



Renewable **Fuels** and **Chemicals** for Switzerland*

Catalyst layer stability during long-term pulsed CO₂ electrolysis

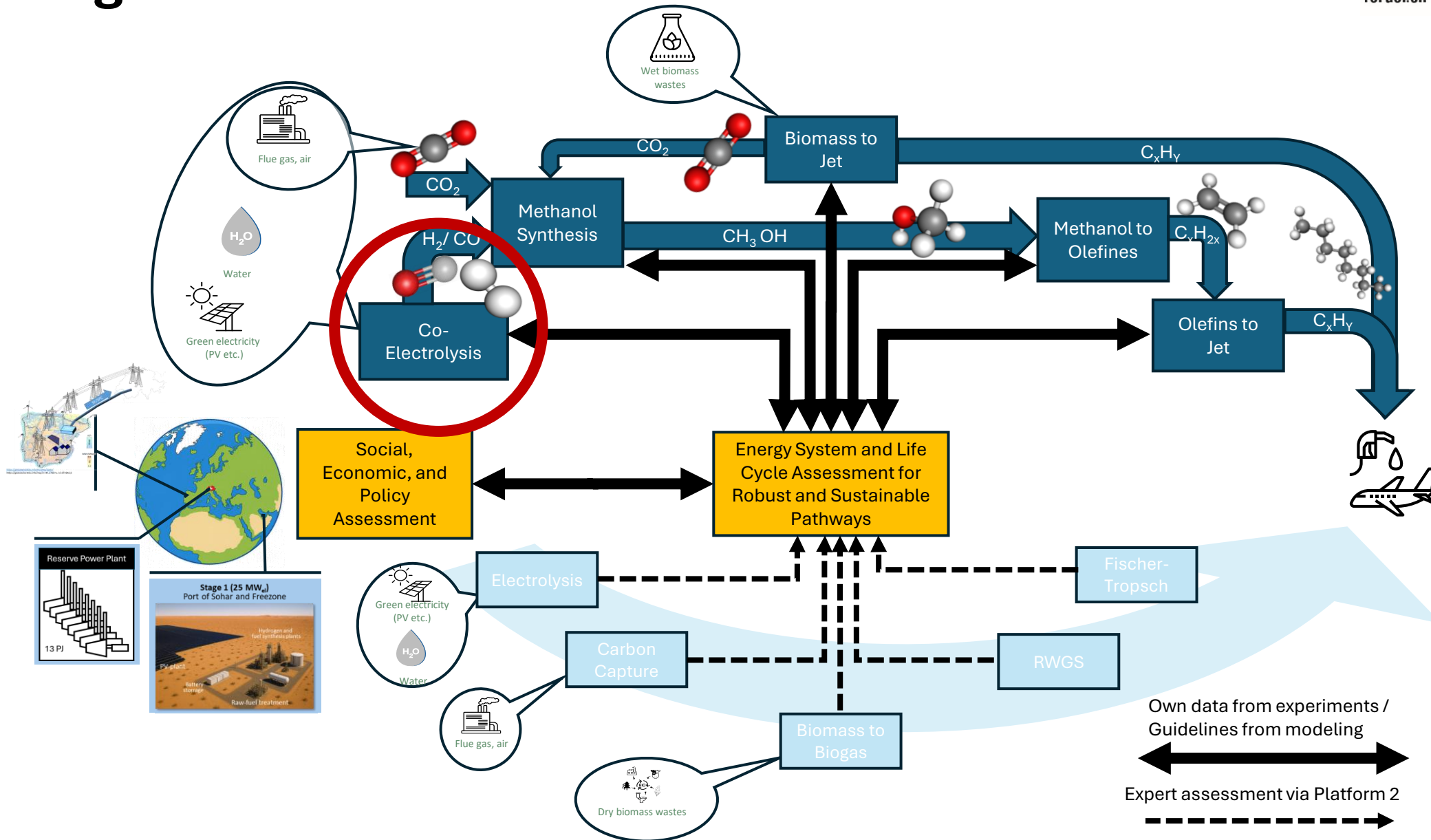
Presenter: Claudia Bissattini Alessi



*reFuel.ch is a consortium sponsored by the Swiss Federal Office of Energy's SWEET programme and coordinated by Empa.



High-level introduction & link to consortium



CO₂ electrolysis at industrial scale

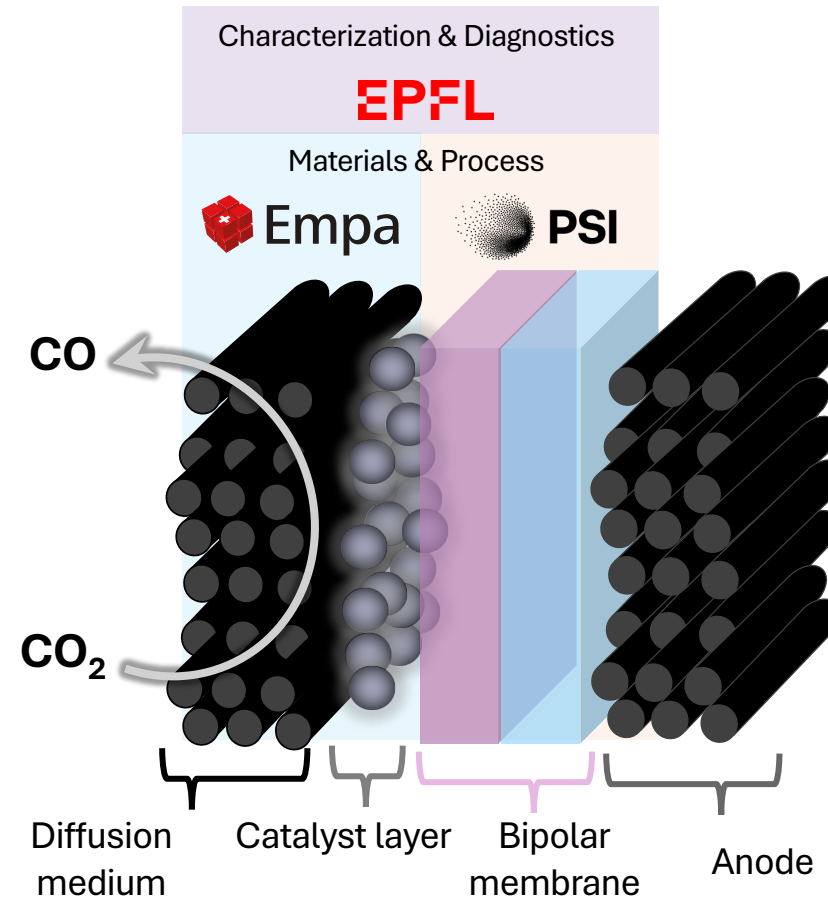


sweet swiss energy research
for the energy transition
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What we have

H₂ electrolysis

- Electrolyzer infrastructure
- Existing supply chain
- Mild operating conditions



WP4 objectives

- Lower the energy demand (<3 V)
- Increase CO production rate (>0.2 A cm⁻²)
- Maintain high selectivity (>1000 h)

CO₂ electrolysis at industrial scale



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What we have

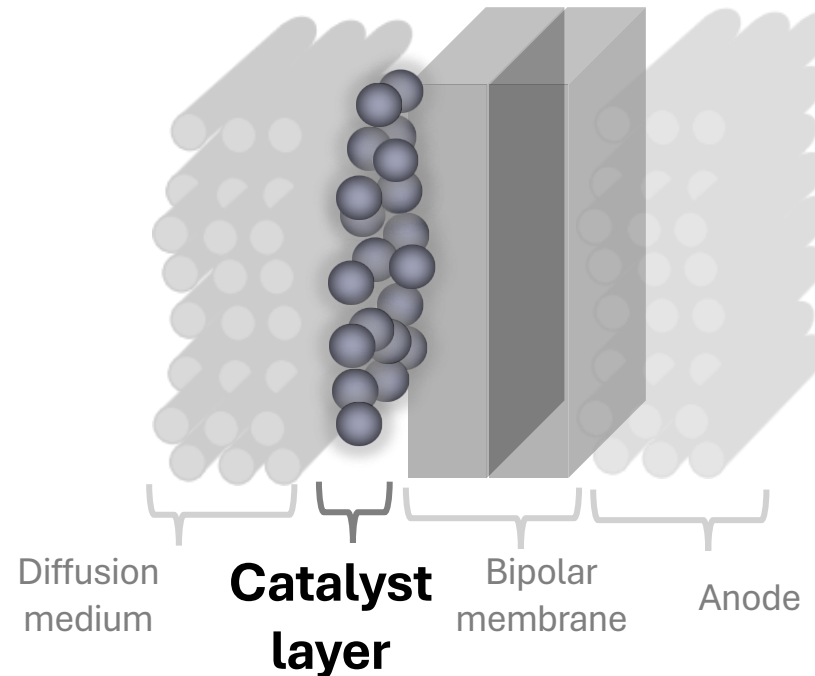
H₂ electrolysis

- Electrolyzer infrastructure
- Existing supply chain
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EPFL



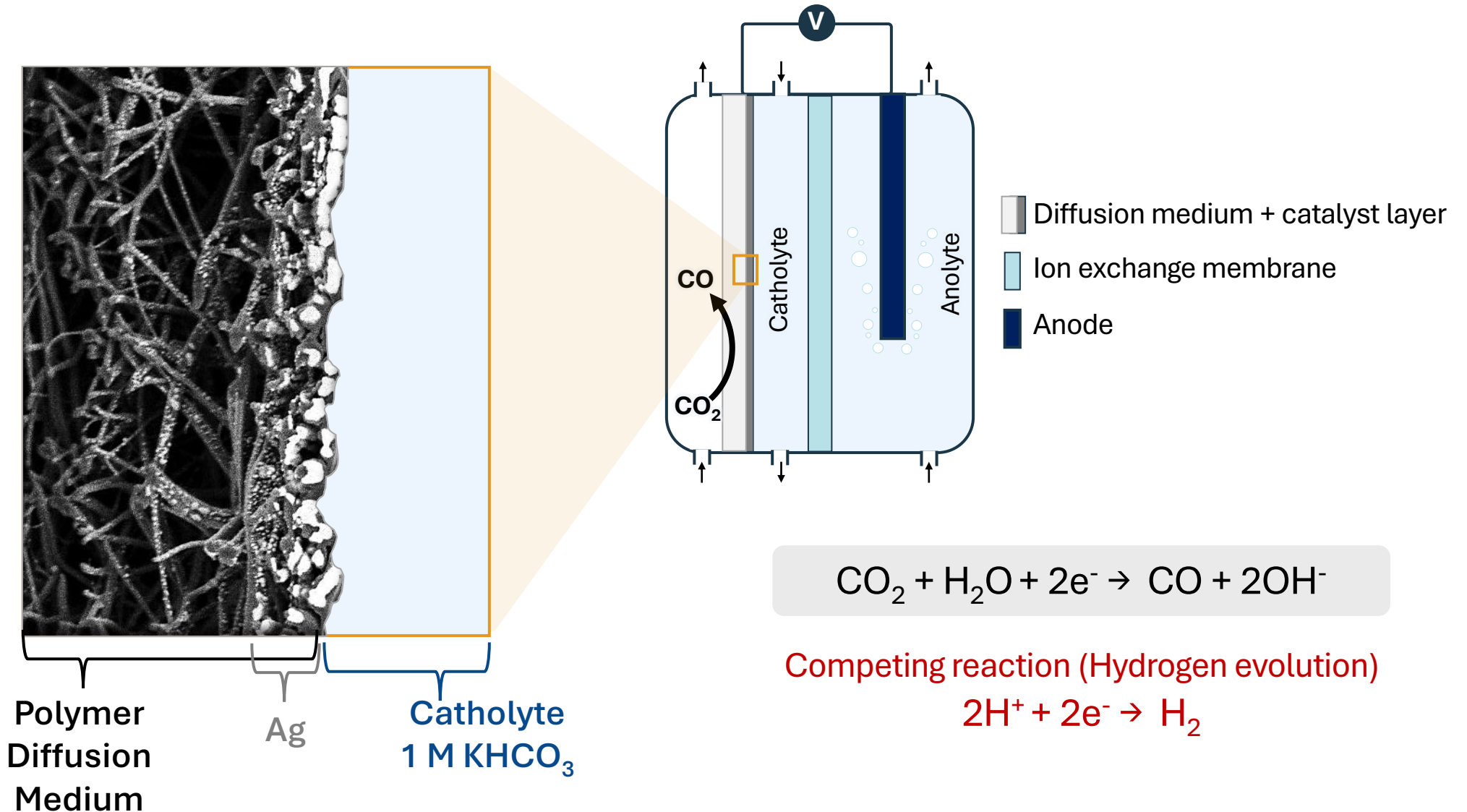
Empa



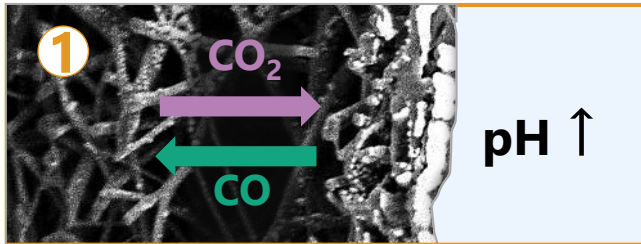
WP4 objectives

- Lower the energy demand
(<3 V)
- Increase CO production rate
(>0.2 A cm⁻²)
- Maintain high selectivity**
(>1000 h)

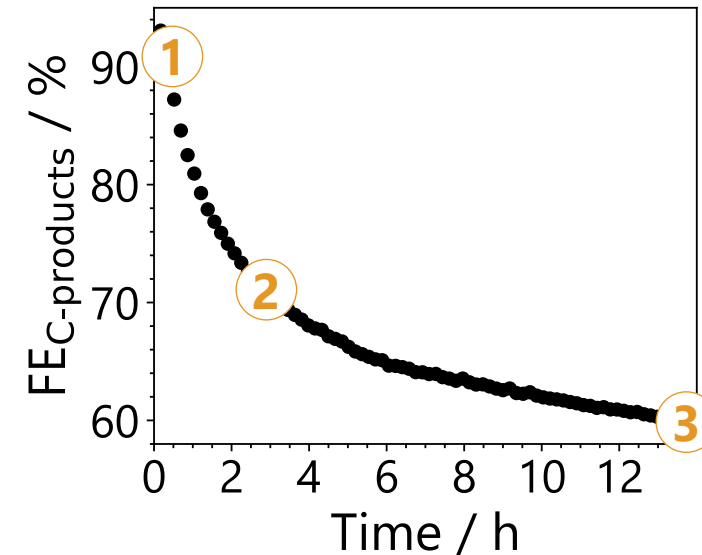
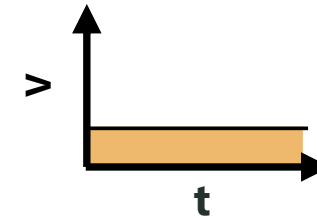
Electrolyzer for catalyst layer studies



How does CO₂ electrolysis work?

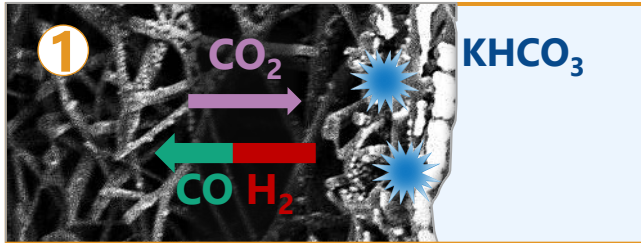


Continuous eCO₂R: -4 V vs SHE @ -200 mA cm⁻²

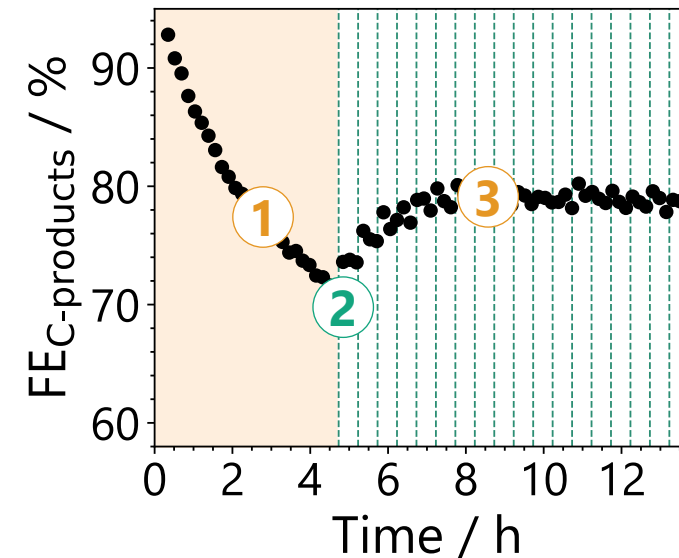
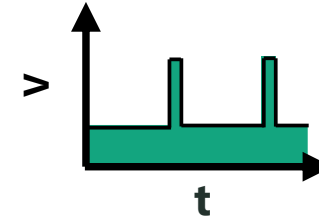


- (Bi)carbonate salt precipitation leads to progressive shift of selectivity towards H₂

How to maintain high selectivity?



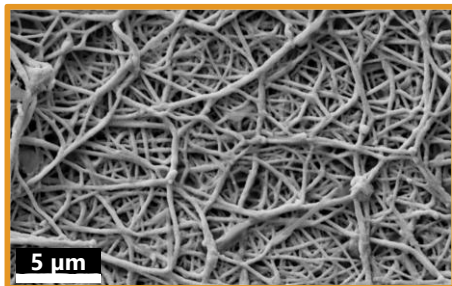
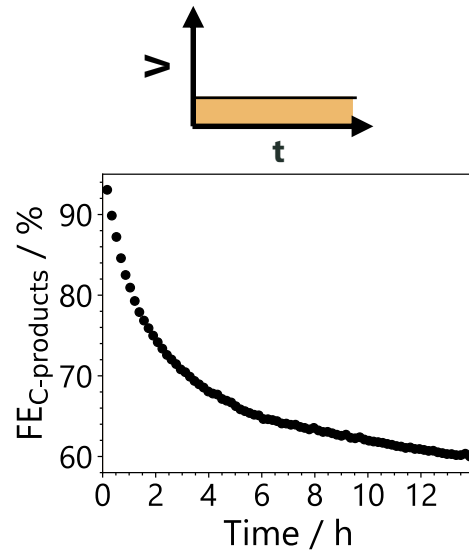
Pulsed eCO_2R : $V_{\text{pulse}} = +0.50 \text{ V vs SHE}$



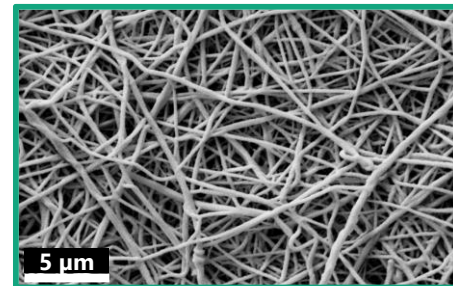
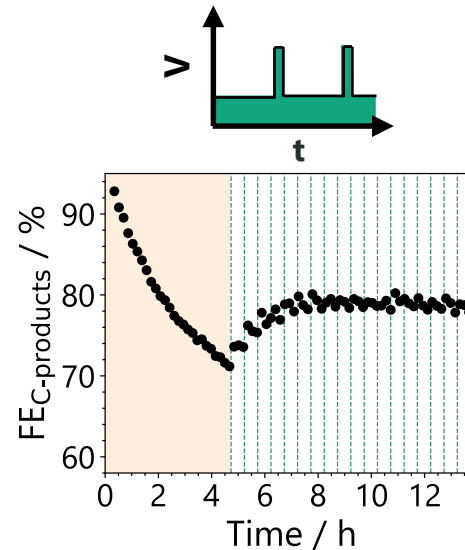
- Dissolution of salts upon pulsing allows to recover and maintain CO selectivity

Pulsed electrolysis parameters have limitations

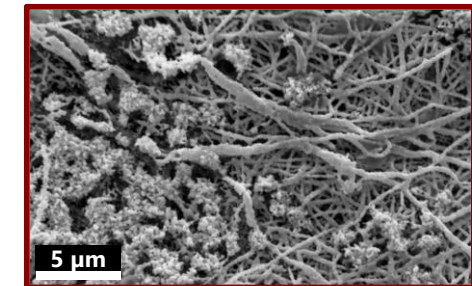
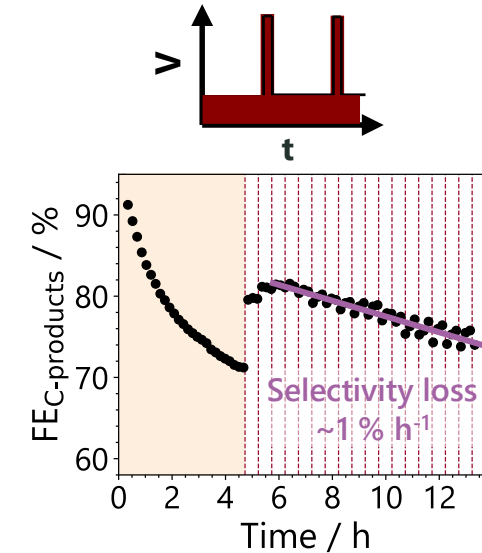
Continuous eCO₂R: -4 V vs SHE @ -200 mA cm⁻²



Pulsed eCO₂R: $V_{\text{pulse}} = +0.50$ V vs SHE

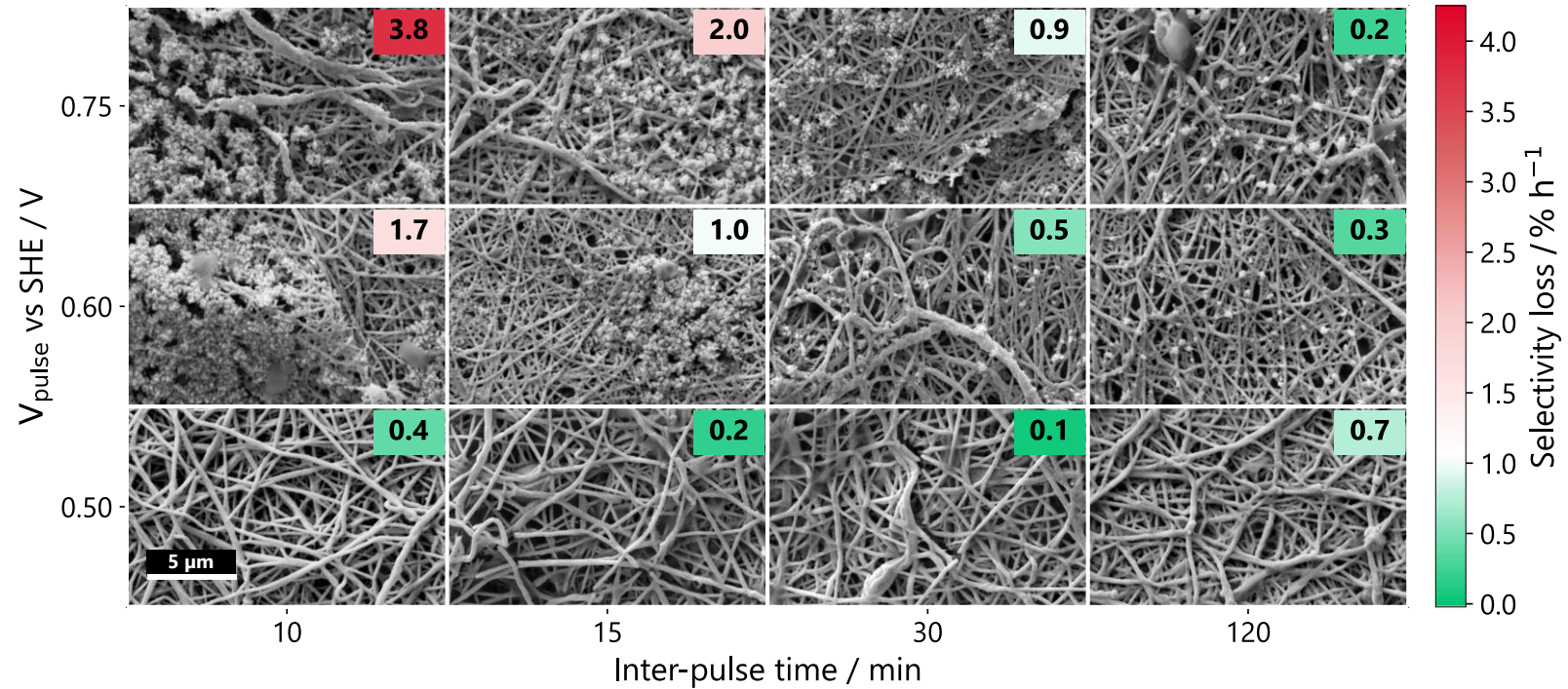
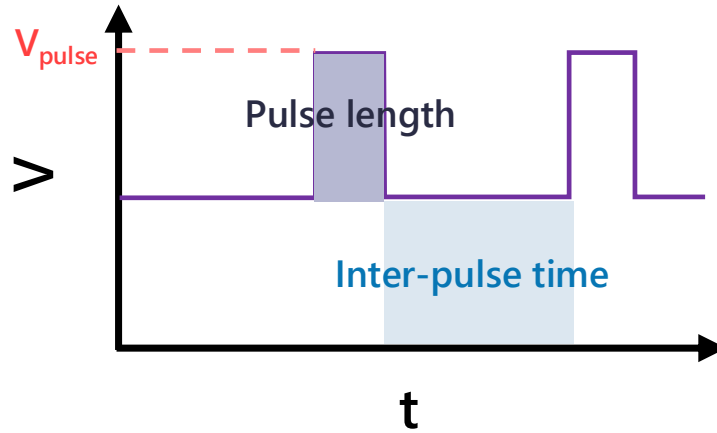


Pulsed eCO₂R: $V_{\text{pulse}} = +0.75$ V vs SHE



- Understanding the impact of different pulse parameters is necessary to improve stability

Mapping the pulse parameter space

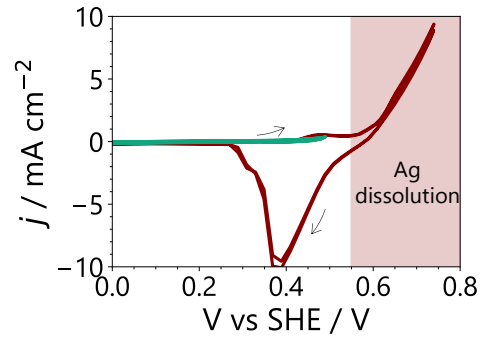


- Frequent high-voltage pulses cause catalyst restructuring and faster selectivity loss
- Low selectivity loss can be achieved at low voltage and long inter-pulse time

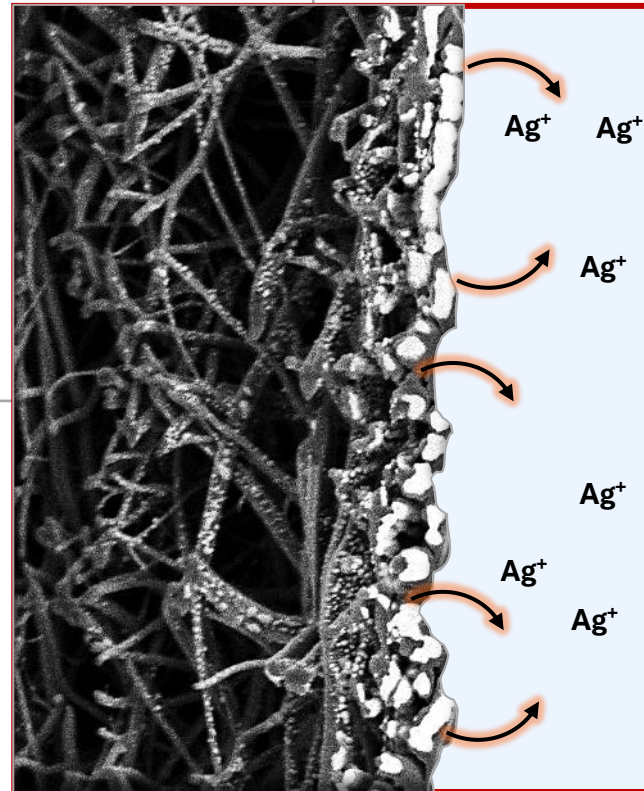
Catalyst restructuring mechanism



Dissolution and plating at $V > 0.55$ V



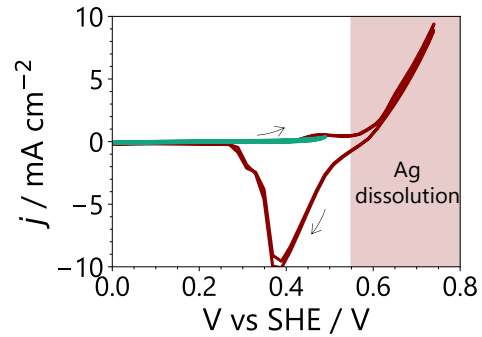
0.75 V for 10 s



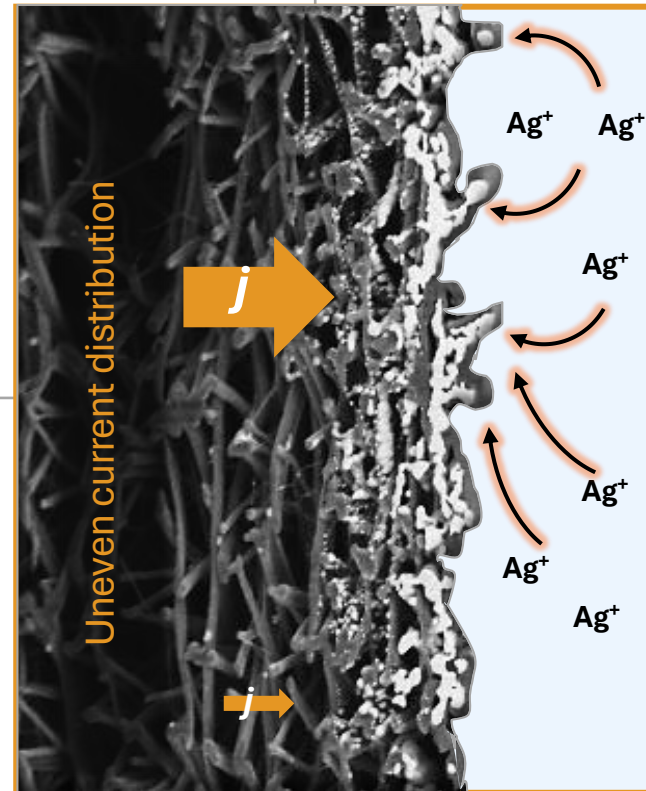
Catalyst restructuring mechanism



Dissolution and plating at $V > 0.55$ V



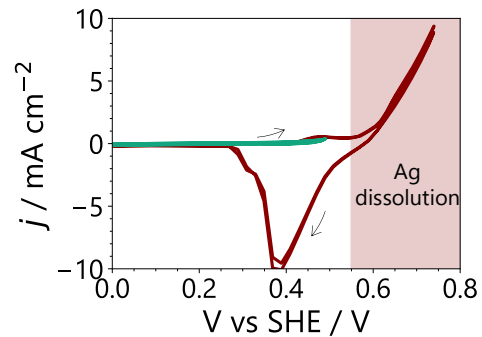
Apply -200 mA cm^{-2}



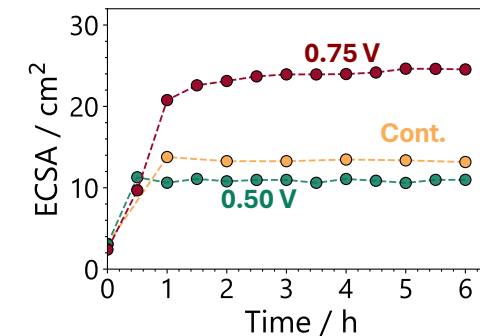
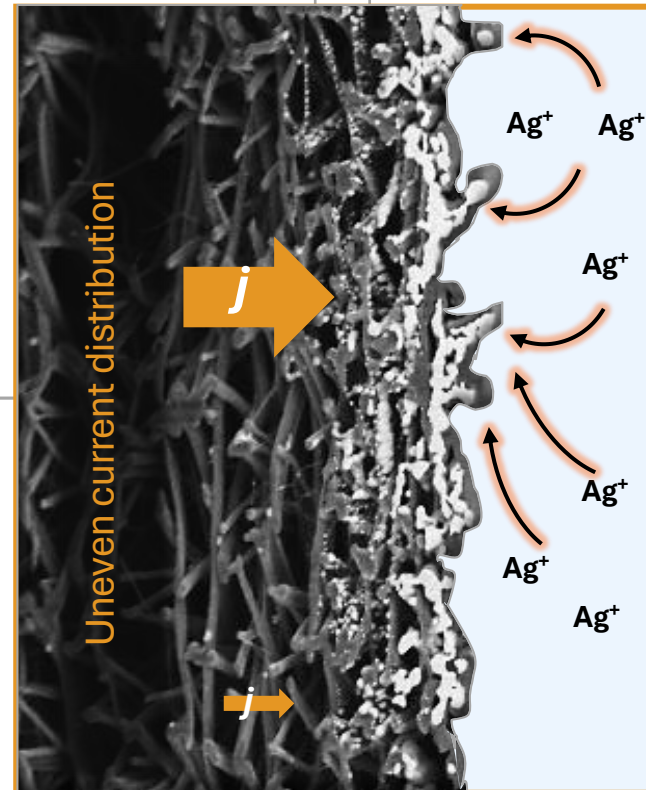
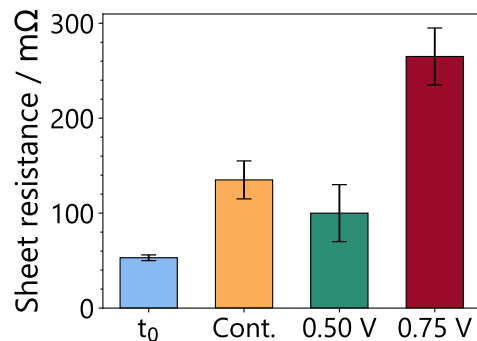
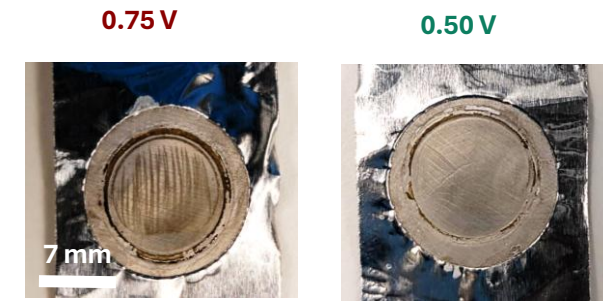
Catalyst restructuring mechanism



Dissolution and plating at $V > 0.55$ V



Clusters appear darker to the naked eye

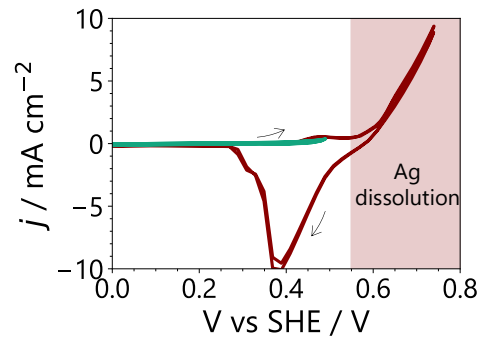


Disconnected clusters increase ohmic losses

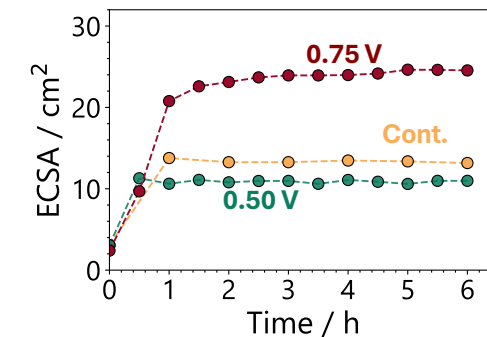
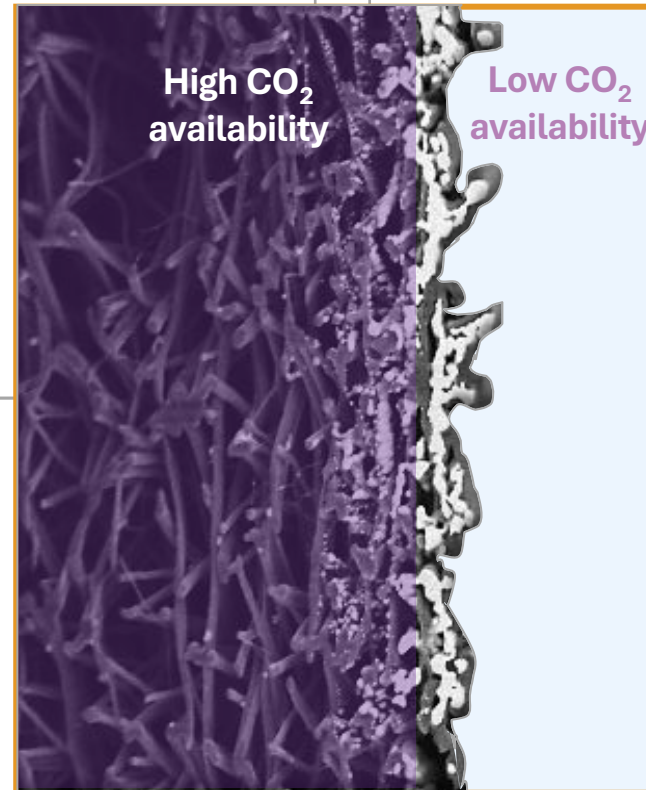
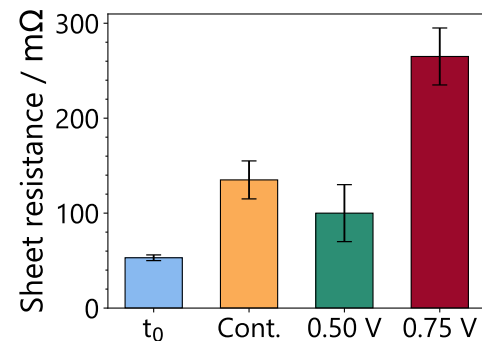
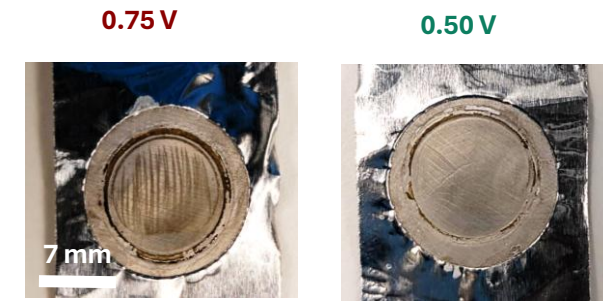
Clusters protruding in the electrolyte increase surface area

Catalyst restructuring mechanism

Dissolution and plating at $V > 0.55$ V



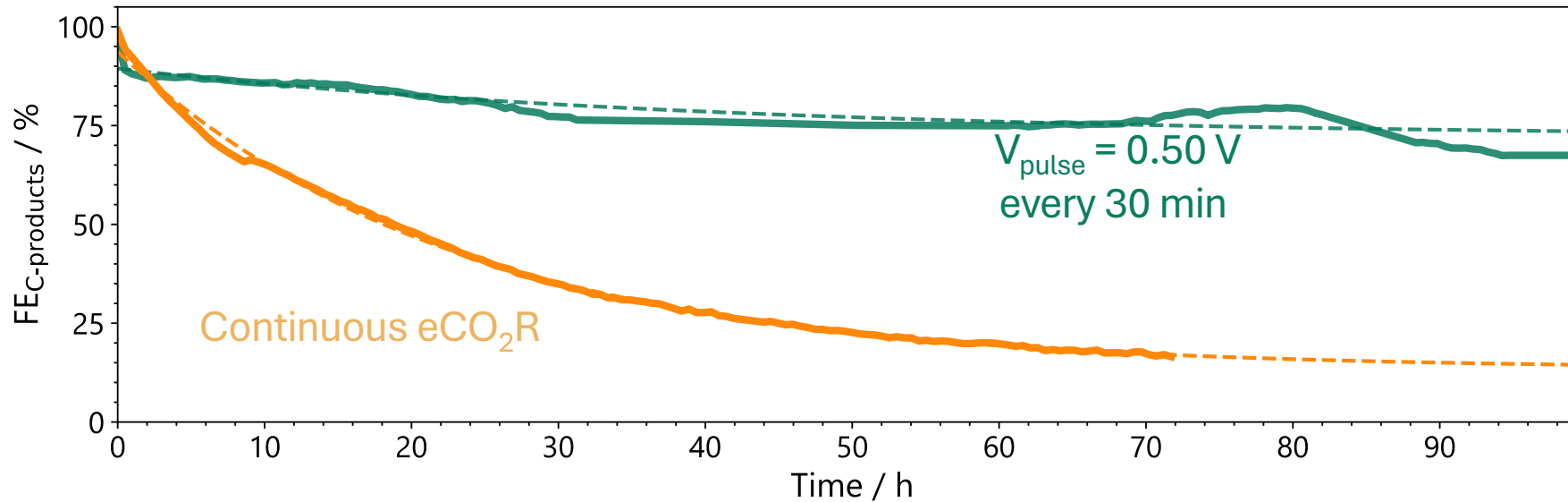
Clusters appear darker to the naked eye



Disconnected clusters increase ohmic losses

Clusters protruding in the electrolyte increase surface area

Maintaining long-term CO selectivity



- Continuous electrolysis leads to a selectivity plateau
- Pulsing at 0.50 V disrupts steady state with local pH regeneration
- Five-fold improvement in selectivity compared to continuous

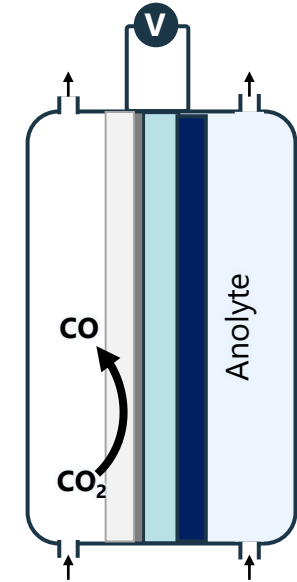
Conclusions and outlook



- Pulsing at $V < \text{Ag dissolution potential}$ restores local pH and dissolves salt precipitates
- Pulsing at $V > \text{Ag dissolution potential}$ leads to catastrophic Ag restructuring

Other projects in WP4

Using machine learning to extract insights from post-mortem GDEs
Developing novel bipolar membranes for longer lifetime and lower energy demand



Acknowledgements

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[Full paper](#)



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reFuel.ch - Renewable Fuels and Chemicals for Switzerland

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The authors bear sole responsibility for the conclusions and the results presented.

