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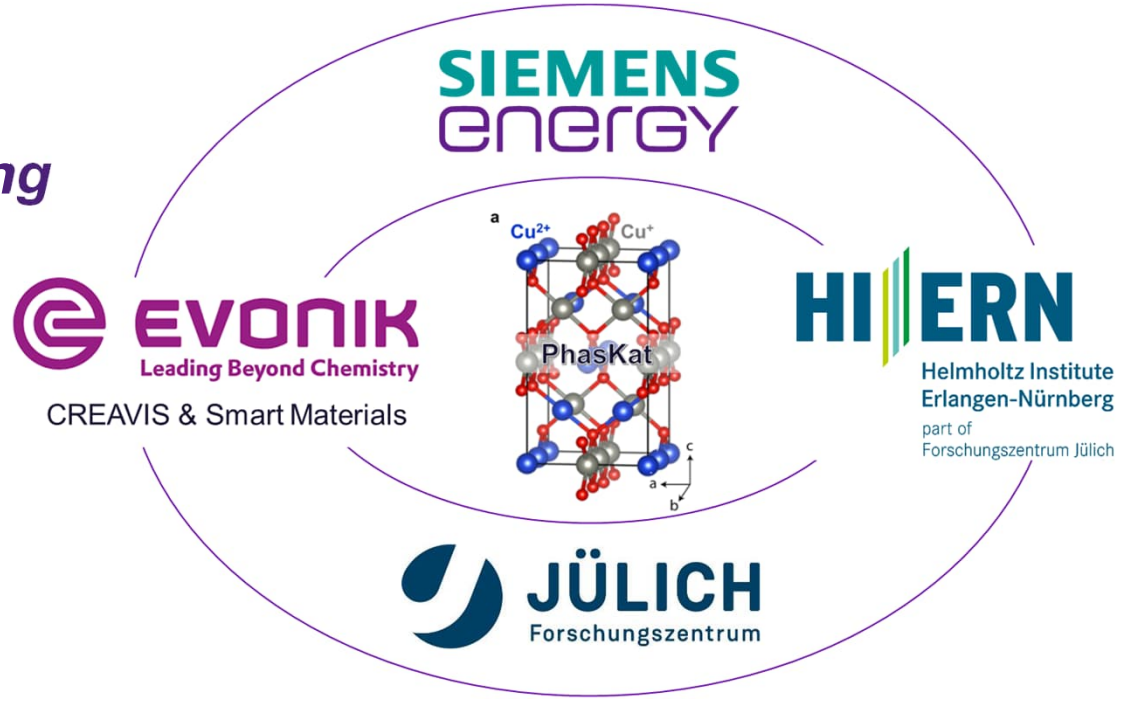
PhasKat

Phase-pure electrocatalysts and adjustment of conditions regarding the reduction of CO_2



Duration: 01.02.2020 – 31.01.2023
Funding code: 033RC028

CO_2-WIN Final Conference

Sept. 28th / 29th, 2023

Dr. Wiebke Sarfert-Gast, Siemens Energy Global GmbH & Co. KG

Motivation

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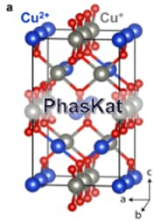

Resources	Direct Electrolysis	Target Products	Use

Solar Power

Wind Power

Renewable energy

H_2O

CO_2

Chemical resources

Electrolysis

Hydrocarbons (C_xH_y)/ Alcohols

TRL 2-3

Ethylene C_2H_4 [2)]

Production:	140 Mio. t / year
Estimated CO_2 saving:	658 Mio. t / year
Estimated price:	850 – 1200 € / t

Ethanol C_2H_5OH [3,4)]

Production:	92,4 t / year
Estimated CO_2 saving:	279 Mio. t / year
Estimated price:	360 € / t

Chemical Industry

Feedstock

Mobility (synthetic fuel)

Aviation

Marine

Heavy Road transportation

1) http://www.ceresana.com/de/marktstudien/chemikalien/ethylen/
2) https://www.statista.com/statistics/274142/global-ethanol-production-since-2000/
3) https://tradingeconomics.com/commodity/ethanol

Objective

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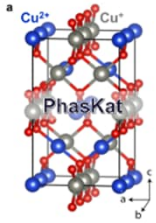
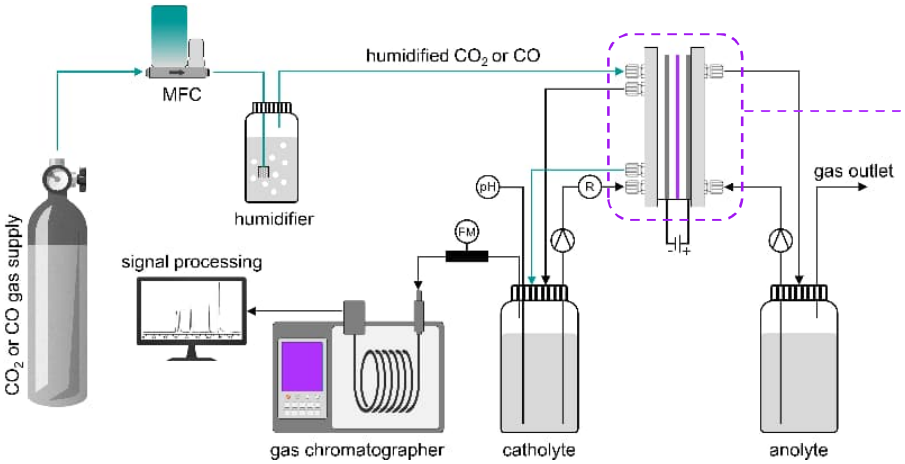
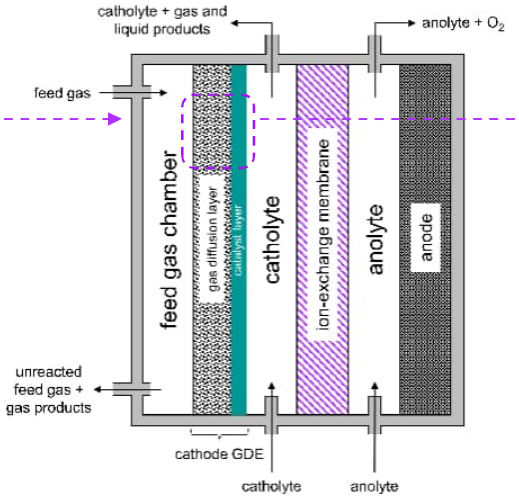


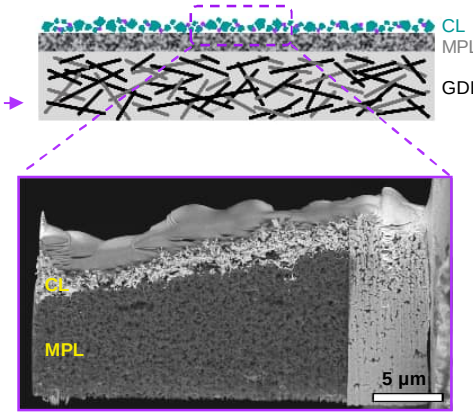
Experimental set-up:



ElectroCell flow reactor



Gas Diffusion Electrode (GDE)



Cross-section SEM image

The performance of the GDE depends on:

- Properties of catalyst material
- Properties of Anion Exchange Ionomers
- Layer composition
- Morphology due to processing conditions
- Operation environment
- Operation mode

→ The aim of PhasKat was to develop a better understanding about the materials and the way of processing in order to be able to optimize the GDE performance at industrial relevant current densities (> 200 mA/ cm²).

WP1: Catalysts

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EVONIK Leading Beyond Chemistry

Objective

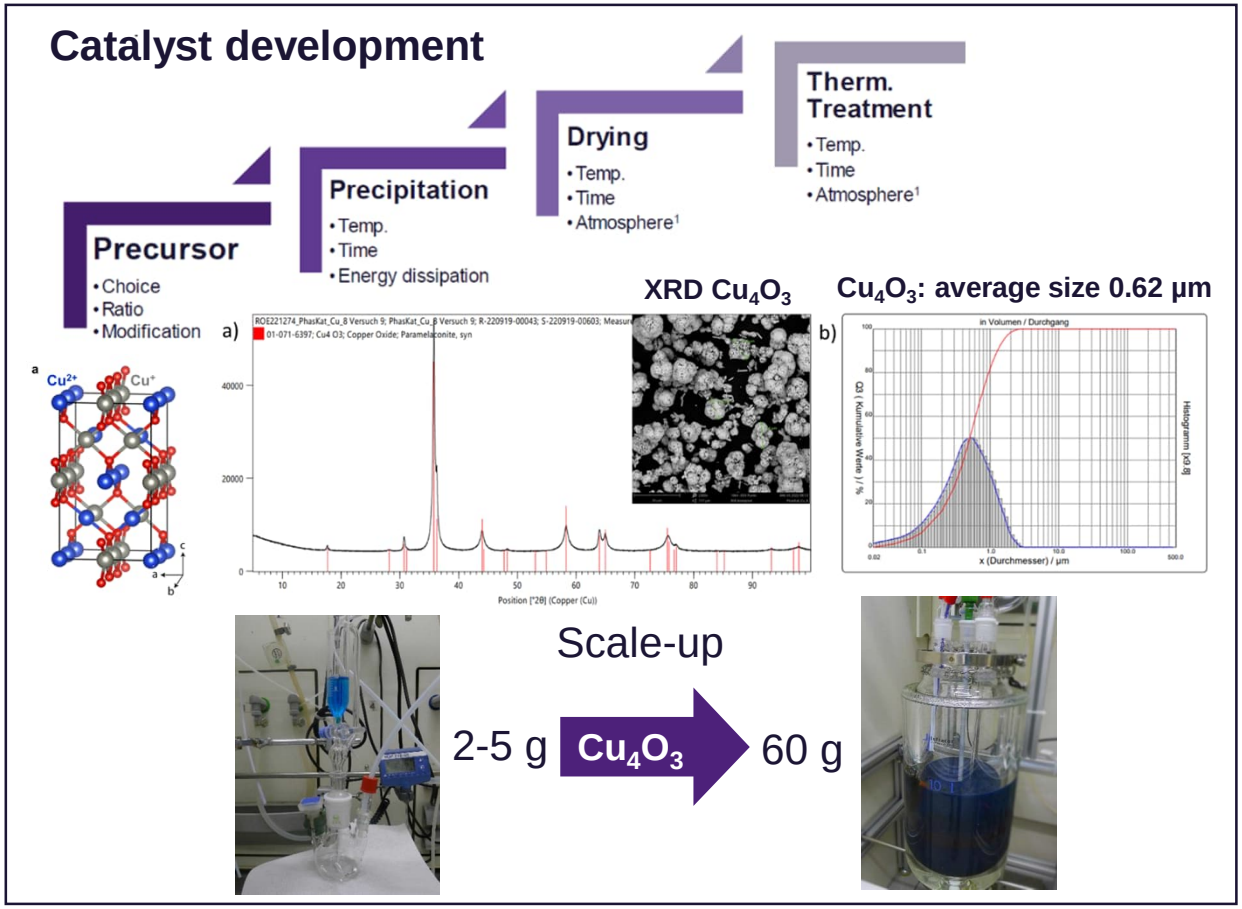
- Catalyst development, optimization and scale-up

Approach

- Lab and scaled synthesis of chosen catalysts based on experience of Evonik and Siemens in materials development:
  - ✓ **Cu_4O_3** * → selected for up-scaling
  - ✓ $Ag_2Cu_2O_3$ **
  - ✓ $BaCuO_{2/2.5}$
  - ✓ Ag_3CuS_2
  - ✓ $CuFe_2O_4$

Outcome

- All materials were synthesized on the gram scale and provided for testing.
- Synthesis of Cu_4O_3 was optimized and upscaled to 60 g.
- The grinding process has been optimized to meet the particle size requirements of < 1 µm.



Involved partners: Dr. A. Reinsdorf, S. Brinkmann, Dr. Y. Markushyna (Evonik SM)

* *Martić et al., Adv. Energy Mater. (2019), 1901228.*
** *Martić et al., Energy and Environ. Sc. (2020), 13, 2993-3006.*

WP2: Anion Exchange Ionomers (AEI)

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EVONIK Leading Beyond Chemistry

Objective

- Development and synthesis of anion exchange ionomers (AEI)

Approach

- Synthesis of AEIs using experience of Evonik in development of high-performance polymers.

Outcome

- Different types of AEIs developed with variation in cationic groups, ion exchange capacity, molar mass, hydrophobicity, counter ion.
- Finally, 6 batches of 800g AEI 4 were synthesized in 5L reactor with molecular weight reproducibility of ± 25%.
- Supply of AEI 4 to partners for further evaluation and optimization studies.

Involved partners: Dr. A. Maljusch, Evonik CREAVIS

WP3: High throughput fabrication of catalyst layer

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HI ERN
Helmholtz Institute Erlangen-Nürnberg
part of Forschungszentrum Jülich

Objective

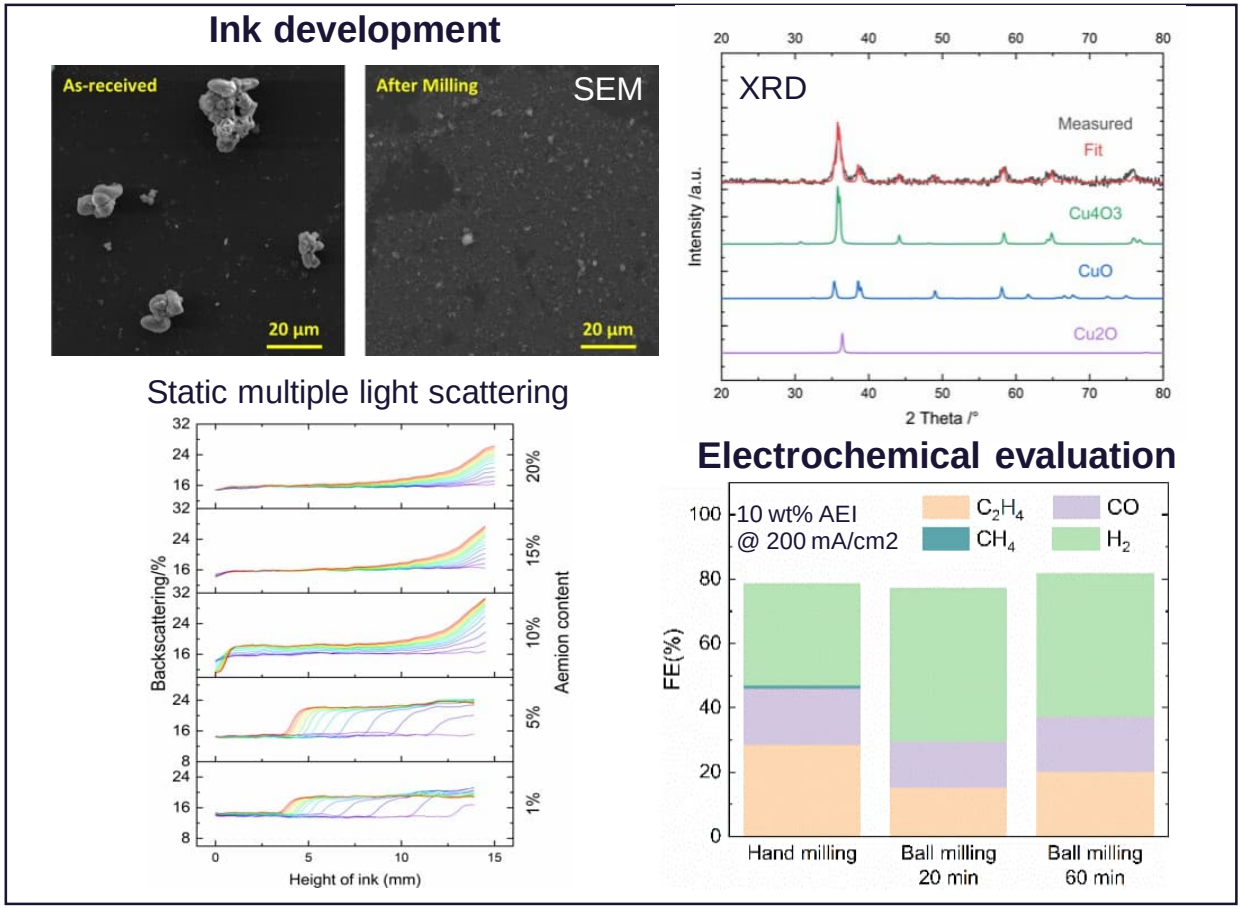
- Developing high throughput fabrication method for GDE via doctor blade coating.

Approach

- Development of stable inks.
- Methodology developed with Ag-catalyst and transferred to selected system Cu_4O_3 + AEI 4.
- Evaluation of the CO_2 electroreduction properties in a flow cell at industrial relevant current densities (> 200 mA/ cm²).

Outcome

- Stable and homogenous inks developed by:
  - optimization of ionomer content
  - particle size (<0.5 µm) reduced by ball milling
  - roller mixer as a dispersion method introduced
- Doctor blading successfully implemented for coating of the catalyst layer.



G. Liu, D. McLaughlin, S. Thiele, C. van Pham, Chemical Engineering Journal 2023, 460, 141757.

WP3: Electrochemical Performance Optimization

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SIEMENS energy

Objective

- Performance optimization of the most promising catalyst-system based on Cu_4O_3 + AEI 4.
- Demonstration of 100 hours operation stability.

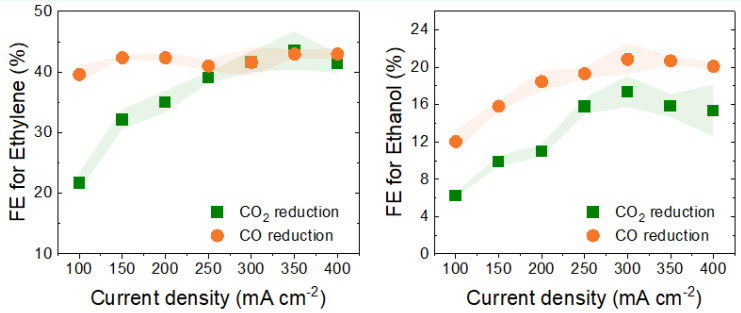
Approach

- Fabrication of GDEs by spray-coating.
- Investigation of CO_2 electroreduction properties in a flow cell at industrial relevant current densities (> 200 mA/ cm²).
- Reactivation of the GDE after flooding.

Outcome

- Max achieved FE of Cu_4O_3 for:
  ethylene: > 40 %
  ethanol: ~ 16 -20 %
- The catalyst layer developed is stable for min. 100 hours. (final milestone demonstrated)

Short-term (1h), galvanostatic catalyst screening of Cu_4O_3



Long-term electrolysis @ 200 mA/ cm² of Cu_4O_3 + AEI 4

Involved partners: Dr. N. Martic, Dr. G. Schmid, S. Szyszkowski, A. Maltenberger

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WP4: Characterization of Electrodes by Impedance Analysis

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JÜLICH Forschungszentrum

Objective

- Analysis of double-layer capacitances of gas diffusion layers and electrodes and their flooding behavior.

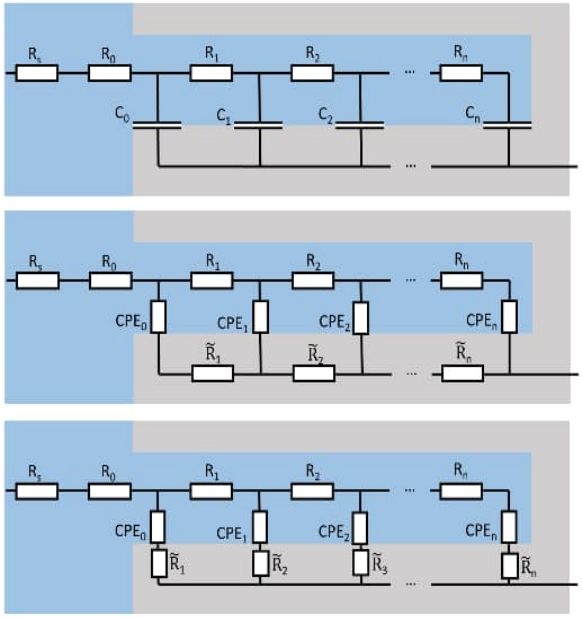
Approach

1. Impedance analysis of different carbon materials with variation in porosity and conductivity to model the flooding behavior.
2. Impedance analysis of flooded GDEs.

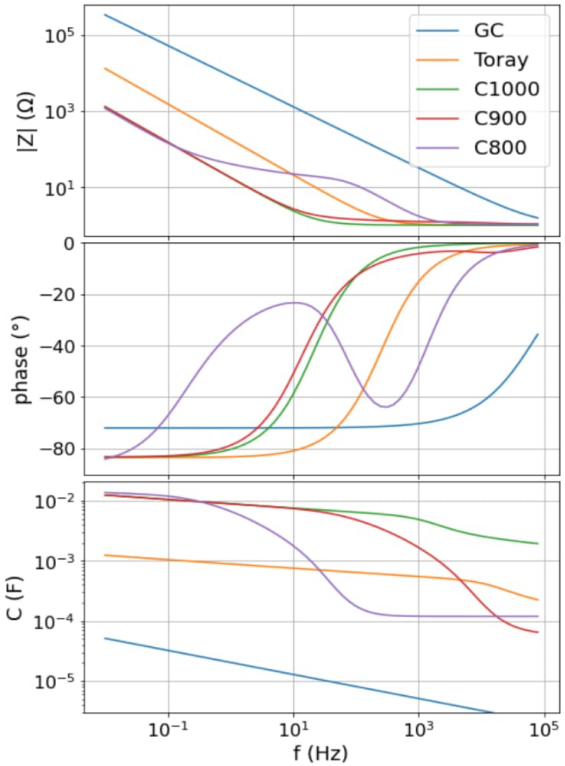
Outcome

- A model describing the influence of porous structures on the bilayer capacity was created to better understand the impedance spectrum.
- Based on the model, the flooding of the electrodes during CO_2 electrolysis can be interpreted better.

Description by advanced equivalent circuit model



Modeled impedance spectra of model electrodes



Involved partners: Dr. H. Tempel, Dr. Y. Emre, Dr. M. Schalenbach

WP 3.5 System Analysis

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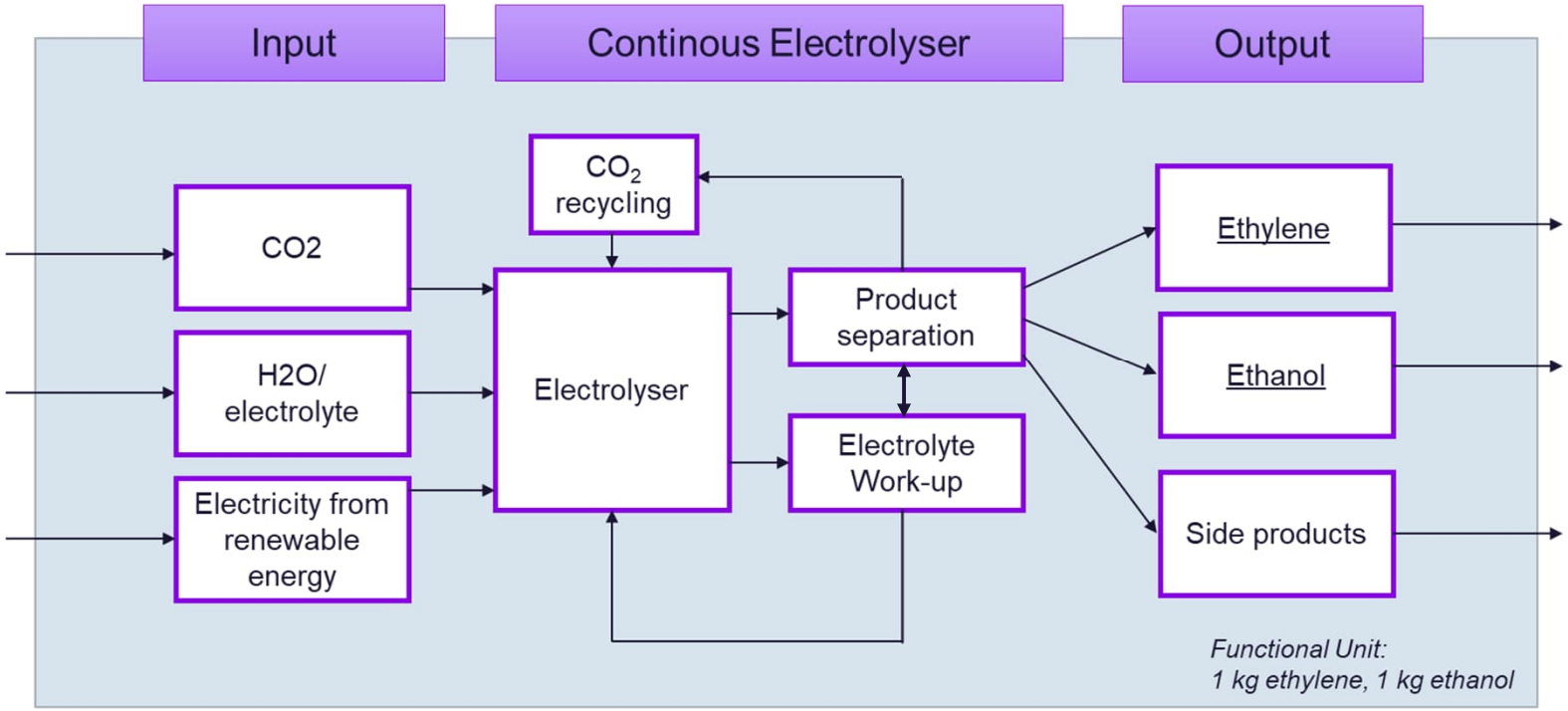
Objective: Consideration of system aspects regarding the continuous operation of an CO_2-to-HC electrolyzer.



Outcome: Solutions developed in terms of product separation and electrolyte work-up.

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Summary & Outlook

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- ☑ Cu_4O_3 has been shown to be an efficient and selective catalyst for the electrolysis of CO_2 to ethylene and ethanol.
- ☑ Scale up of the Cu_4O_3 synthesis to 60 g demonstrated with possibility for further upscaling up to industrial level.
- ☑ Tailor-made ionomers (AEI) have been realized and up-scaled which enable improved ion transport in the cell.
- ☑ The foundations for a high throughput fabrication of catalyst layers by means of doctor blade coating have been created.
- ☑ A basic understanding of the flooding behavior at the electrolyte/electrode interface was developed.
- ☑ Performance targets were achieved for Cu_4O_3 / AEI 4 (final milestone).
- ☑ Concepts for continuous operation of an electrolyzer developed that potentially allow an energy efficient product separation and work-up of electrolyte.

Outlook

- ➢ Increase in efficiency, CO_2 usage efficiency, product yield and stability.
- ➢ Availability of renewable energies at affordable electricity costs and a corresponding amount of CO_2 required.

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Acknowledgement

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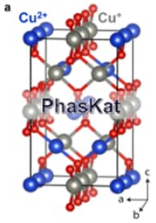

Thank you

for your attention!

Dr. Wiebke Sarfert-Gast

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