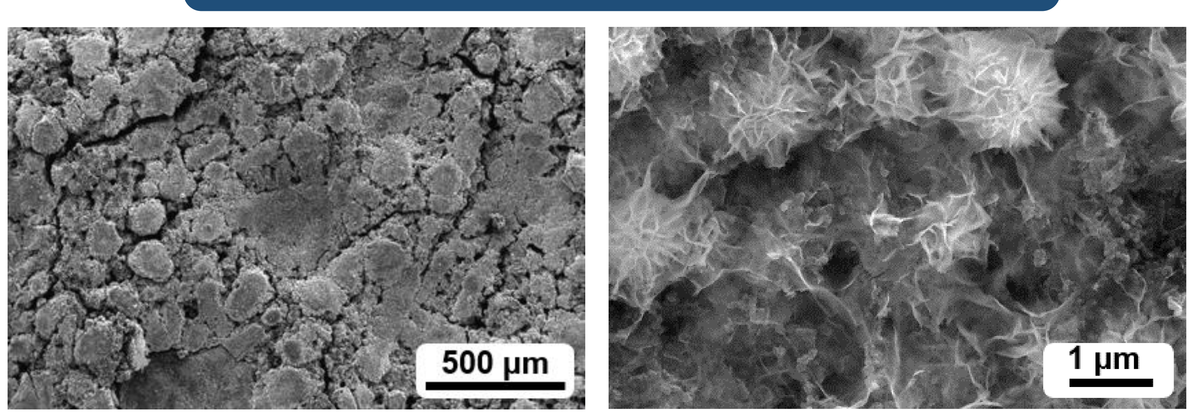
Catalyst: Bi_2O_3
Binder: PiperION
Additive: Carbon powder
Dispersion medium: Ethanol

Substrate: TGP-H-120 (30%)
Catalyst loading: 4 mg cm^{-2}

Cathodic GDE as prepared



Cathodic GDE after electrolysis



Results

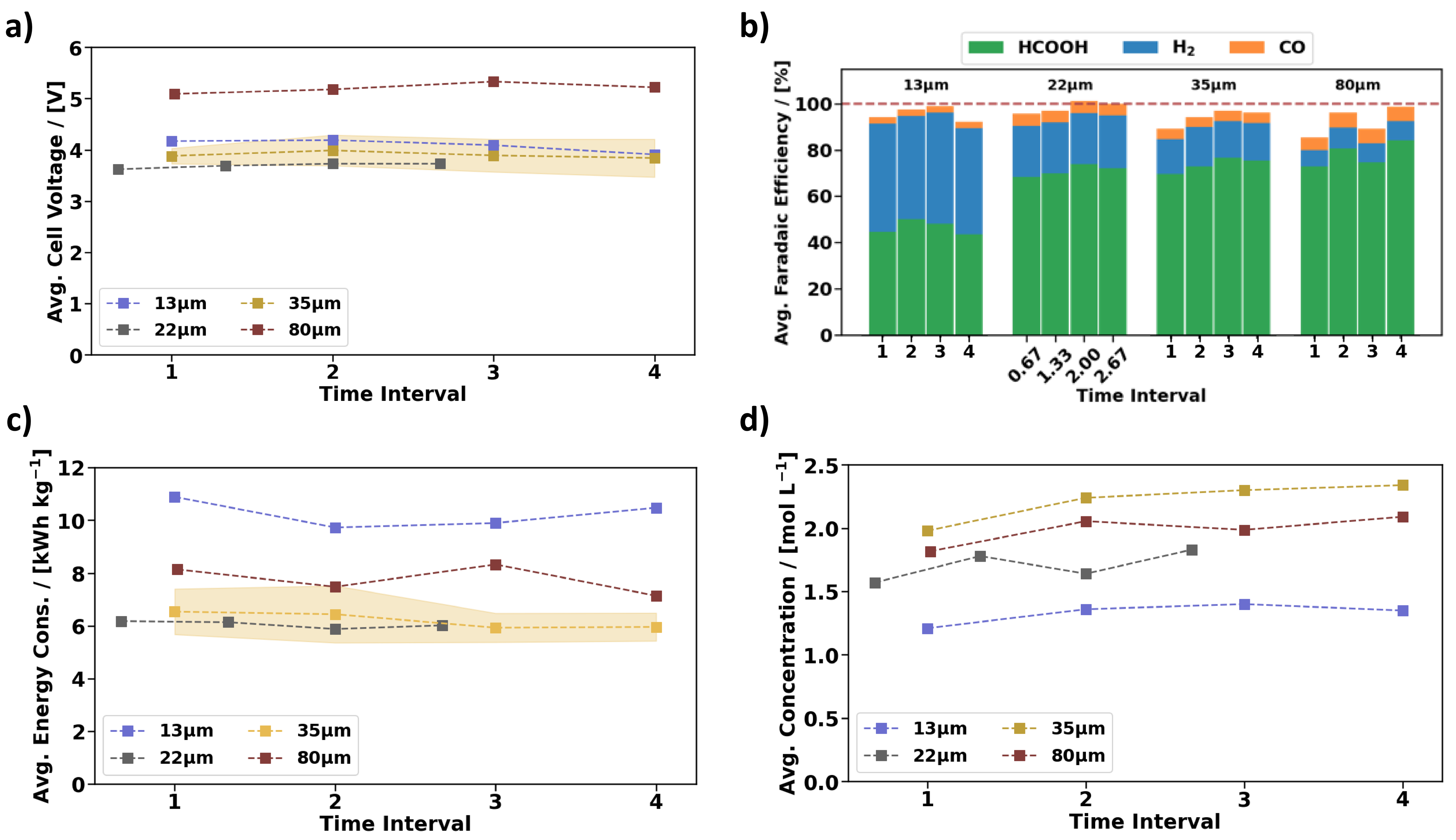


Fig.1. Electrolyzer performance in the electroreduction of CO_2 to formic acid as a function of the AEM thickness under continuous operation at 200 mA cm^{-2} for 4 hours. a) Average cell voltage, b) average faradaic efficiency of formic acid, H_2, and CO, c) average energy consumption, and d) average concentration of resulting formic acid.

Conclusion

The performance of a three-compartment flow cell for direct formic acid production via CO_2 electroreduction was investigated using PiperION AEMs of 13 µm, 22 µm, 35 µm, and 80 µm thicknesses over 4 hours at 200 mA cm^{-2}. Among the tested membranes, medium-thick membranes (22 and 35 µm) delivered the best electrolysis performance, achieving ~76% FE_{HCOOH}, an energy consumption of ~6.0 kWh kg^{-1}, and formic acid concentration of ~2.3 mol L^{-1}. In contrast, the thinnest membrane (13 µm) yields low faradaic efficiencies to formic acid, and the thickest membrane (80 µm) shows cell voltages above 5 V. This study demonstrates that the appropriate thickness of the membrane is critical to establish an alkaline environment around the cathodic catalyst layer, fundamental for the eCO_2R-to HCOOH.

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