Sustainable Plastics Symposium

CO2EXIDE – Electrochemical CO_2 conversion to produce ethylene and ethylene oxide derivates

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March 25, 2021

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768789.

CO_2EXIDE Project

- **Aim:** Development of an electrochemical, energy-efficient and near-to CO_2-neutral process to produce the bulk chemical ethylene oxide and further derivates from CO_2, water, and renewable energy
- **Duration:** January 2018 – June 2021
(6-month extension due to COVID-19)
- 3.5-years funding by **Horizon2020**

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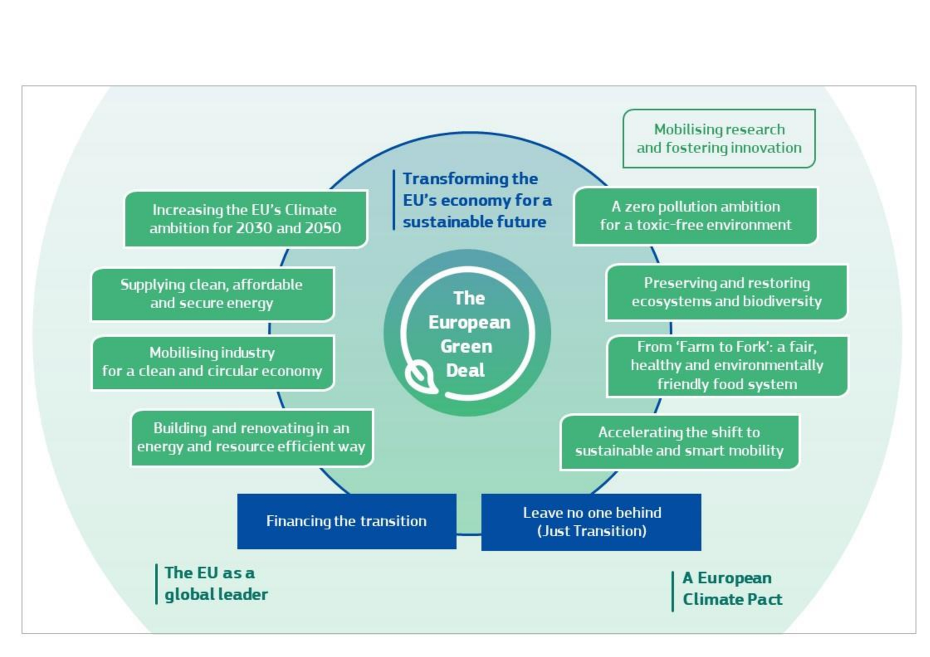
Motivation: Climate Protection and Circular Economy

- Paris Agreement 2015 (COP 21) → 1.5/2 °C target
  - Global economy to be carbon-neutral by mid-century
- European Green Deal
  - EU to become GHG-neutral by 2050
  - Economic growth is decoupled from resource use
- National legislations are taking shape
  - All sectors need transition to sustaineble energy and feedstock base



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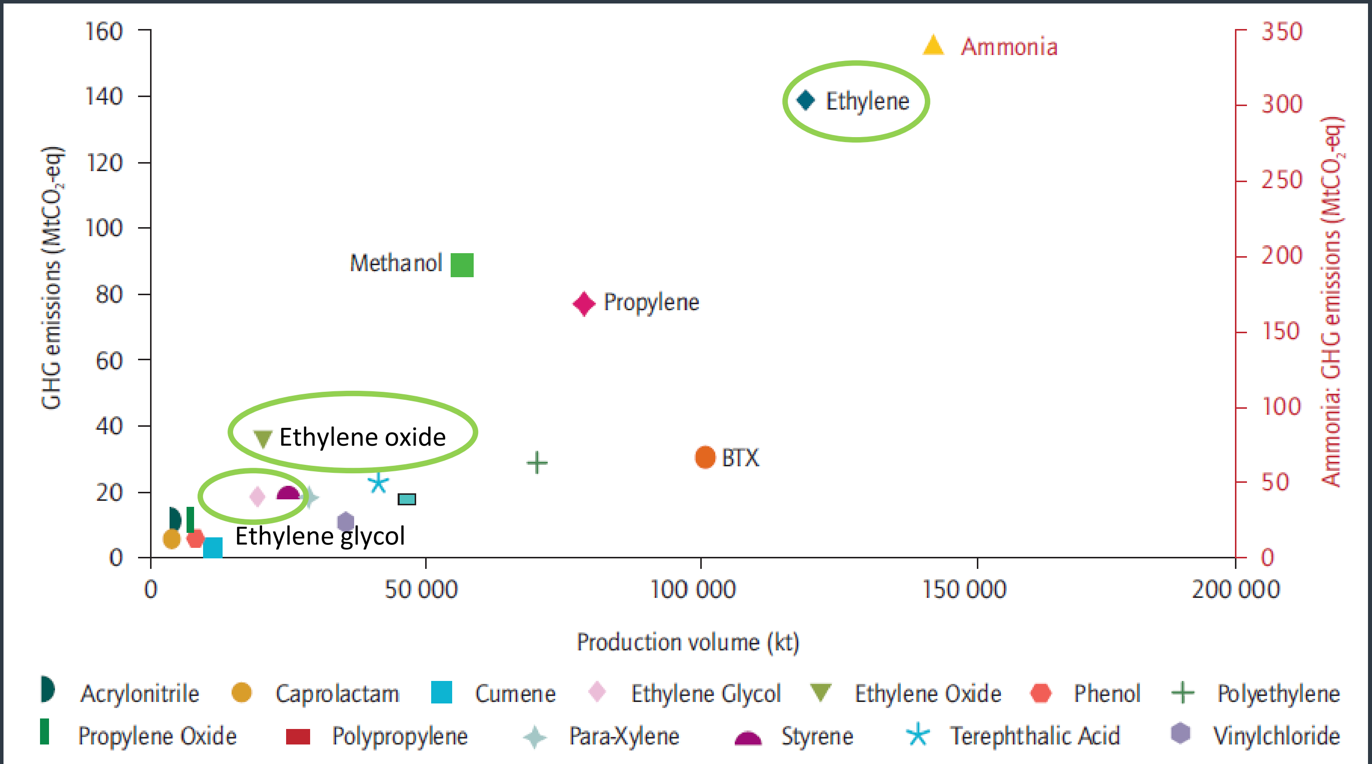
Chemical industry

- (Petro-)chemical processes:
  - 1.24 Gt CO_2-eq/yr (ref. 2012)
  - 3-4% of total global GHG emissions
- Transition to sustainable chemical industry requires:
  - Renewable energy
  - Renewable (carbon) feedstock
    - not only biomass and recycling
    - CO_2 as important carbon source



Source: Technology Roadmap - Energy and GHG Reductions in the Chemical Industry via Catalytic Processes, Dechema, IEA, ICCA, 2013.

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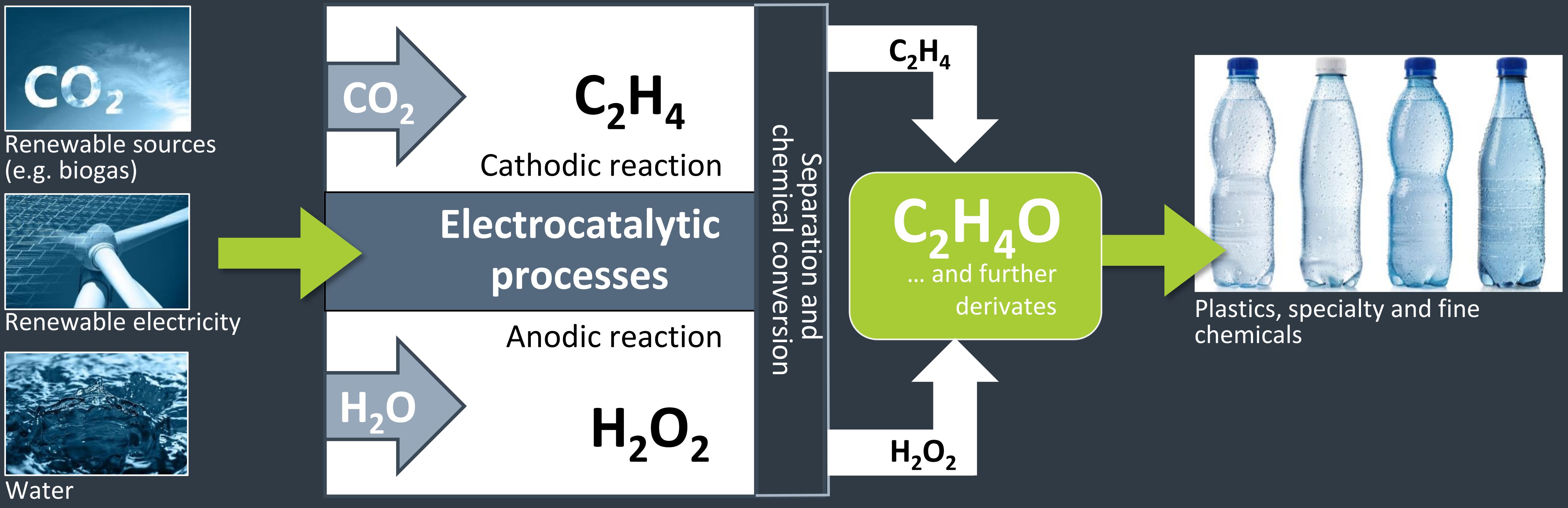
CO_2EXIDE Process



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Central Innovations

- Parallel value-adding electrocatalytic processes (“200 % cell”)
- Integrated conversion → electro- and chemo-catalysis
- Development of materials: electrocatalysts and electrodes
- Electrochemical cell
    - compact design
    - dynamic operation mode
- Synthesis of important platform chemicals: Ethylene, ethylene oxide, glycols

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CO_2EXIDE Process

Renewable sources (e.g. biogas)

Renewable electricity

Water

Feedstock supply

→ CO_2 purification

→ Feedstock potentials (CO_2 and renewable electricity)

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axiom

Plastics, specialty and fine chemicals

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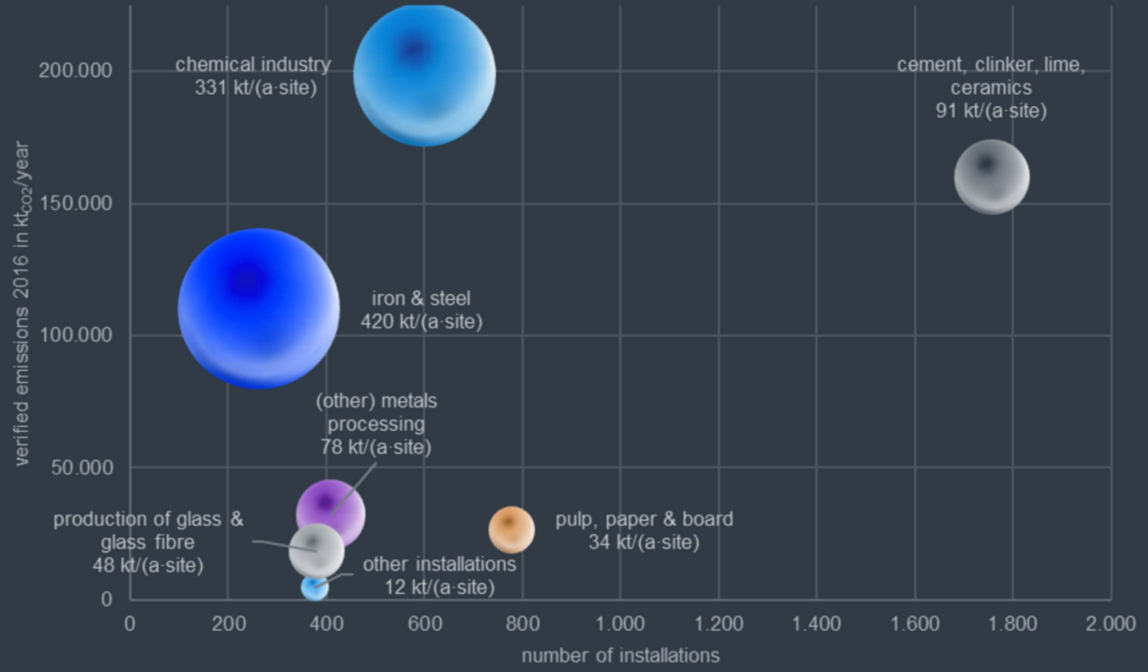
Potential of CO_2 point sources in EU

- Potential of CO_2 from renewable and fossil point sources evaluated
- Comprehensive statistical analysis in terms of available volumes, distribution and CO_2-purity
- CO_2 from biogas has currently a potential of ~ 23 Mt/y in Europe
- Public Report D2.1 (Potential of green CO_2 sources for ethylene synthesis) (Link)



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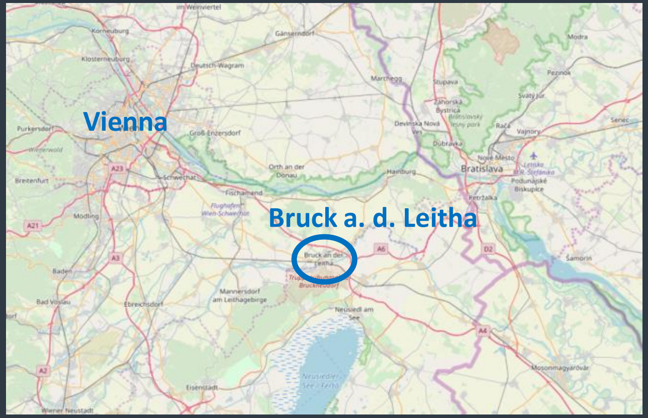
CO_2 source in CO2EXIDE

- Biogas plant in Bruck an der Leitha (Austria)
- Biogas plant utilizes up to 34.000 t/y biowaste and produces 5 million sm^3/y of biogas
- CO_2 offgas stream from biogas upgrading totals 1,6 million sm^3/y (~3.400t. of CO_2)
- Enrichment to 99.4% CO_2



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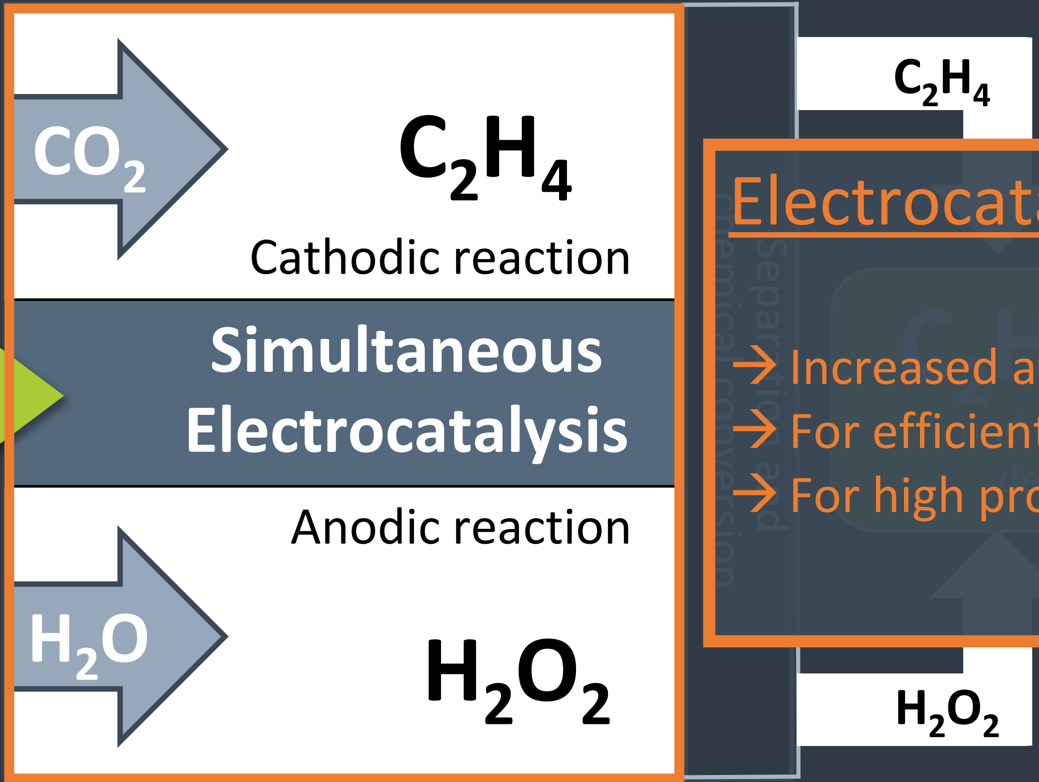
CO_2EXIDE Process

University of Southampton
Academic Centre for Materials and Nanotechnology AGH
Fraunhofer IGB
Latvijas Universitātes Cietvielu Fizikas Institūts
SCHAEFFLER



Electrocatalysis

→ Increased activity, selectivity, stability
→ For efficient use of CO_2 and electric energy
→ For high product concentrations

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Electrocatalysis

- Cathodic reaction:
  $2\,CO_2 + 8\,H_2O + 12\,e^- \rightleftharpoons C_2H_4 + 12\,OH^-$

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Electrocatalysis

- Cathodic
  2 CO_2 + 8

Reaction	E^0/[V vs RHE]	(Product) Name, abbreviation
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	1.23	Oxygen Evolution Reaction, OER
$2H^+ + 2e^- \rightarrow H_2$	0	Hydrogen Evolution Reaction, HER
$xCO_2 + nH^+ + ne^- \rightarrow product + yH_2O$		*CO_2 Reduction, CO_2R*
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH_{(aq)}$	−0.12	Formic acid
$CO_2 + 2H^+ + 2e^- \rightarrow CO_{(g)} + H_2O$	−0.10	Carbon monoxide
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH_{(aq)} + H_2O$	0.03	Methanol, MeOH
$CO_2 + 4H^+ + 4e^- \rightarrow C_{(s)} + 2H_2O$	0.21	Graphite
$CO_2 + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	0.17	Methane
$2CO_2 + 2H^+ + 2e^- \rightarrow (COOH)_{2(s)}$	−0.47	Oxalic acid
$2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH_{(aq)} + 2H_2O$	0.11	Acetic acid
$2CO_2 + 10H^+ + 10e^- \rightarrow CH_3CHO_{(aq)} + 3H_2O$	0.06	Acetaldehyde
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH_{(aq)} + 3H_2O$	0.09	Ethanol, EtOH
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_{4(g)} + 4H_2O$	0.08	Ethylene
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_{6(g)} + 4H_2O$	0.14	Ethane
$3CO_2 + 16H^+ + 16e^- \rightarrow C_2H_5CHO_{(aq)} + 5H_2O$	0.09	Propionaldehyde
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH_{(aq)} + 5H_2O$	0.10	Propanol, PrOH

Nitopi et al., Chemical Reviews 2019, 119(12), 7610-7672.

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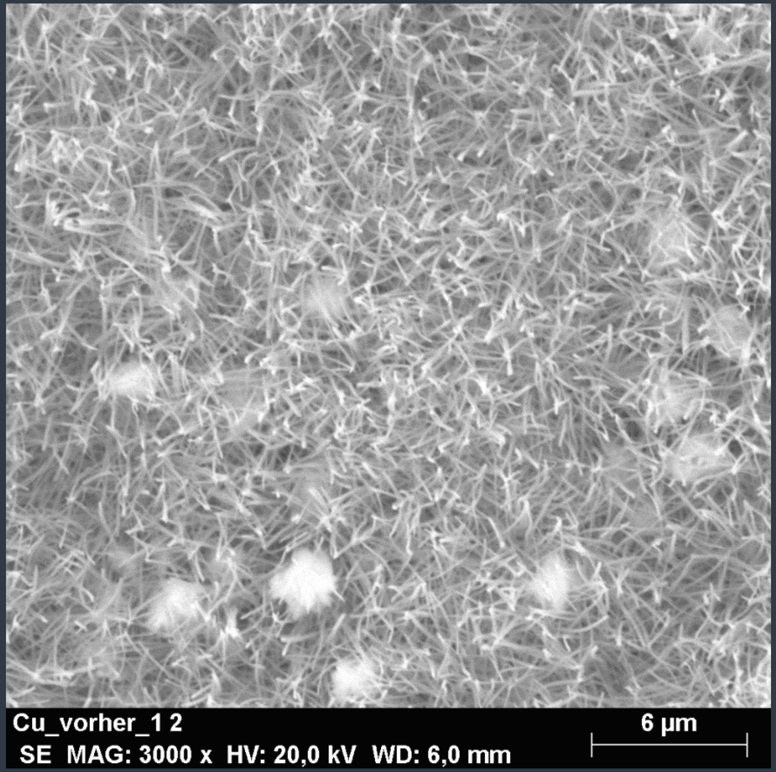
Electrocatalysis

- Cathodic reaction:
  $2\ CO_2 + 8\ H_2O + 12\ e^- \rightleftharpoons C_2H_4 + 12\ OH^-$

- Numerous competing reaction pathways for eCO_2R
- Water reduction at similar potential → H_2 evolution
- Good catalysts needed



Nano-structured Cu layer on GDE

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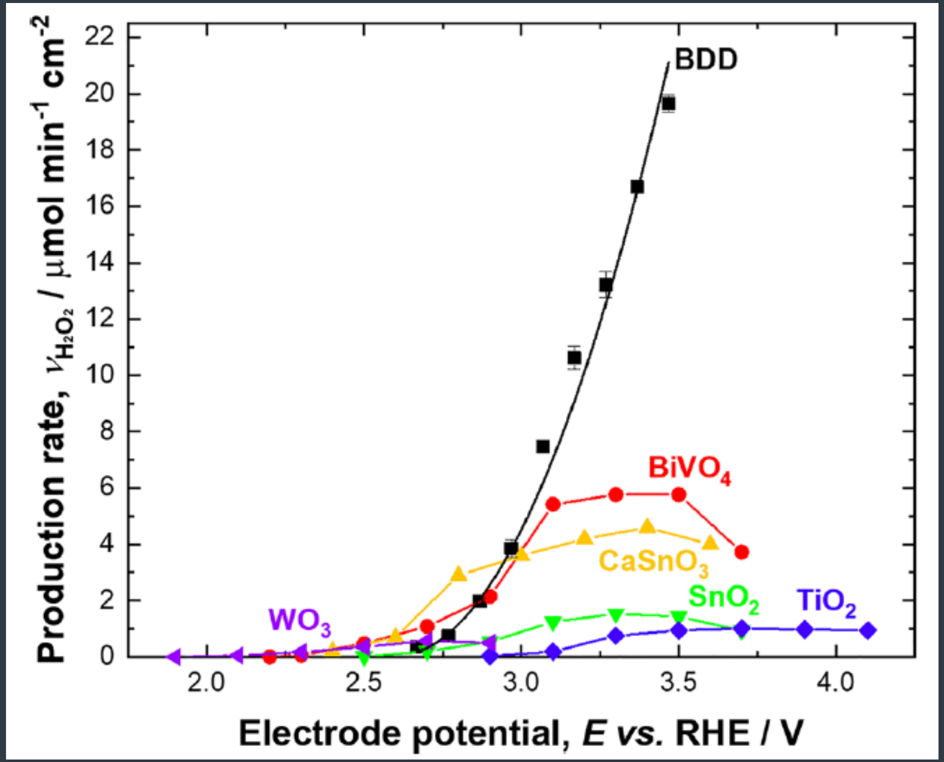
Electrocatalysis

- Anodic reaction:
  $2\ H_2O \rightleftharpoons H_2O_2 + 2\ H^+ + 2\ e^-$

- Challenge to achieve relevant concentrations (>0.1 M)
- Balancing reaction rate and selectivity
- Carbon material suitable → boron-doped diamond (BDD)



Mavrikis et al., ACS Applied Energy Materials 2020, 3(4), 3169-3173.

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UNIVERSITY OF Southampton

CO_2EXIDE Process

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UNIVERSITY OF Southampton

ACADEMIC CENTRE FOR MATERIALS AND NANOTECHNOLOGY AGH

SIEMENS energy

LATVIJAS UNIVERSITĀTES CIETVIELU FIZIKAS INSTITŪTS

CO_2 → C_2H_4

Cathodic reaction

Simultaneous Electrocatalysis

Anodic reaction

H_2O → H_2O_2

chemical conversion

C_2H_4

H_2O_2

Electrochemical cell

→ PEM cell design to combine CO_2 reduction and water oxidation

→ Development of membranes and electrodes

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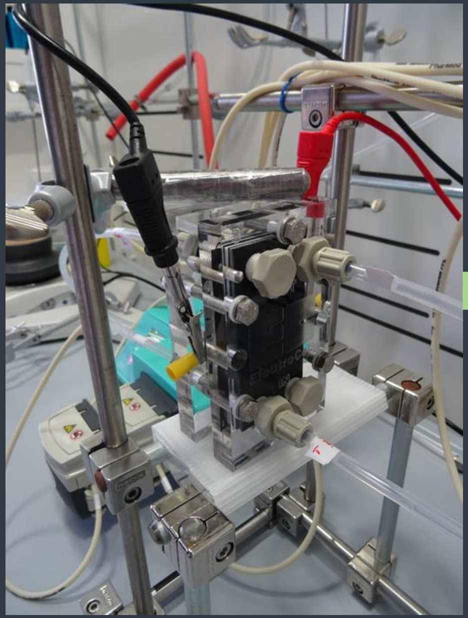
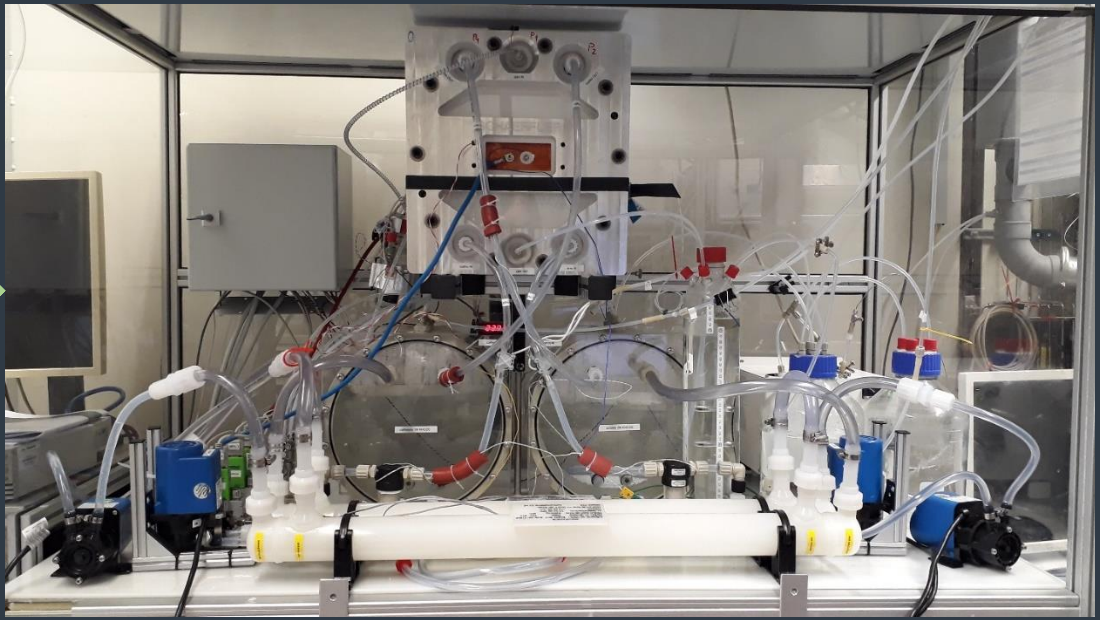
Scale-up from small to large lab-scale



7-10 cm²

25 cm²



300 cm²

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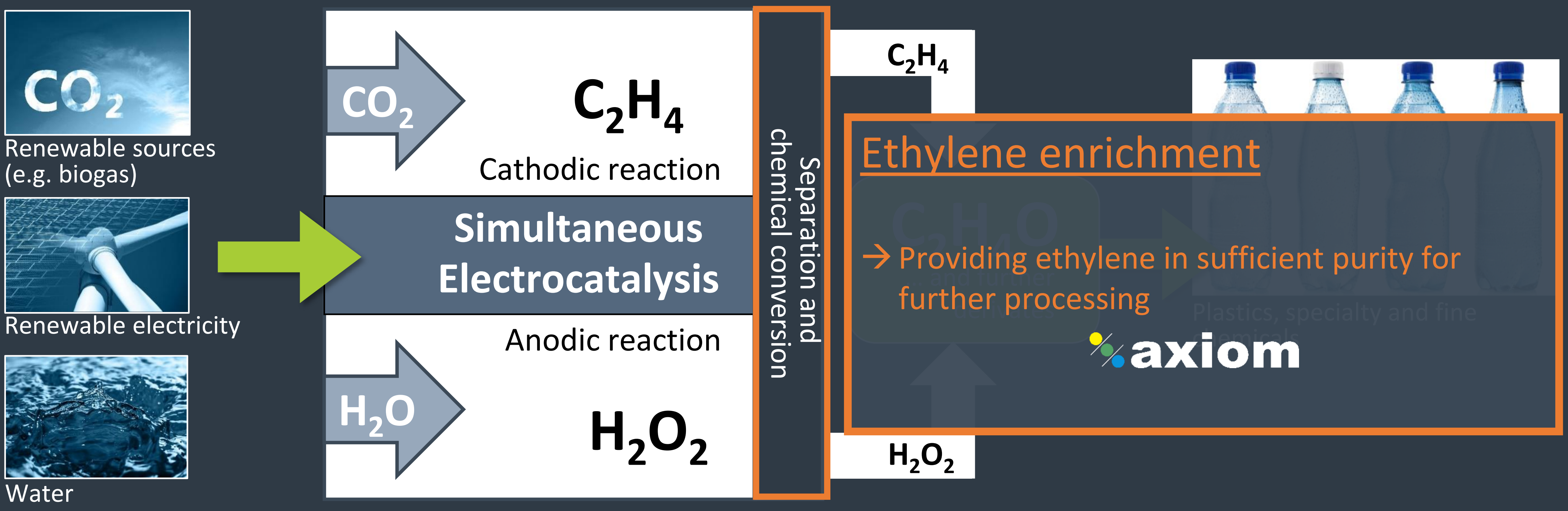
CO_2EXIDE Process



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Ethylene enrichment unit (EEU)

- High ethylene concentration needed
- Depletion of H_2 and CO_2
- Membrane technology, max 5 L/min, 10 bar
- Enrichment from 1% to 14-32% ethylene (>80% recovery)
- Almost full removal of H_2 from 15% to ~0%

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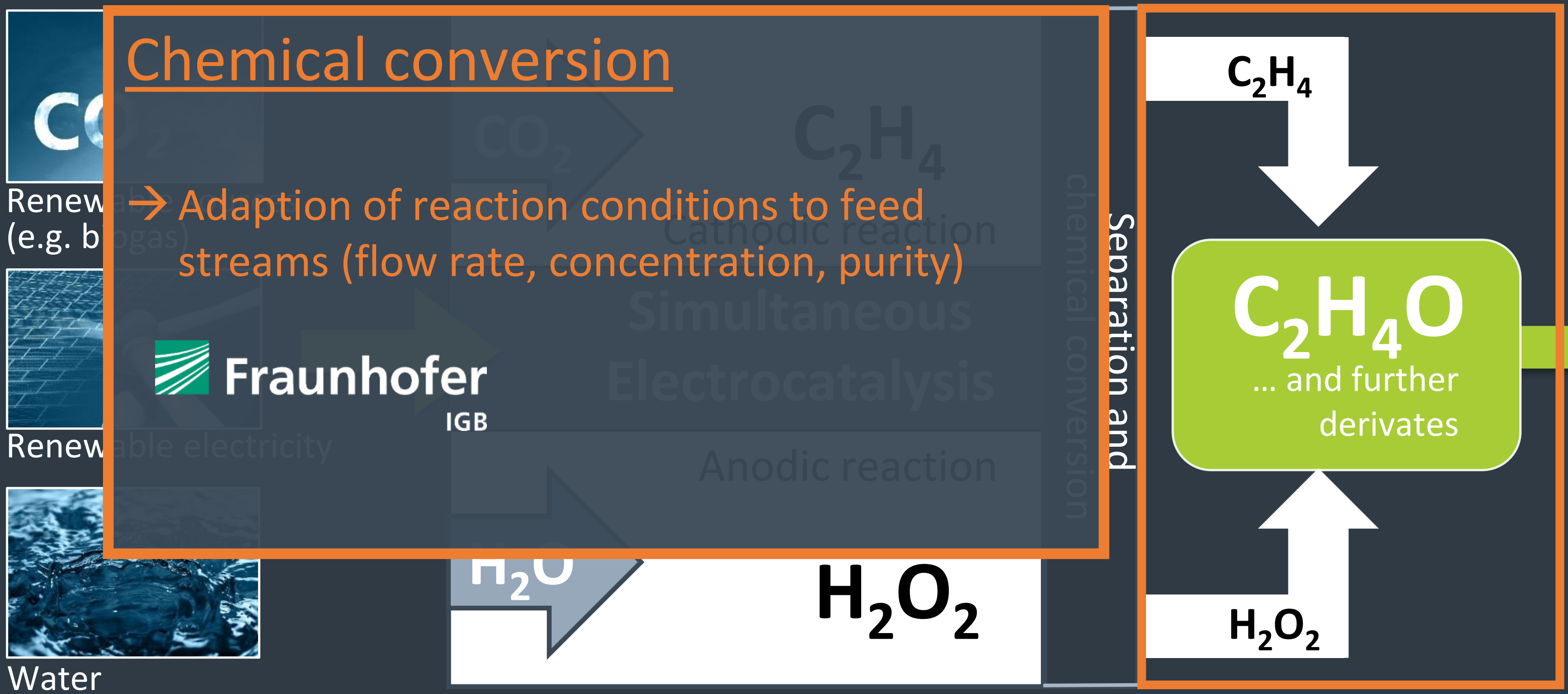
CO_2EXIDE Process



Chemical conversion

→ Adaption of reaction conditions to feed streams (flow rate, concentration, purity)

Fraunhofer IGB

Plastics, specialty and fine chemicals

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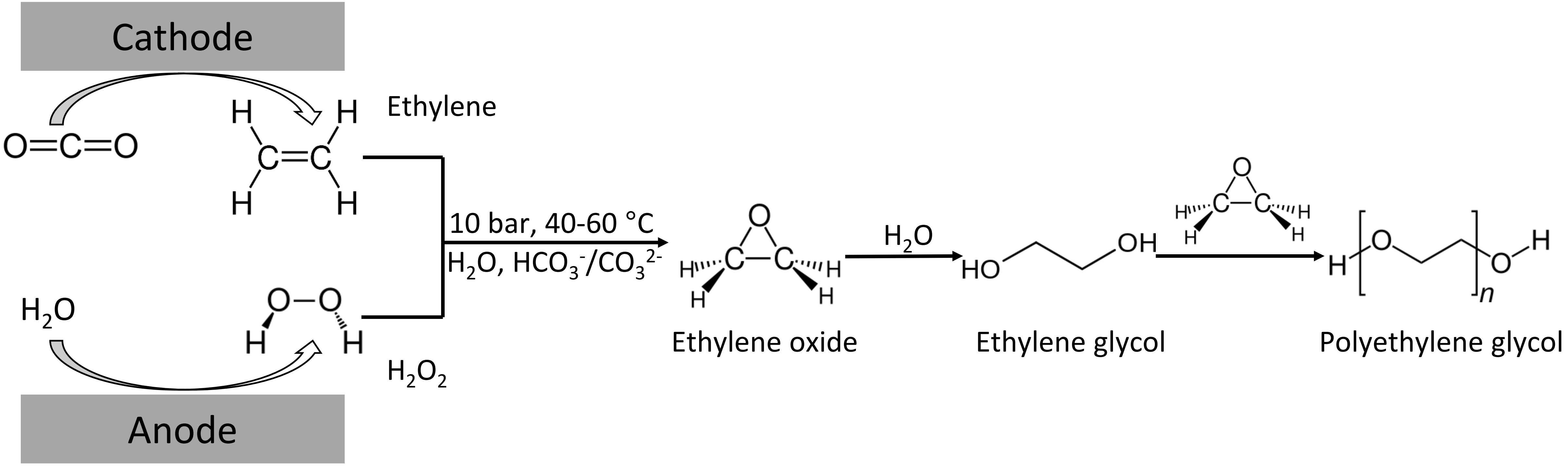
Chemical conversion: Ethylene oxide synthesis



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Fraunhofer IGB

Chemical conversion: Ethylene oxide synthesis

4 parallel 100 mL autoclave reactors

2 L reactor

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Fraunhofer IGB

CO_2EXIDE Process

Renewable sources (e.g. biogas)


Renewable electricity


Water

CO_2

C_2H_4

Cathodic reaction

Simultaneous Electrocatalysis

Anodic reaction

H_2O

H_2O_2

Separation and chemical conversion

C_2H_4

C_2H_4O

… and further derivates

H_2O_2

Demonstration

→ Coupling of process steps

→ Stable operating conditions

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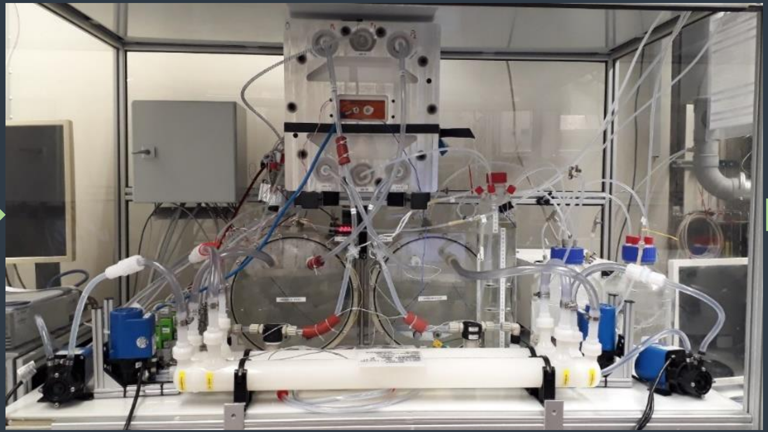
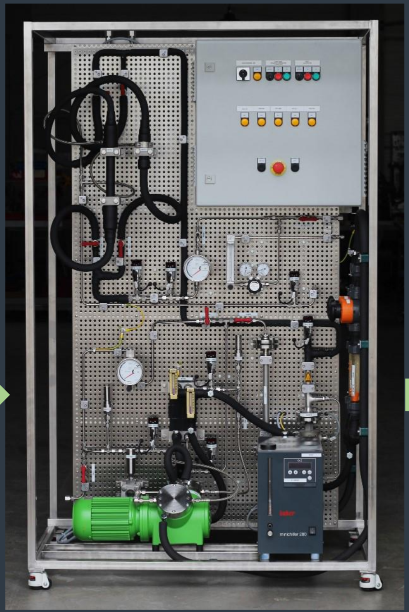
Demonstration @AGH in Krakow

CO_2 from biogas



Electrochemical cell (300 cm^2)



Ethylene enrichment

Chemical conversion (ethylene oxide synthesis)

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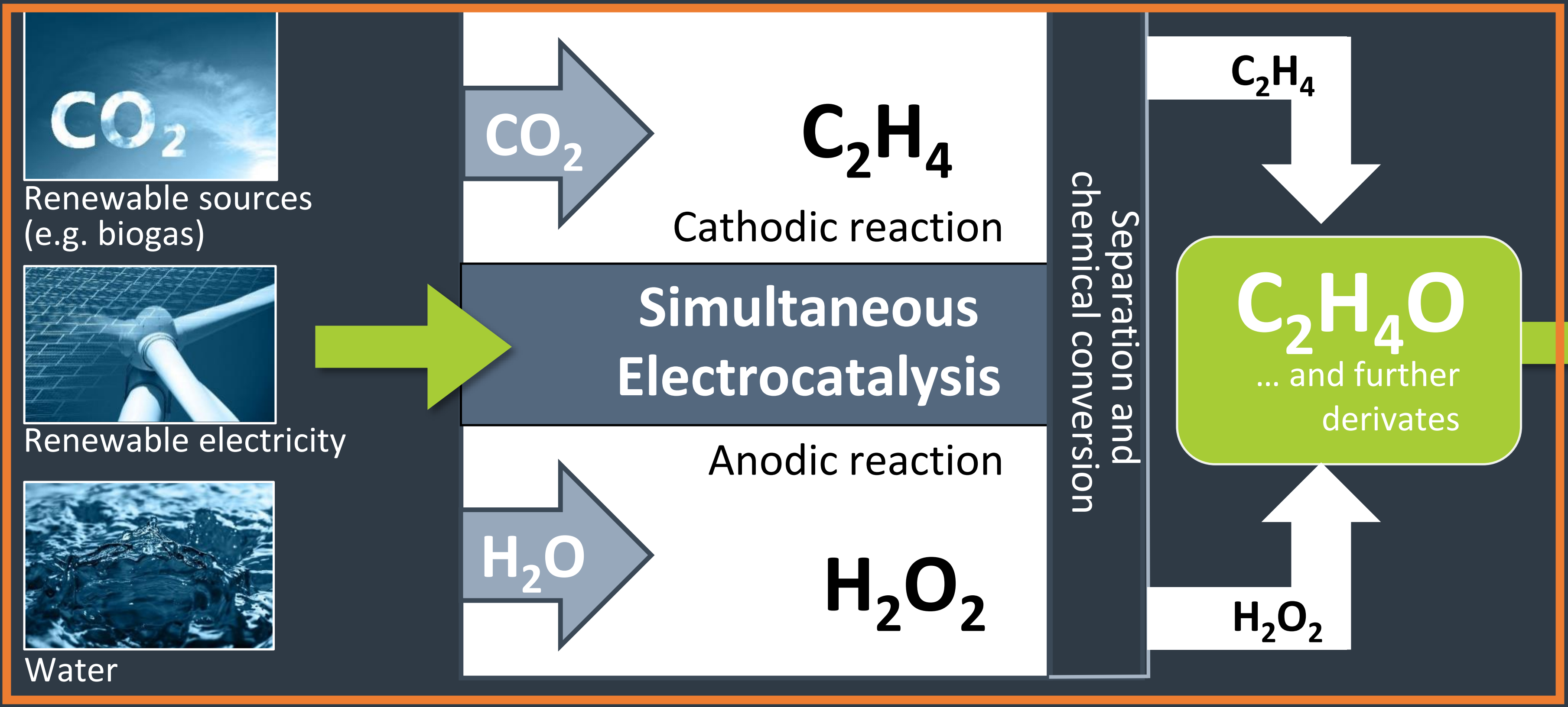
CO_2EXIDE Process



System-level assessment

→ Environmental & (socio-) economic performance

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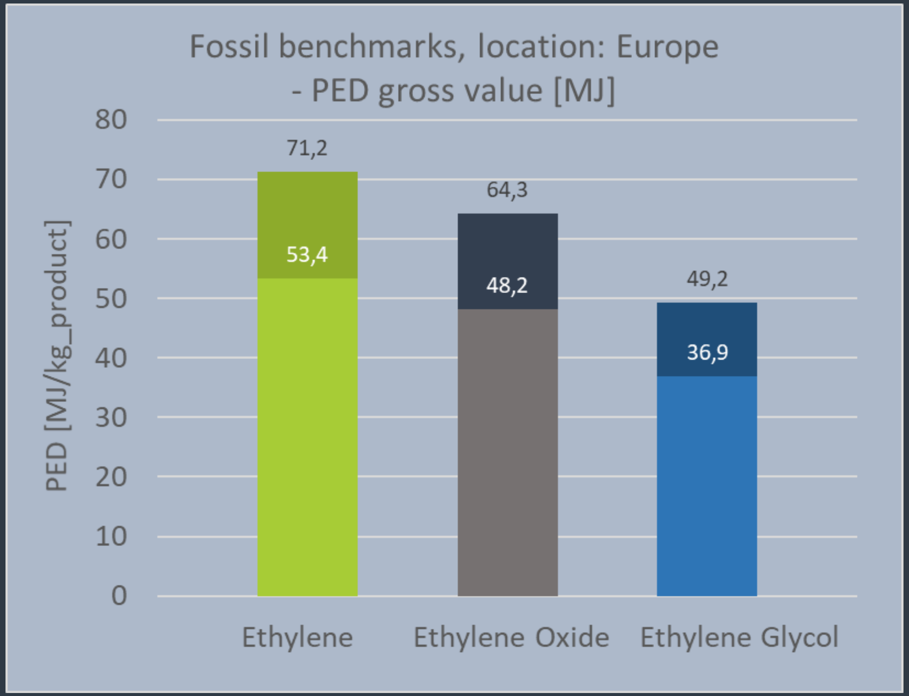
Techno-economic/life cycle assessment

- (Potential) environmental impacts?
  - Benchmarking to relevant reference systems
- Techno-economic performance potentials
- Relating technology (performance) scenarios to environmental/economic impacts
- Identification of critical R&D and deployment targets



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Ten partners in six countries

ACADEMIC CENTRE FOR MATERIALS AND NANOTECHNOLOGY AGH	Development of CO_2 reduction catalyst
axiom	CO_2 feedstock preparation, CO_2 recovery from biogas, ethylene enrichment, ethylene separation
MŰEGYETEM 1782	Electrolysis parameters, stable operating conditions, catalyst stability, contaminants, surface analysis
ENERGIE INSTITUT an der Johannes Kepler Universität Linz	Life Cycle Assessment, Techno-economic process and product assessment
EPC	Communication and dissemination, coordination support
Fraunhofer IGB	Coordination, electrocatalytic oxidation reaction, ethylene oxidation, chemical conversion
LATVIJAS UNIVERSITĀTES CIETVIELU FIZIKAS INSTITŪTS	Cathode, catalyst graphene stacks, theoretical calculations, electrolysis half-cell, SPEEK / ionic liquid
SCHAEFFLER	Nanostructured coatings for catalyst, coating process development, electrochemical cell design
SIEMENS energy	Electrochemical cell design, system integration, scale-up, testing and validation
UNIVERSITY OF Southampton	3D printed electrodes; anodic hydrogen peroxide; carbon dioxide reduction; flow cell, gas diffusion electrodes

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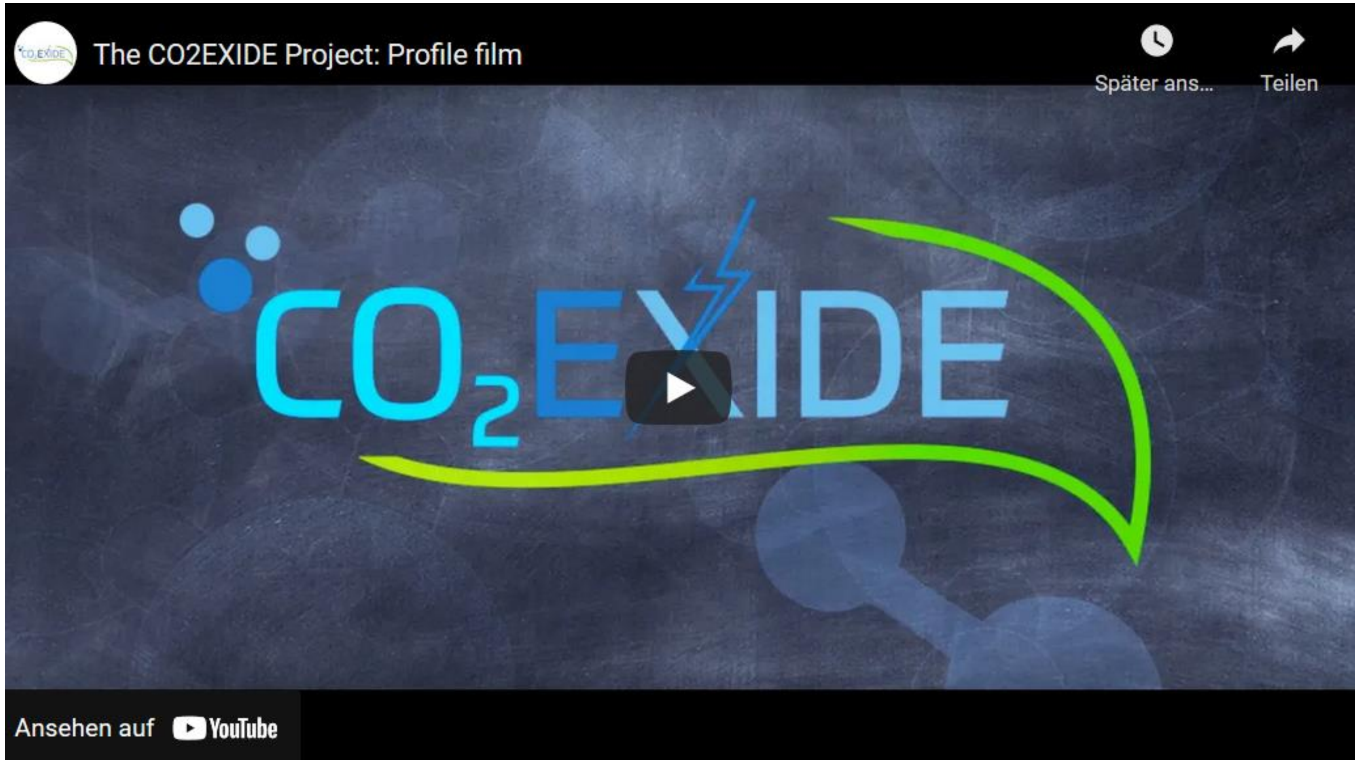
CO2EXIDE Project Film



http://www.co2exide.eu/

https://www.youtube.com/watch?v=dxZhxTGqJ7s

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Many thanks for your attention!

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Further Information

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