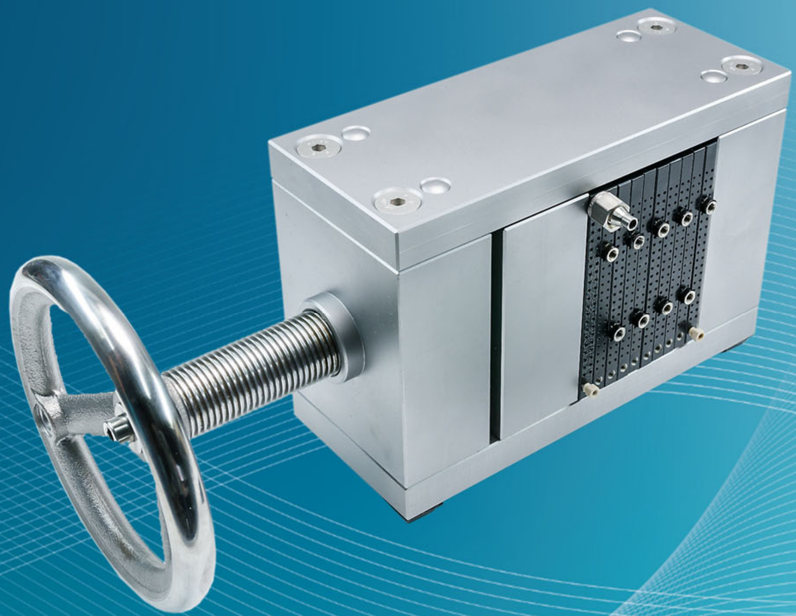


Fraunhofer IMM

Fraunhofer Institute for Micro-engineering and Microsystems IMM

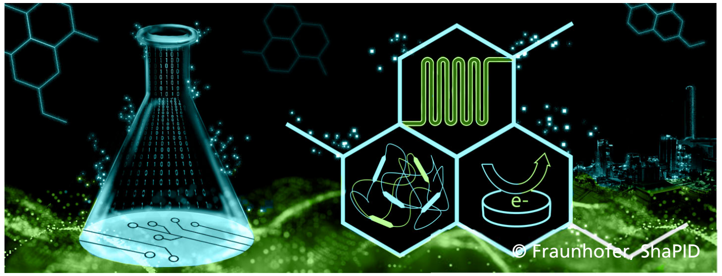
Flow reactors for the electrochemical CO_2 reduction to formate / formic acid and beyond

25.03.2025, Webinar “Unlocking CCU Potential Through Electrochemistry“

Dr. Patrick Löb, Deputy Head of Division Chemistry & Head of Group Flow Chemistry, Mainz, Germany

Introduction – background and context

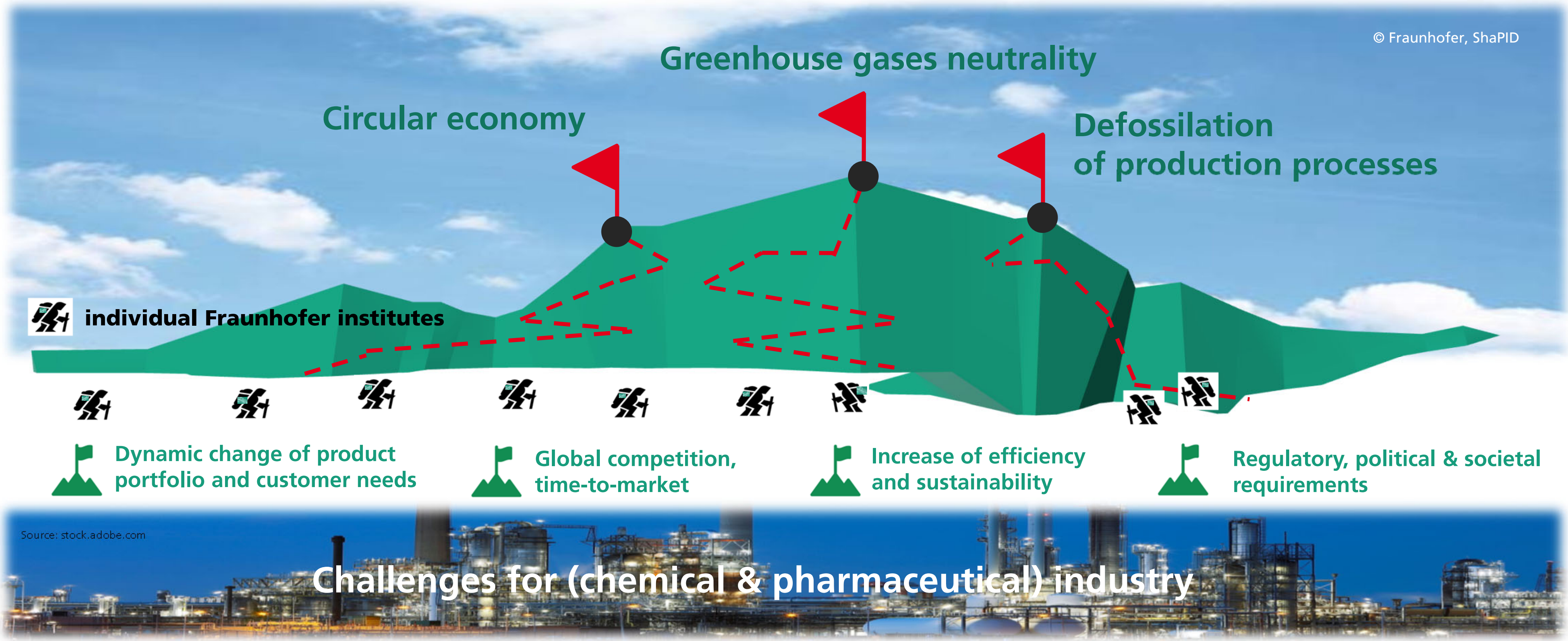
Introduction to Fraunhofer Lighthouse project ShaPID



- **Fraunhofer** is tackling current challenges faced by industry.
- Its internal **lighthouse projects** put the focus on strategic objectives with a view to developing practical solutions from which especially German and European economies can benefit.
- By **pooling their expertise** and involving industrial partners at an early stage (advisory board), the **Fraunhofer institutes** involved in the projects aim to turn original scientific ideas into marketable products as quickly as possible.
- **ShaPID** (**Sha**ping the Future of Green Chemistry by **P**rocess **I**ntensification and **D**igitalization) is one of these project (01/2021-06/2024)
- **Involved Fraunhofer institutes**: ICT (coordination), IAP, IFF, IGB, **IMM**, IME, ISC, ITWM, UMSICHT
- More information: https://www.shapid.fraunhofer.de/en.html (last access: 24.03.2025)

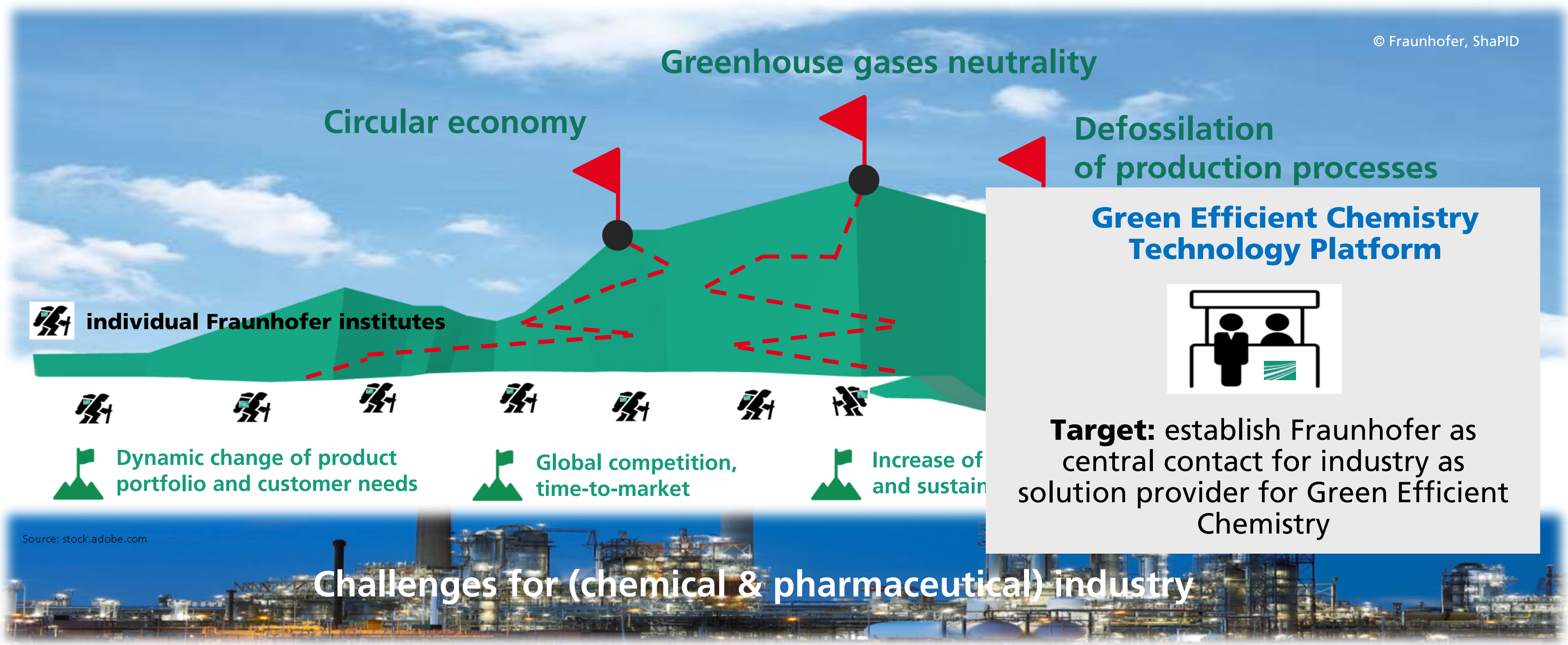
Introduction – background and context

General motivation and target in ShaPID – pooling of Fraunhofer competences



Introduction – background and context

General motivation and target in ShaPID – pooling of Fraunhofer competences



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Introduction – background and context – demonstration process in ShaPID

Process cascade for the production of green polymers from CO_2 and electric energy

- Transformation of society to more sustainablity → use of renewable materials for the manufacturing industry → polymer materials about 400 million tons worldwide (2021) → largest share produced from fossil resources → move to renewable feedstock basis like from mechanical or chemical recycling of plastic materials, biomass, and CO_2.
- CO_2 as raw material offer high scalability and sustainability.
- Different approaches, e.g.:
  - Direct reaction of CO_2 with expoxides to form polycarbonates
  - Synthesis of traditional or new monomers through reductive conversion of CO_2
    - E.g. reduction to methanol followed by conversion via Methanol-to-Propylene process into propylene
    - Processes targeting other and more complex and valuable polymer building blocks → ShaPID example

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

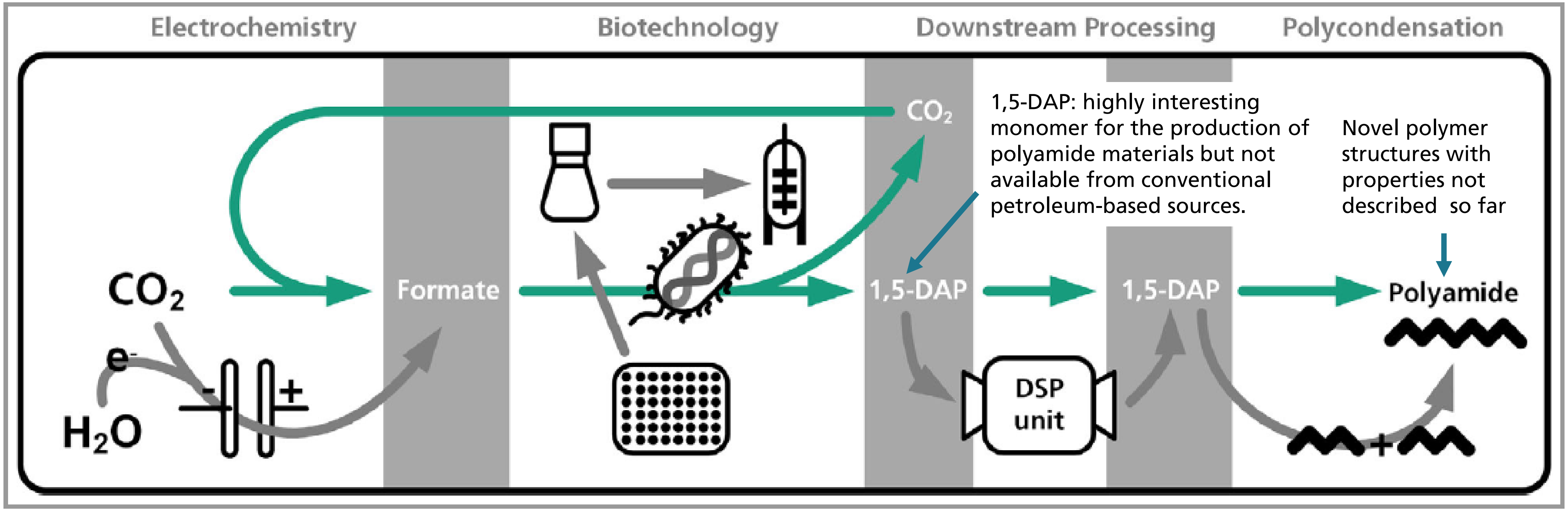
Introduction – background and context – demonstration process in ShaPID

Process cascade for the production of green polymers from CO_2 and electric energy

- **Novel process cascade** combining advantages of electrochemical CO_2 conversion with the synthetic potential of industrial biotechnology:
  - Electrocatalytic reduction of CO_2 to formic acid
  - Formic acid as substrate for the metabolically engineered bacterium *Methylorubrum extorquens*: production of 1,5-diaminopentane (cadavarine) via L-lysine as precursor
  - Purification of cadaverine via targeted downstream processing
  - Usage in a polycondensation process to produce polyamide materials

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

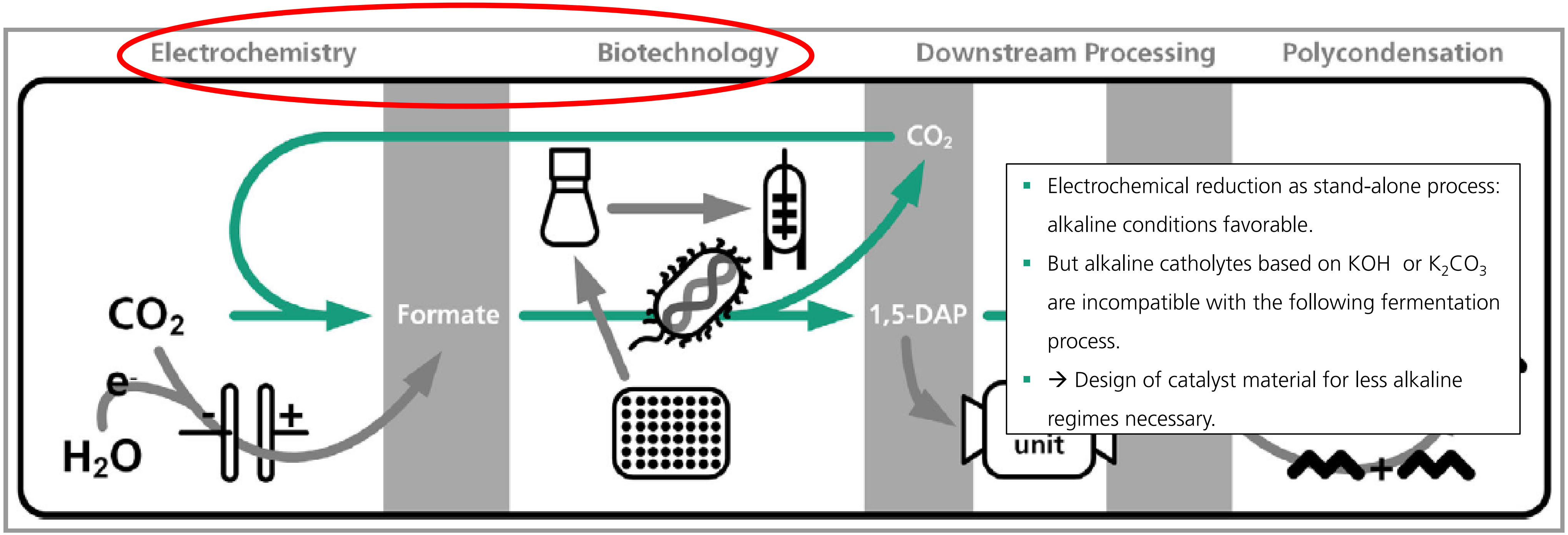
Process cascade for the production of green polymers from CO_2 and electric energy



J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

1,5-DAP: 1,5-diaminopentane
DSP: downstream processing

Process cascade for the production of green polymers from CO_2 and electric energy



- Electrochemical reduction as stand-alone process: alkaline conditions favorable.
- But alkaline catholytes based on KOH or K_2CO_3 are incompatible with the following fermentation process.
- → Design of catalyst material for less alkaline regimes necessary.

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

1,5-DAP: 1,5-diaminopentane
DSP: downstream processing

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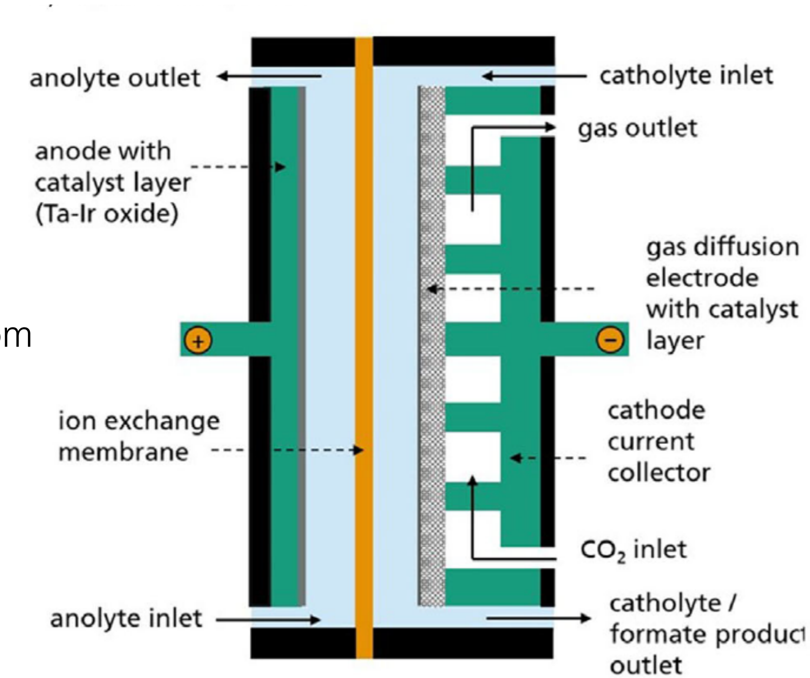
Electrocatalysis platform in ShaPID for the demo process

Approach: electrochemical formate production – electrolysis cell

- **Liquid catholyte**
- Phosphate buffer at pH >> 7 as electrolyte
  - Ir mixed metal oxide anode from Special Anodes B.V.
  - 1.6 mm thick compartments



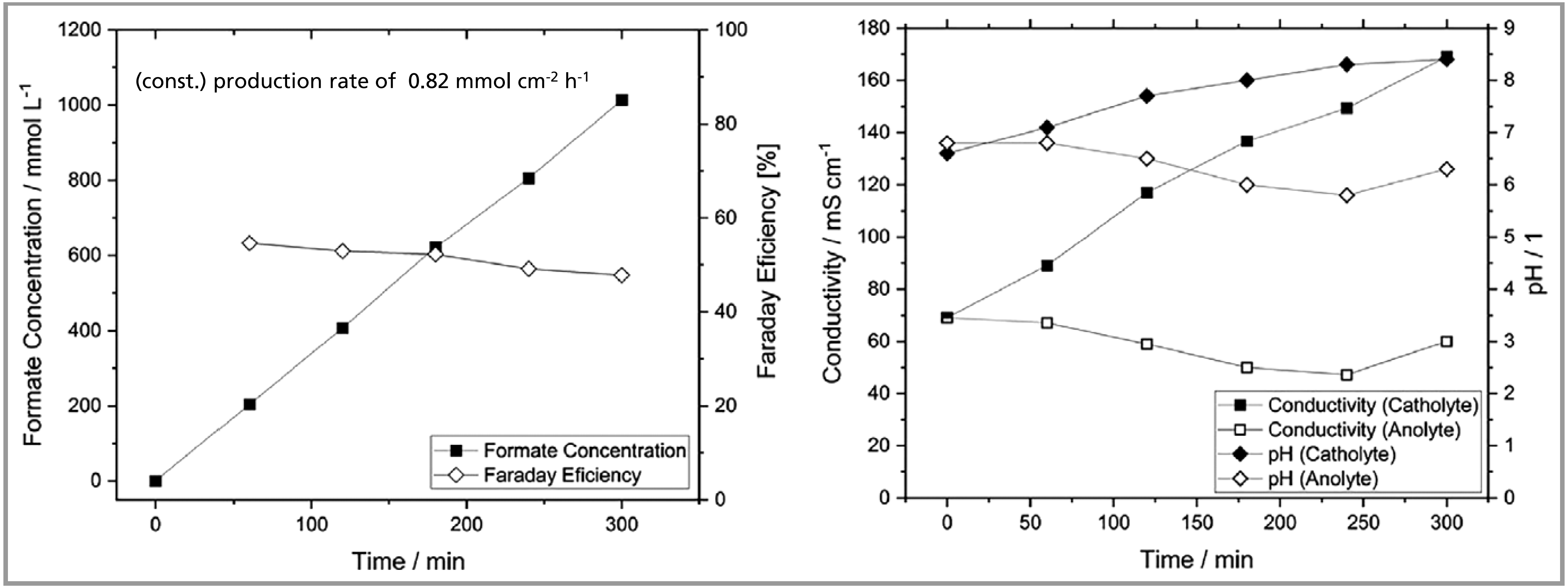
- Cathode area: 123 cm^2
- GDL: Freudenberg GmbH + coating with tin-based electro catalysts

- Cation exchange membrane: Fumasep F-10150-PTFE

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

Approach: electrochemical formate production – experimental results

Recirculation of 500 mL 1 M phosphate buffer. Current density: 81 mA cm^{-2}.



J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

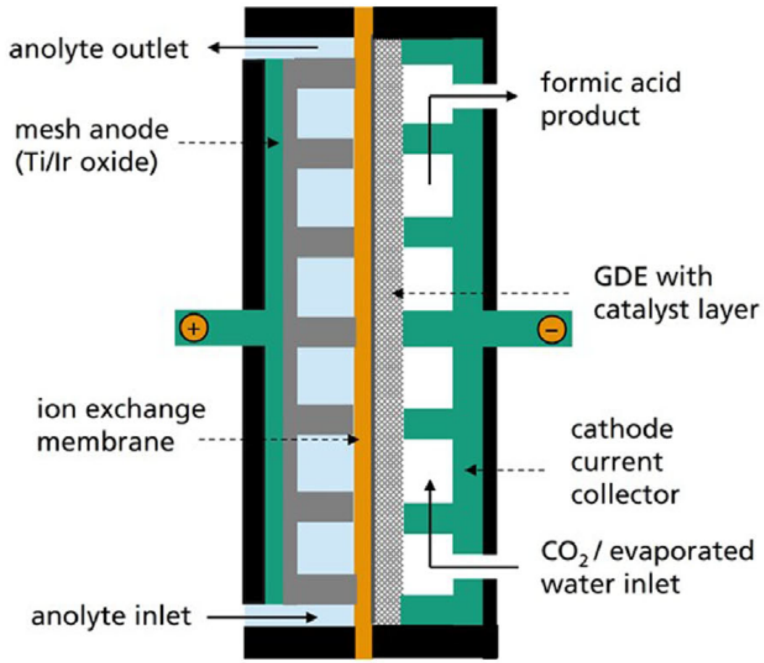
Electrocatalysis platform in ShaPID for the demo process

Approach: electrochemical formic acid production – electrolysis cell

- **Catholyte-free process***

  *K. T. Park et *al.*, *Angew. Chem. Ing. Tech.* **2018**, *57*, 6883-6887.

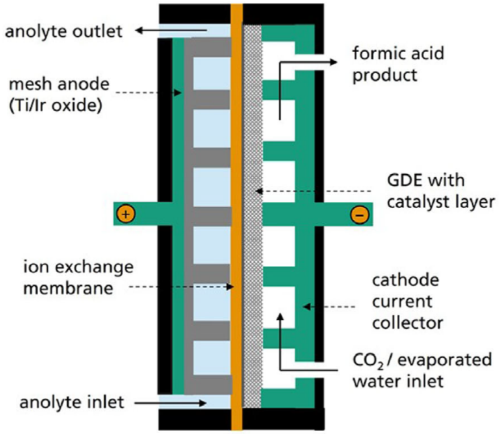
  - Formic acid solutions free of electrolyte salts are advantageous as feed stream for fermentation.
  - Exploration of cell configuration zero-gap cathodic and anodic half-cells.



J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

Electrocatalysis platform in ShaPID for the demo process

Approach: electrochemical formic acid production – first experimental results



1 M KOH aq

- First investigations done, more needed.
- Mixture of formic acid, formate formed, FE 12%.
- **Potential:***
  - no loss of formic acid/formate by diffusion into the anolyte observed
  - stable process parameters
  - performance tunable by CO_2/water vapor ratio
- Further studies to improve process – parameters: anolyte composition, electrocatalyst, current density, temperature, type of membrane, etc.

*Exemplary results from K. T. Park et *al.*, *Angew. Chem. Ing. Tech.* **2018**, *57*, 6883-6887: 41.5 g L^{-1} formate concentration, 343 K, PCD 51.7 mA cm^{-2} , FE 93.3% at 2.2 V. Energy efficiency (other parameters) at best 64.7%. Commercial tin catalyst.

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 . CC BY-NC-ND 4.0 - https://creativecommons.org/licenses/by-nc-nd/4.0/

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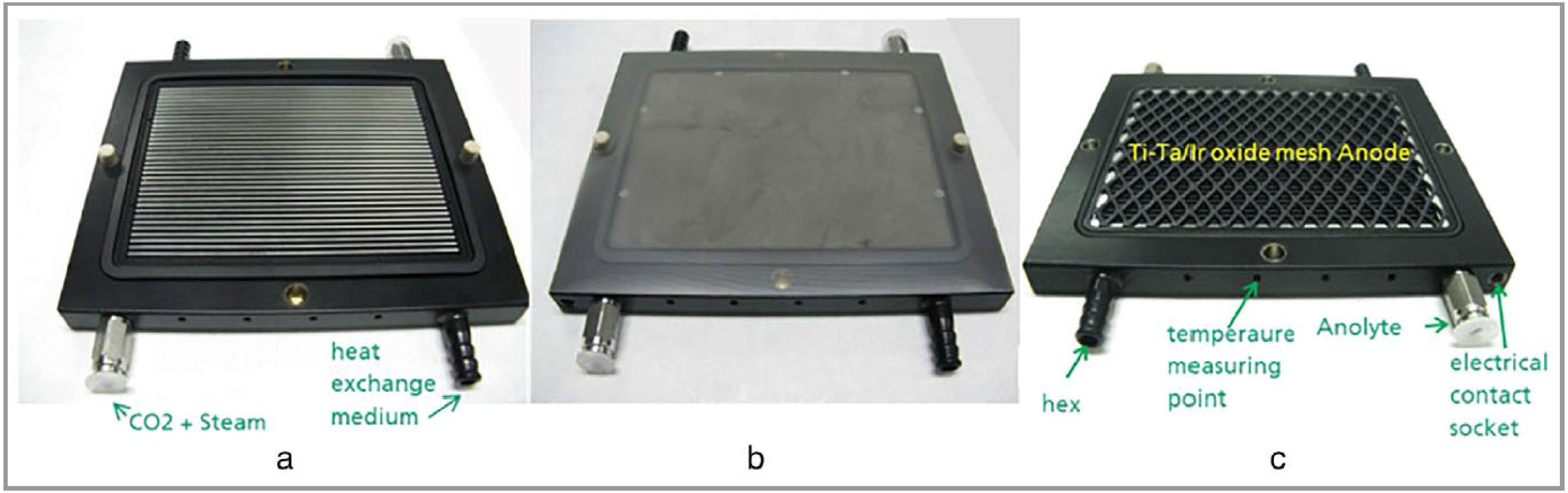
Electrocatalysis platform in ShaPID for the demo process

Approach: electrochemical formic acid production – cell development



J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 . CC BY-NC-ND 4.0 - https://creativecommons.org/licenses/by-nc-nd/4.0/

Electrocatalysis platform in ShaPID for the demo process

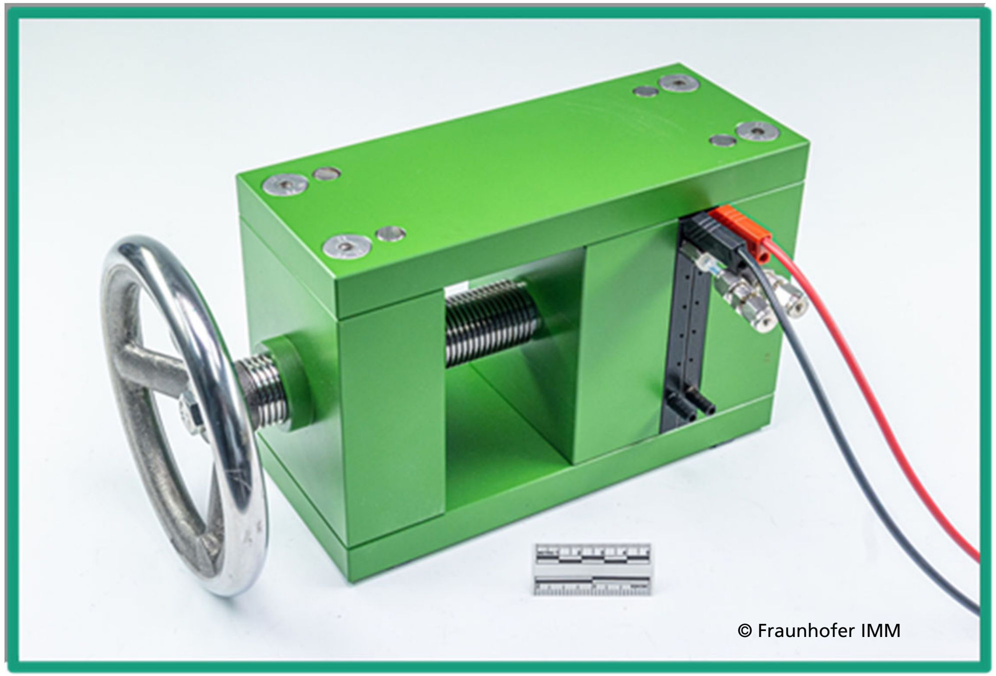
Approach: electrochemical formic acid production – fabrication steps

- Additive manufacturing to produce the current collector plates with their complex internal fluid distribution structures.
- Creation of microchannels as fluid distribution structures on the smooth surface of the plates by milling.
- Surface coating (e.g., with PTFE) of the plates.
- Removal of the polymer coating from the channel bar (cathode side) and from the periphery frame (anode side) by milling to enable the electrical contacting of the electrodes.
- Galvanic deposition of platinum on the free metal surface areas for better electrical contact and corrosion protection.

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 .

Electrocatalysis platform in ShaPID for the demo process

Approach: electrochemical formic acid production – complete reactor

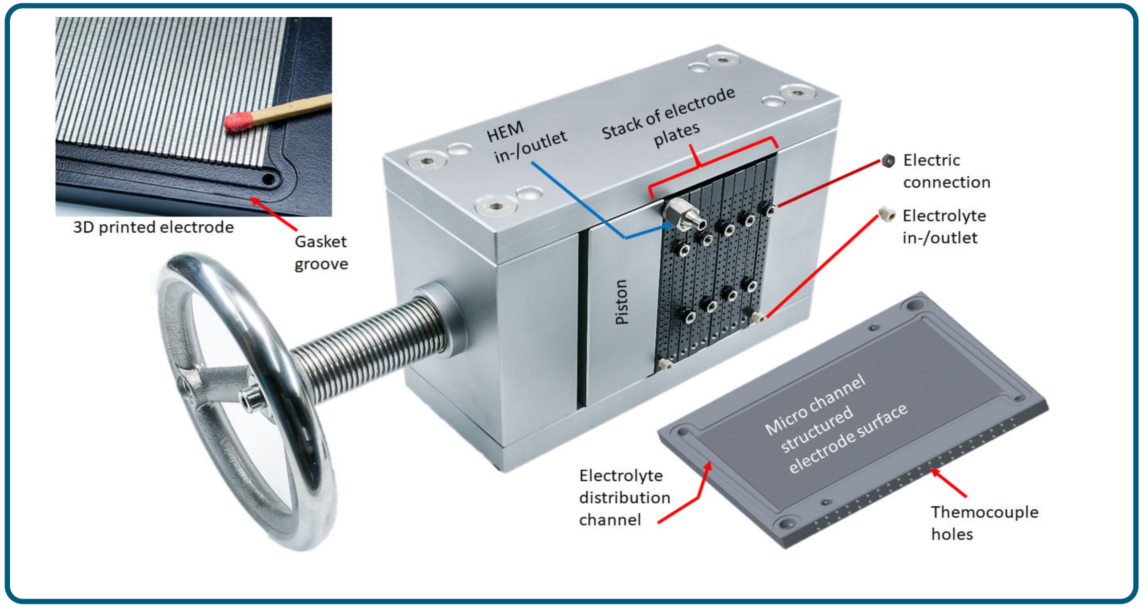


- Scale-up will be adressed through stacking of multiple cells
- The design both for electrode plates and press follows a general concept applicable, adjustable for other purposes

J. T. Fabarius et *al.*, *Chem. Ing. Tech.* **2024**, *96*, No. 5, 698-712. DOI: 10.1002/cite.202400002 . CC BY-NC-ND 4.0 - https://creativecommons.org/licenses/by-nc-nd/4.0/

Modular and Scalable Electrochemical Microreactor for Versatile Applications

Reactor concept



➡ Up to 20 cells in parallel operation

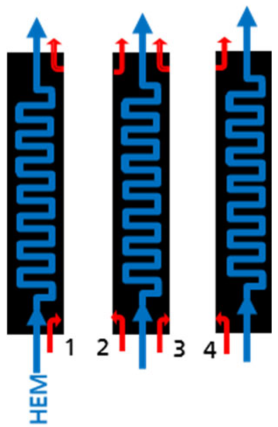
- Flexible and scalable reactor concept
- 3-D printed electrodes with integrated heat exchanger
- PTFE coating for insulation
- Microstructured electrode surface

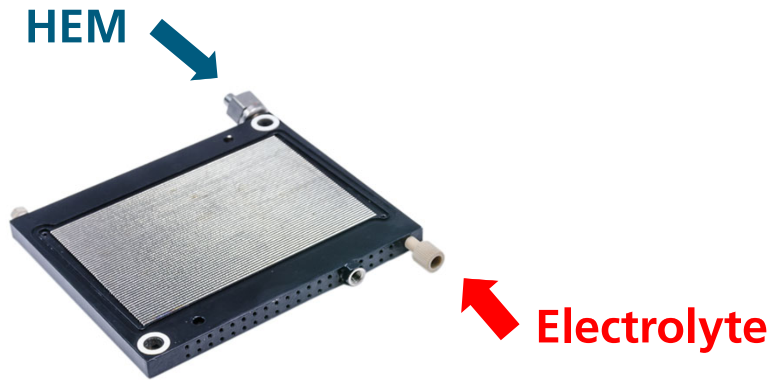
Parameter	Value
#Microchannels	56
Electrode distance	150 µm
A_{ges}	42.6 cm^2
V_{ges}	0.64 cm^3

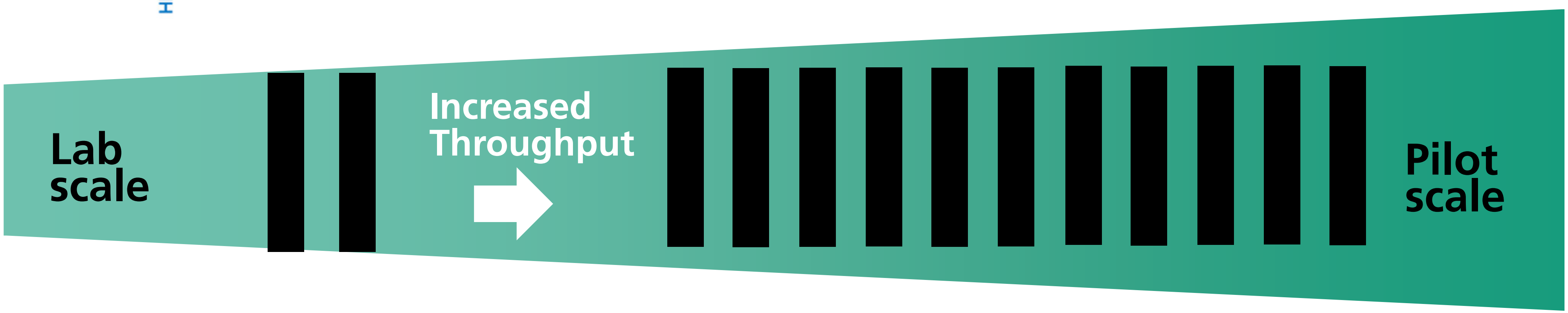
A. Ziogas, C. Hofmann, S. Baranyai, P. Löb, G. Kolb, *Chemie Ingenieur Technik* **2020**, *92*, 513.

Modular and Scalable Electrochemical Microreactor for Versatile Applications

Reactor concept & concept for scale-up







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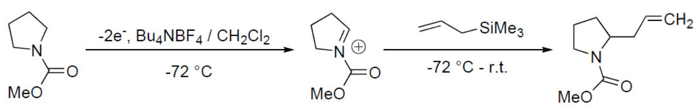
Application examples

Cation-Flow-Methode

+ 7 °C

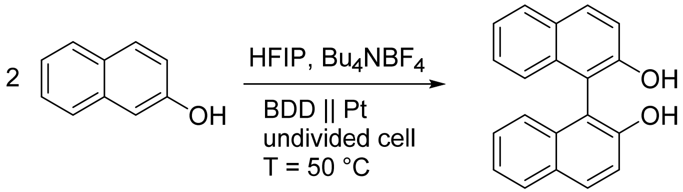


Peroxodicarbonate

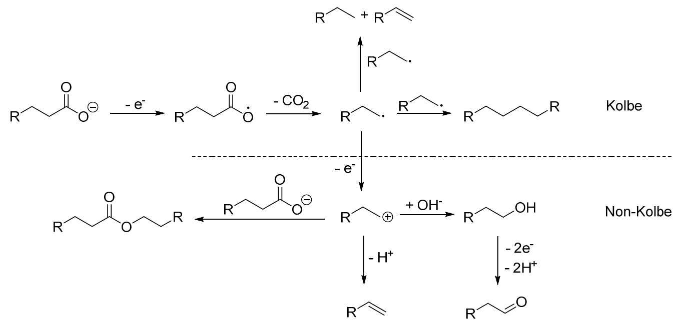
$$2CO_3^- \xrightarrow{-2e^-} C_2O_6^{2-}$$

$$2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$$

C-C Coupling of Phenols



Kolbe Electrolysis



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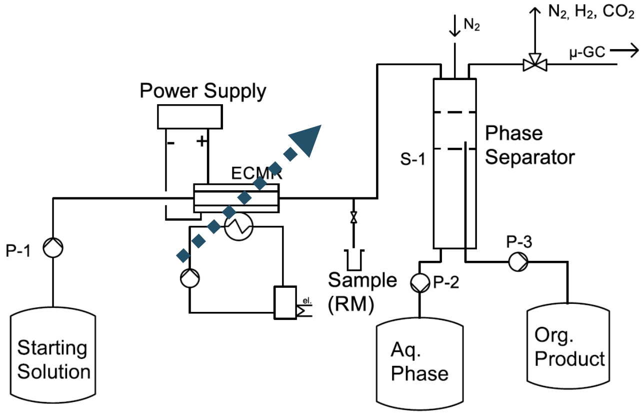
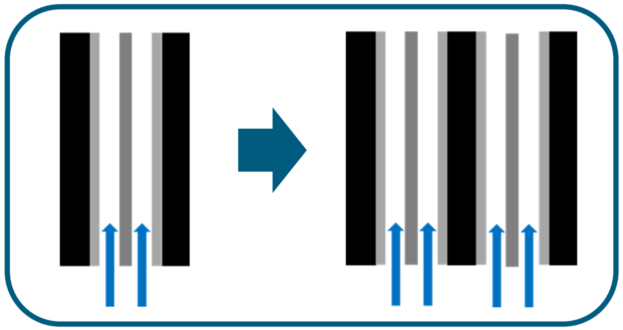
Modular and Scalable Electrochemical Microreactor for Versatile Applications

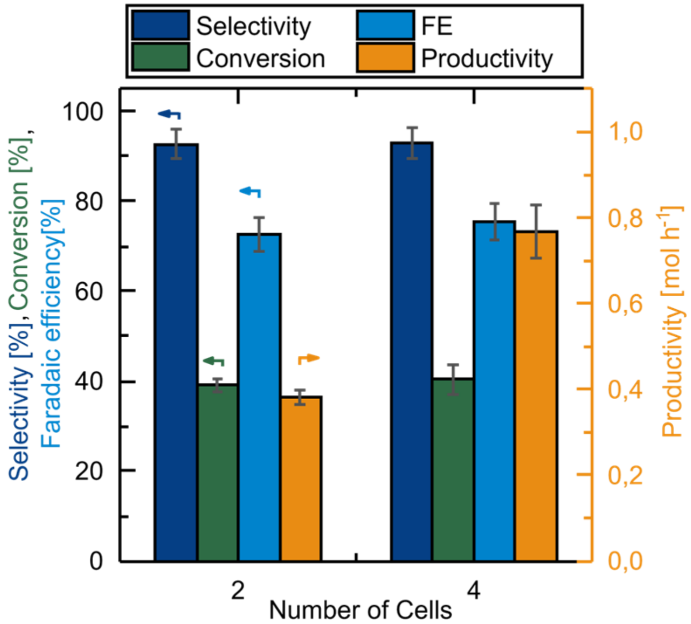
Validation of scalability of reactor concept by numbering-up

N. Baumgarten, B. J. M. Etzold, J. Magomajew, A. Ziogas, *ChemistryOpen* **2022**, *11*, e202200171513. doi.org/10.1002/open.202200171

▪ Validation for Kolbe Electrolysis







Proof-of-Concept scalability by numbering-up

Kolbe Electrolysis with up to 10 cells in parallel

→ ca. 1.4 kg/h fatty acid conversion; 0.85 kg/h productivity

→ 20 cells: 3-5 kg/h conversion, 2-3 kg/h productivity (depending on substrate)

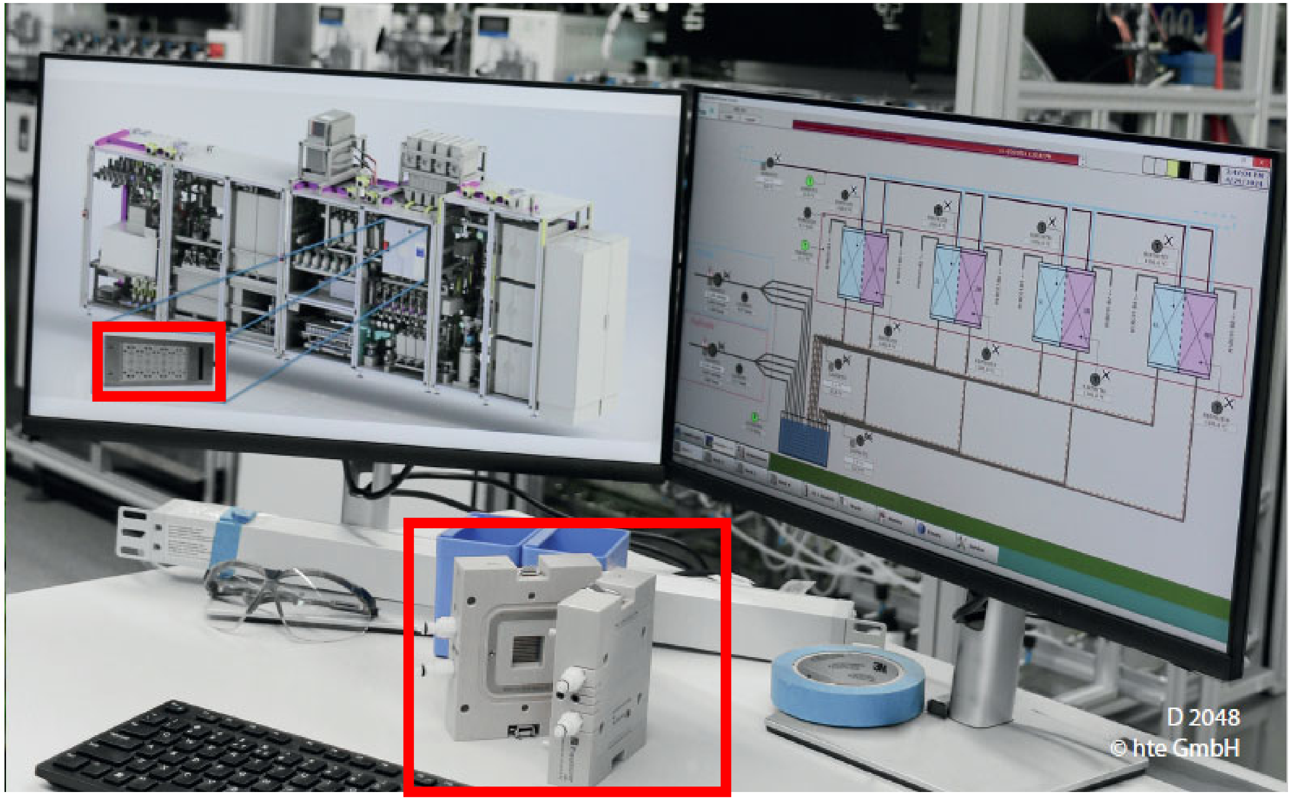
Modular electrochemical cells for screening purposes

Chemie Ingenieur Technik   Short Communication   1

High-Throughput Experimentation in Electrochemistry for Alkaline Water Electrolysis

Inka Dessel, Deniz Dogan, Rüdiger-Albert Eichel, Burkhard Hecker, Christian Hofmann, Florian Huber, Asha Jakob, Hans-Joachim Kost, Patrick Löb, Andreas Müller, Sarifahnurliza Sahehmahamad, Volkmar M. Schmidt, Fabian Schneider, Hermann Tempel, Guido Wasserschaff* and Athanassios Ziogas

DOI: 10.1002/cite.202300234



Modular electrochemical cells for screening purposes

https://www.fraunhofer.de/en/press/research-news/2023/september-2023/modular-flow-cells-for-sustainable-chemistry.html (last access 06.01.25)

Summary

1. Integration of electrochemical CO_2 reduction in a novel process cascade to produce novel green polymers
2. Promising catholyte free process route to formic acid explored
3. Modular and scalable reactor design for broader applicability introduced
4. Application for screening purposes outlined

Acknowledgements:

ShaPID team from involved Fraunhofer institutes:

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IMM team: A. Ziogas, N. Baumgarten, H.-J. Kost, C. Hofmann, J. Magomajew, S. Baranyai, J. Rocker, …

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Thank you for your attention!