The CO2EXIDE electrochemical cell: Simultaneous ethylene and Hydrogen peroxide production

Sustainable Plastics Symposium 25.03.2021

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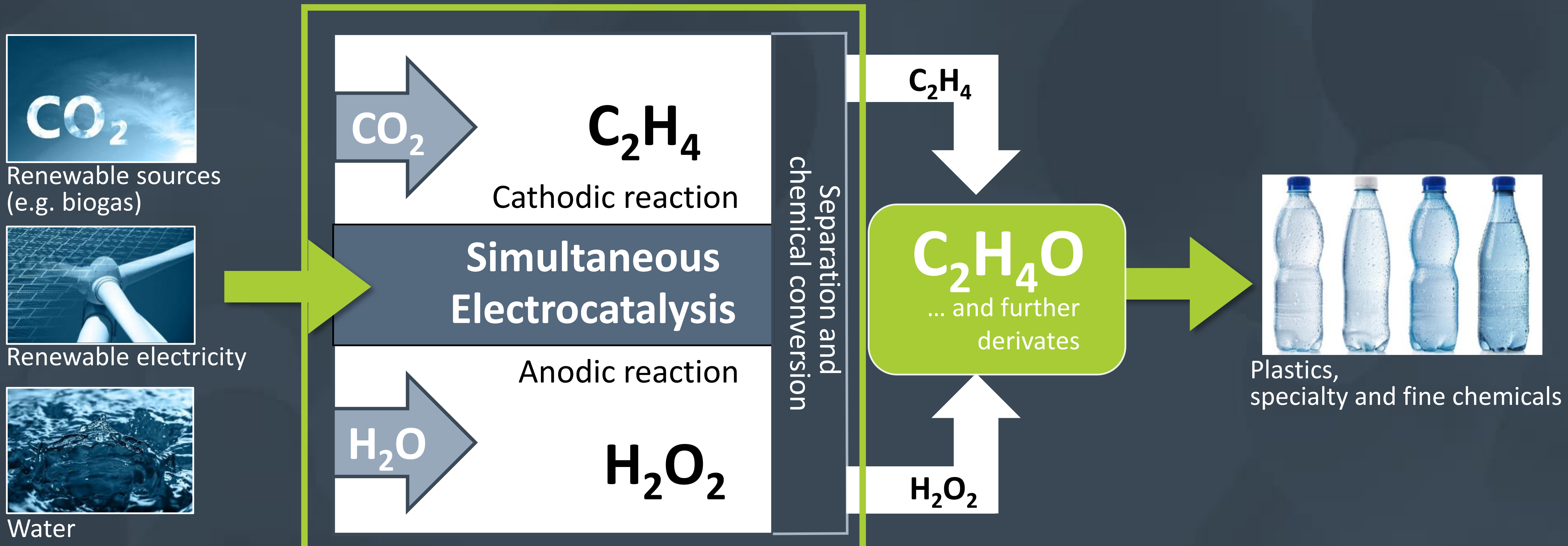
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768789.

Introduction
CO_2EXIDE Technology - Overview



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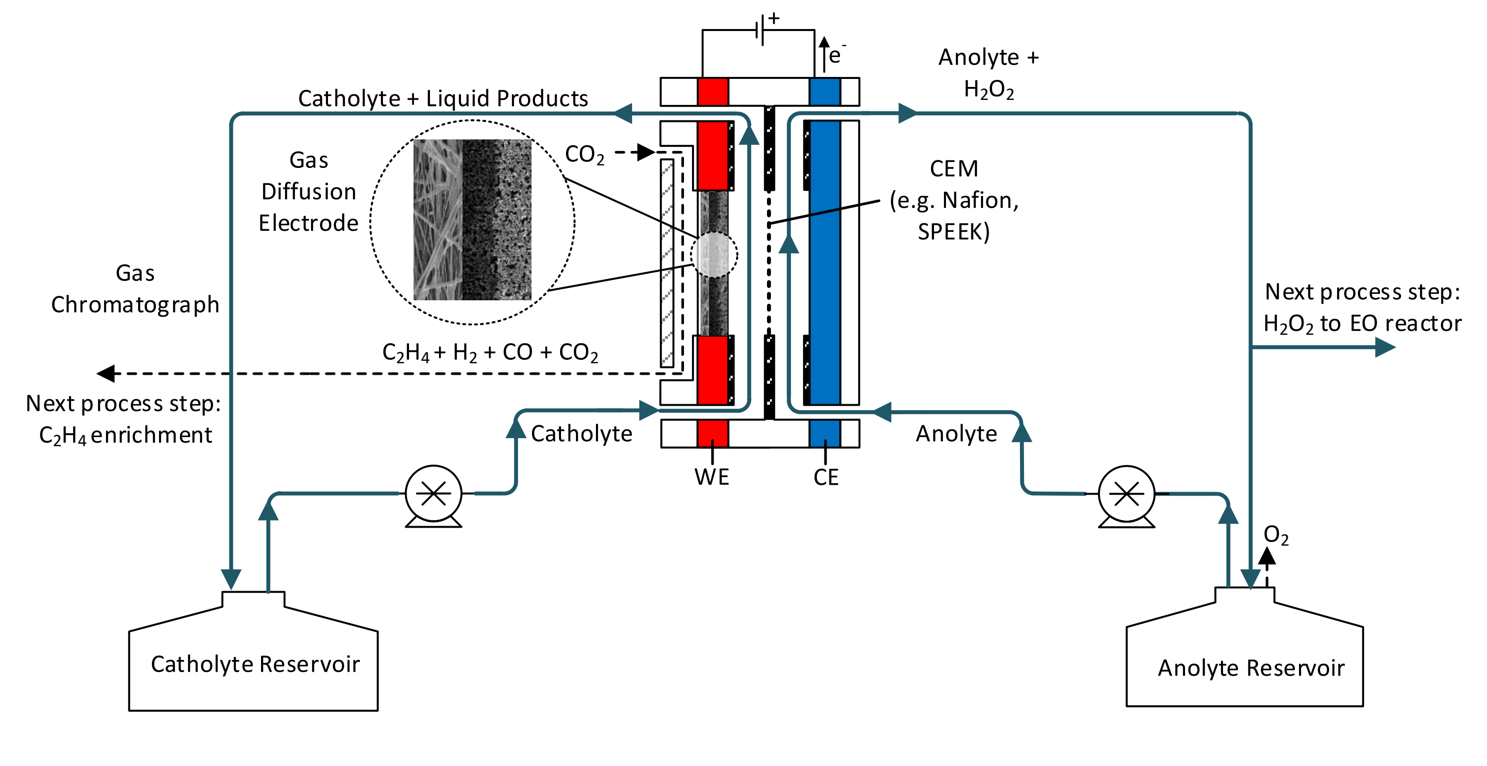
Simultaneous Electrocatalysis



Cathodic reaction:

$2\ CO_2 + 8\ H_2O + 12\ e^- \rightleftharpoons C_2H_4 + 12\ OH^-\ E^0 = -1.17$ V *vs.* RHE

Anodic reaction:

$2\ H_2O \rightleftharpoons H_2O_2 + 2\ H^+ + 2\ e^-,\ E^0 = 1.76$ V *vs.* RHE

The generic concept of the CO2EXIDE flow cell is based on a three chamber cell

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Electrochemical CO_2 reduction CO2RR

CO_2- Reduction product formation is strongly dependent on the electrocatalyst material

- CO2RR is a complex multi-step reaction
- adsorption of CO_2 is typically the rate-determining step
- reaction mechanisms for the various products are affected by the binding strength of reactants and intermediates on the catalyst surface
- key step in the formation of C2 species proposed to be the dimerization of neighbouring *CO

Copper is the only one to produce *hydrocarbons* →

Main product *CO* →

Main product *Formate* →

Main product *Hydrogen* →

Electrode	CH_4	C_2H_4	C_2H_5OH	C_3H_7OH	CO	$HCOO^-$	H_2	Total
Cu	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Au	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	0.0	0.0	0.0	0.0	0.0	0.0	99.7	99.7

Y. Hori, "Electrochemical CO_2 reduction on metal electrodes" in Modern Aspects of Electrochemistry, Vol. 42, published by C.G. Vayenas, R.E. White and M.E. Gamboa-Aldeco, Springer, NY, 2008, pp. 89-189

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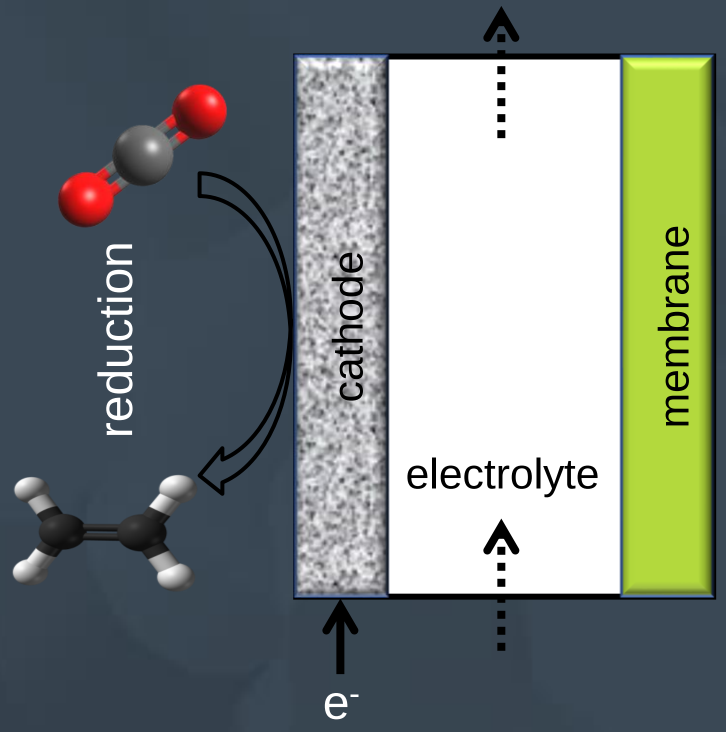
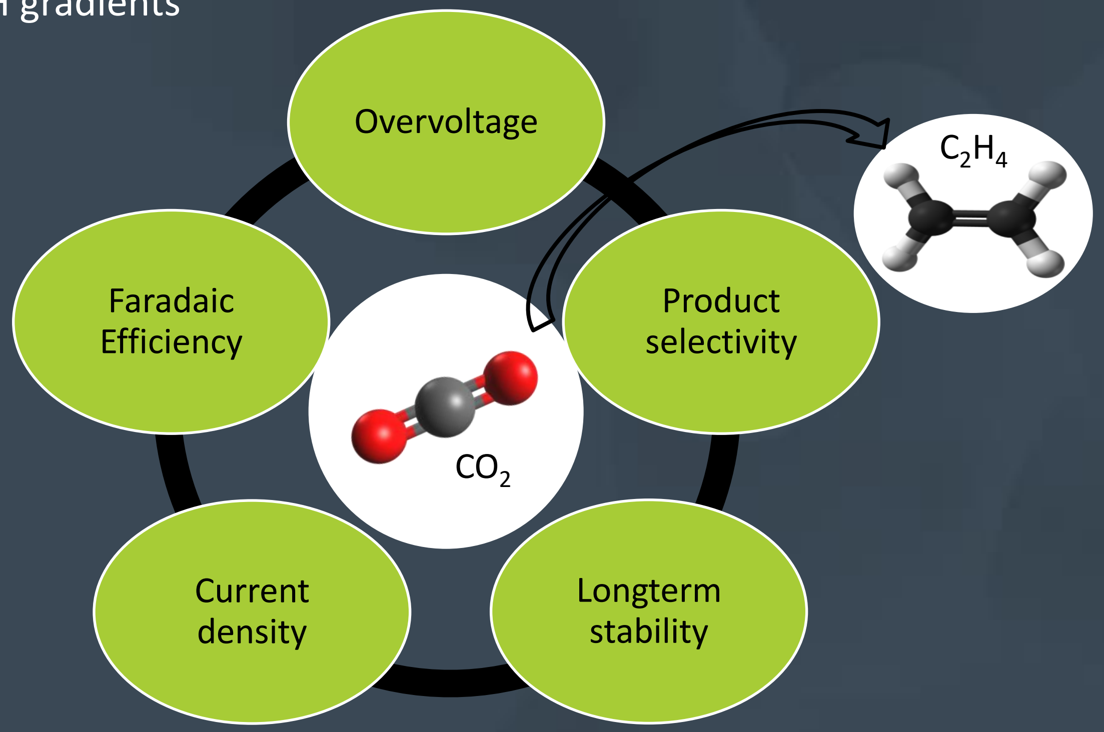
Electrochemical CO_2 reduction CO2RR to ethylene as product - Challenges



Factors influencing the product selectivity on copper surfaces:

- Electrolyte composition, electrolyte buffering strength
- Local CO_2 concentration and pH gradients
- Mass transport effects
- Crystal facets
- Particle size
- Shape effects
- Pore size effects
- …



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Electrochemical CO_2 reduction CO2RR to ethylene as product – Electrode preparation

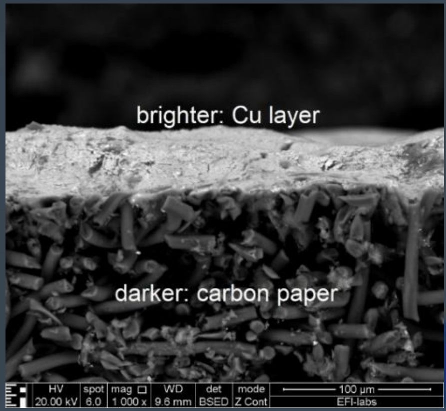
Types of electrodes tested:

- various forms of Cu metallic electrodes (monocrystals, meshes, foams, etc.)
- nanowires electrodeposited in Anodic Aluminium Oxide (AAO) templates
- graphene sheet stacks modified with Cu metal powder
- electrochemically deposited copper on various substrates
- Cu layers sputtered onto metallic substrates (Cu, Fe)
- Cu layers sputtered onto Gas Diffusion Layers → GDEs

produce robust and scalable electrodes, which can be used in the demonstrator

New cathode

Used cathode



- Cathode: 500 nm Cu sputter deposited on Freudenberg H23C2
- Electrochemical experiments at 200 mA/cm^2
- 10 cm^2 MicroFlowCell® (ElectroCell)
  Stability ~ 5h
- Concentration of C_2H_4 in product gas ~ 4%

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MŰEGYETEM 1782

Anodic Electrosynthesis of H_2O_2 via Water Oxidation

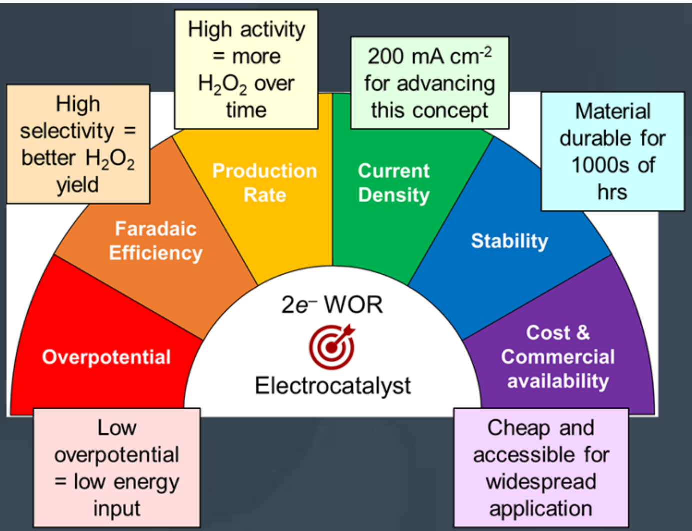
- $2e^-$ WOR: electrochemical production of H_2O_2 from just water and renewable energy:

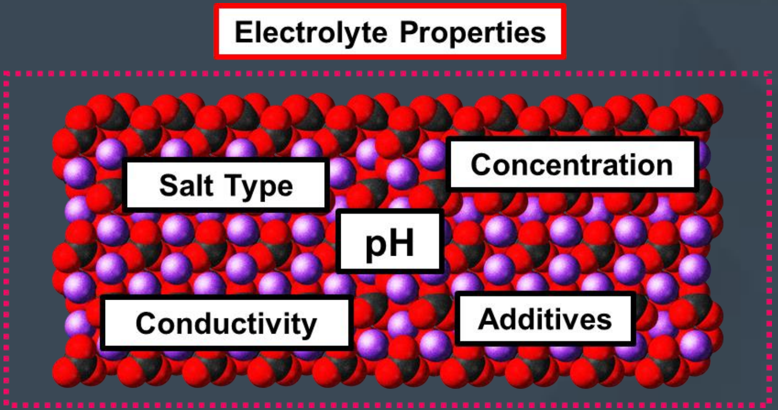
$$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e^-, E^0 = 1.76 \text{ V } \textit{vs.} \text{ RHE}$$

- Unorthodox method for H_2O_2 production due to more favourable competing reactions:

  a) O_2 evolution: $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$, $E^0 = 1.23$ V *vs.* RHE
  b) H_2O_2 oxidation: $H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$, $E^0 = 0.67$ V *vs.* RHE
  c) H_2O_2 decomposition: $2H_2O_2 \rightarrow O_2 + 2H_2O$

- Research: catalyst materials & aqueous supporting electrolyte





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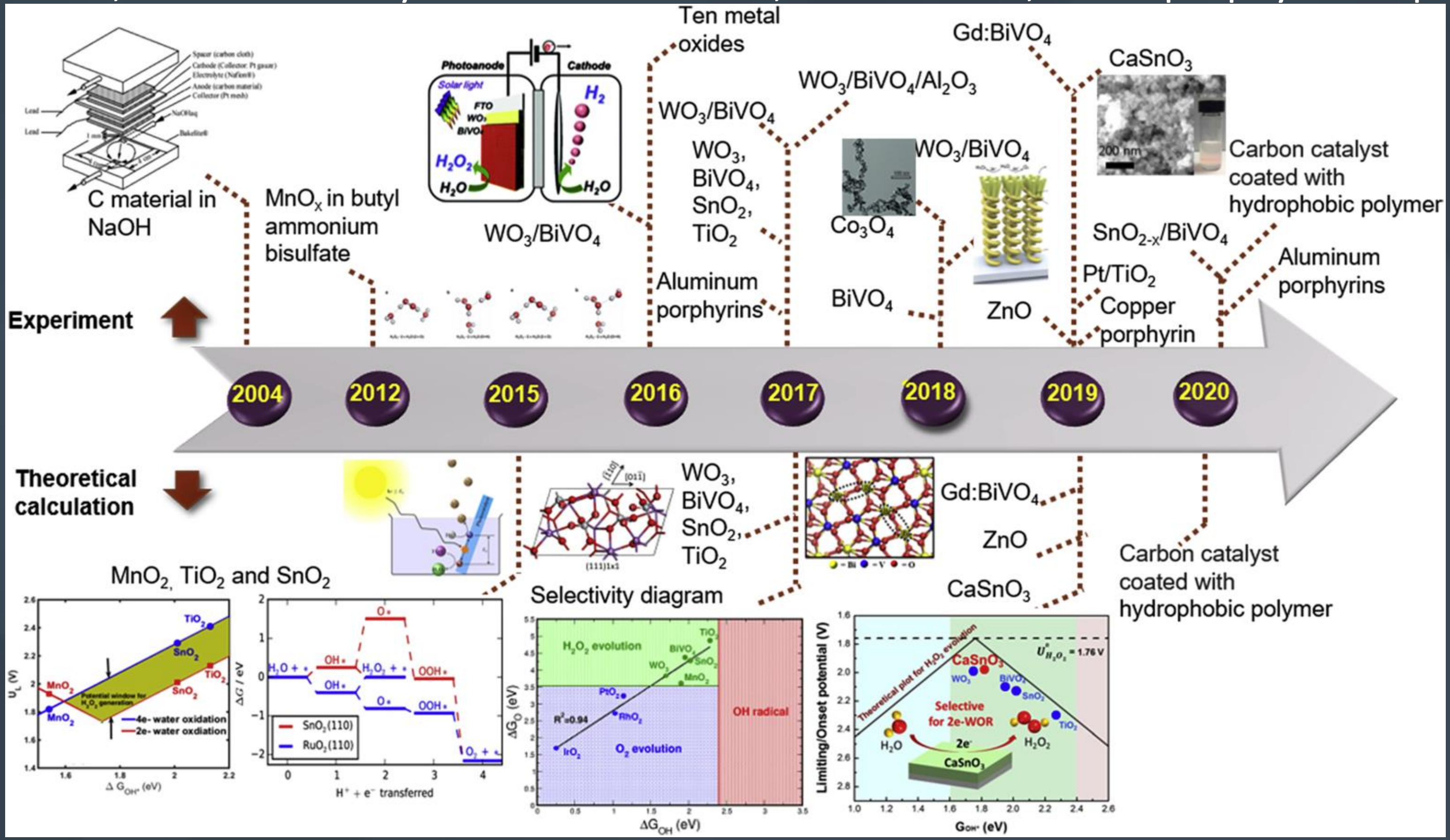
Recent Developments in $2e^-$ WOR to Produce H_2O_2

Since 2004, $2e^-$ WOR catalysts include: C-fibres, metal oxides, metal porphyrins & polymers



- Oxides achieve high %*FE*s and C-fibres reach acceptable H_2O_2 production rates, both at low current densities

- Catalyst disadvantages:
  - Oxides & carbon operate at very low currents (<10 mA cm^{-2})
  - Oxides like $BiVO_4$, $CaSnO_3$ toxic for environment
  - Carbon fibre will degrade easily at high currents

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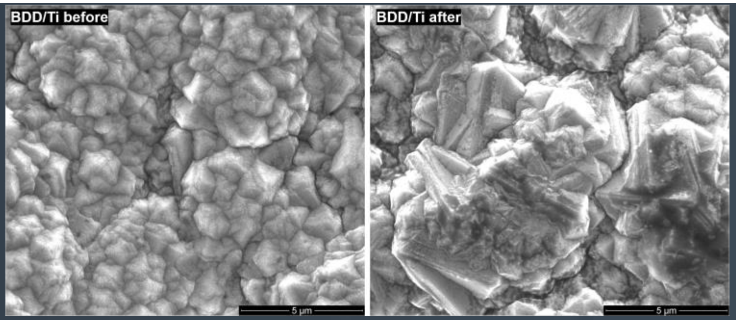
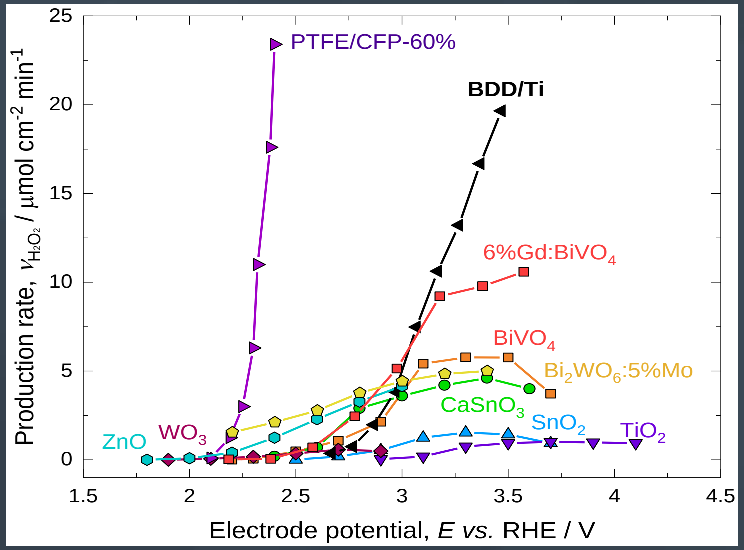
$2e^-$ WOR Research at the University of Southampton SOTON

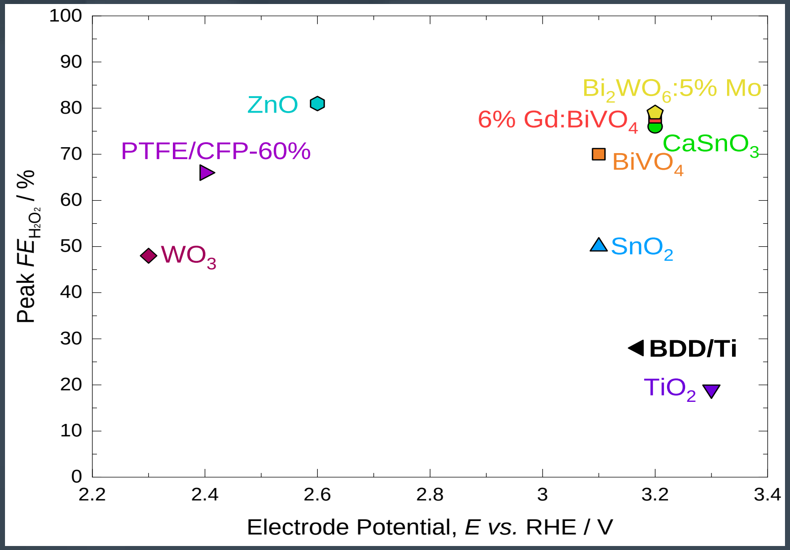
- SOTON: boron-doped diamond (BDD) coated on Ti with a B doping: ~4,000 ppm
- Experiments in 25 mL, 2 M $KHCO_3$, pH 8, applied potential = 0-3.5 V *vs.* RHE
- H_2O_2 results: 29.0 mM; 19.7 µmol cm^{-2} min^{-1} and %*FE* of 28% at current ~ 295 mA cm^{-2}
- Results compare favourable to literature:



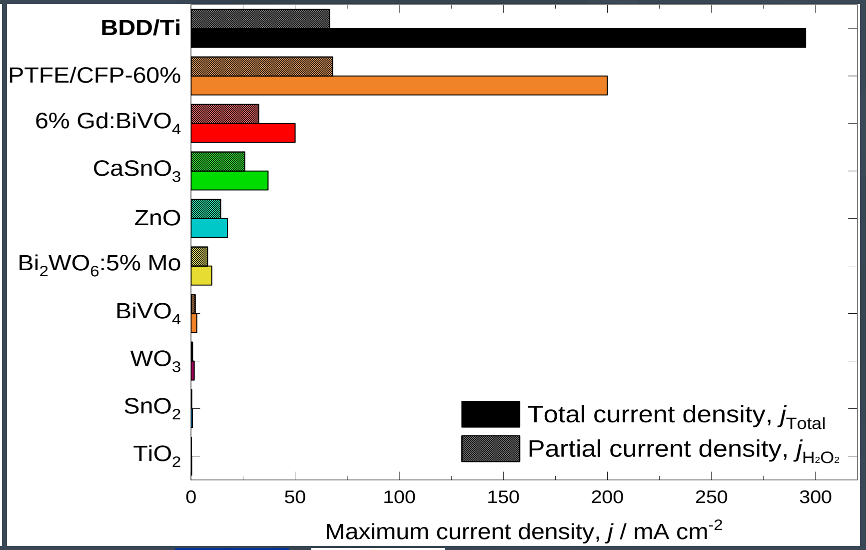
H_2O_2 Production *vs.* Potential



Faradaic Efficiency *vs.* Potential



Current Density Comparison



Southampton

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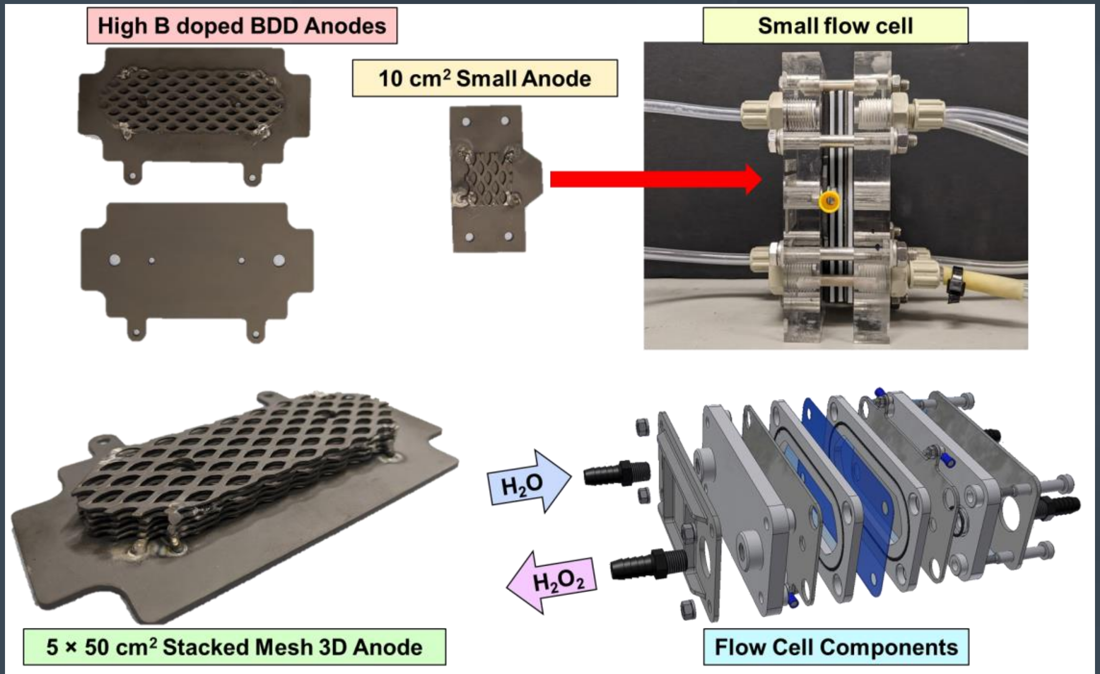
Future SOTON Experiments on 2e⁻ WOR

1. **Investigate influence of various BDD film parameters on H_2O_2 production:**
    a. B doping level
    b. Crystallite texture
    c. Coating thickness
    d. sp^3/sp^2 ratio, etc.

2. **Evaluate influence of electrolyte anions on H_2O_2 production & optimise electrolyte**

3. **Scale up process from small-volume cell to flow reactor**



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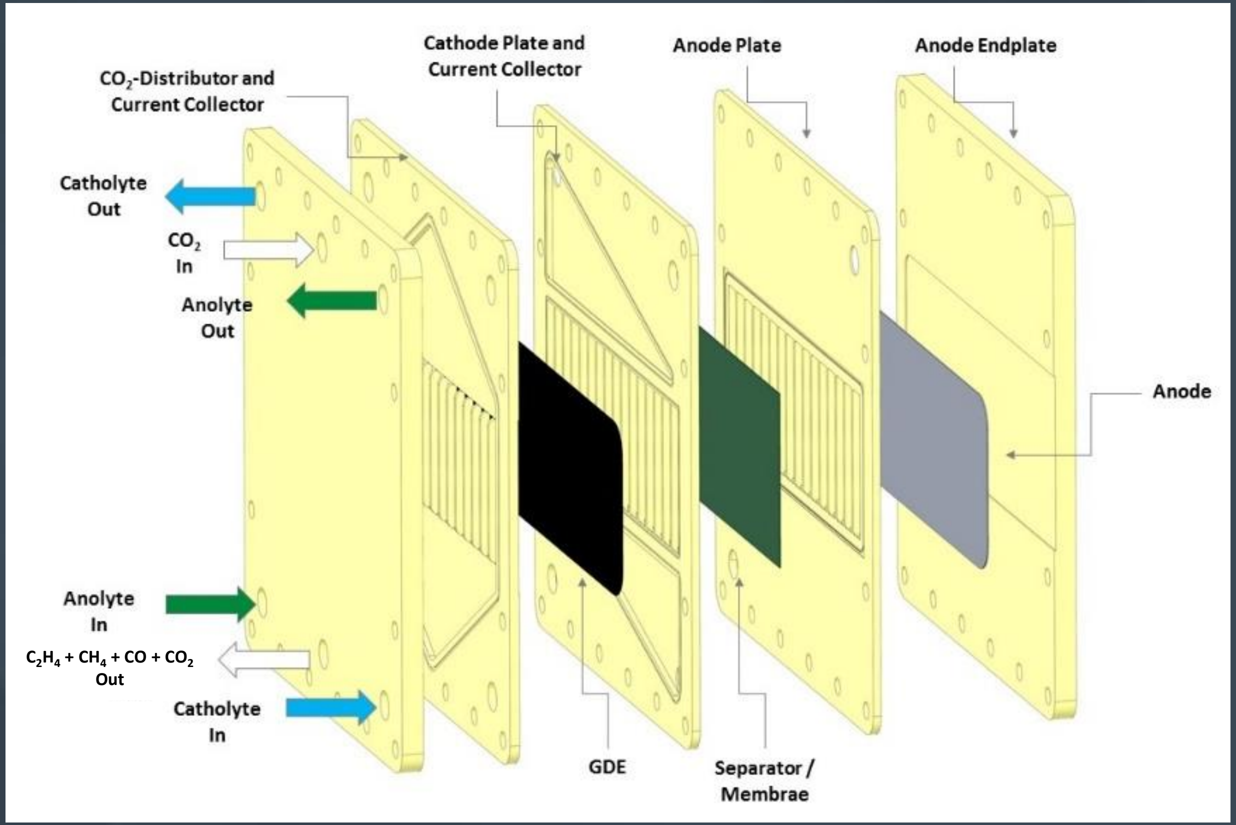
The Cell Concept



- Flow Cell in 3-chamber design
- Anolyte and catholyte flow in the same direction but cross each other
- The gas flow is directed in the opposite direction to the liquid flow

Development strategy for scale-up:

1. Step: Electrolysis cell with 25 cm^2 active area
2. Step: Electrolysis cell with 300 cm^2 active area

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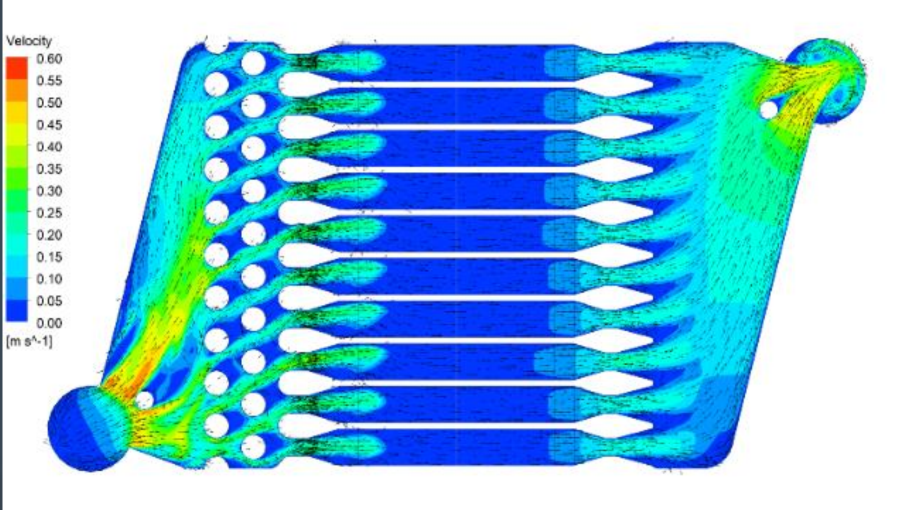
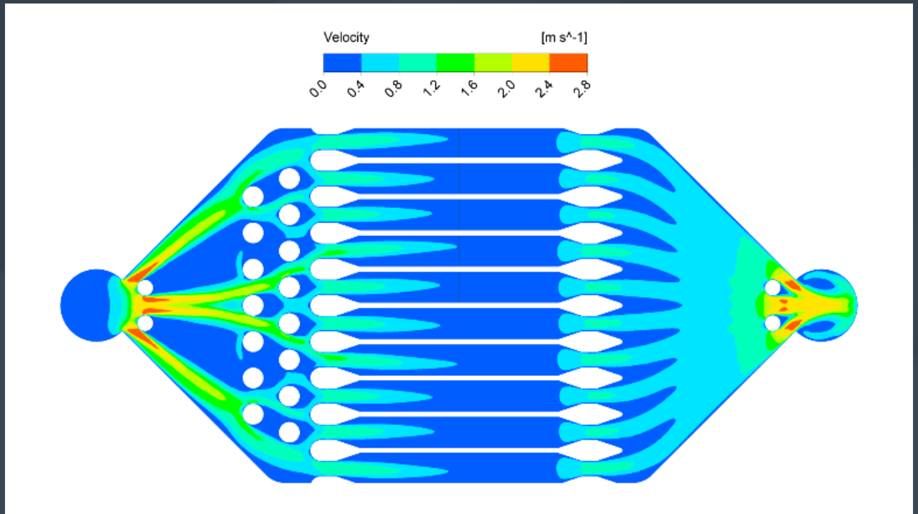
The 25 cm^2 Cell

Velocity in the Anolyte Flow Field (Top View)



Velocity in the CO_2 Flow Field (Top View)



Cell was optimized by computational fluid dynamics (CFD) simulations to assure a homogeneous flow distribution and a low pressure drop in all media-leading chambers.

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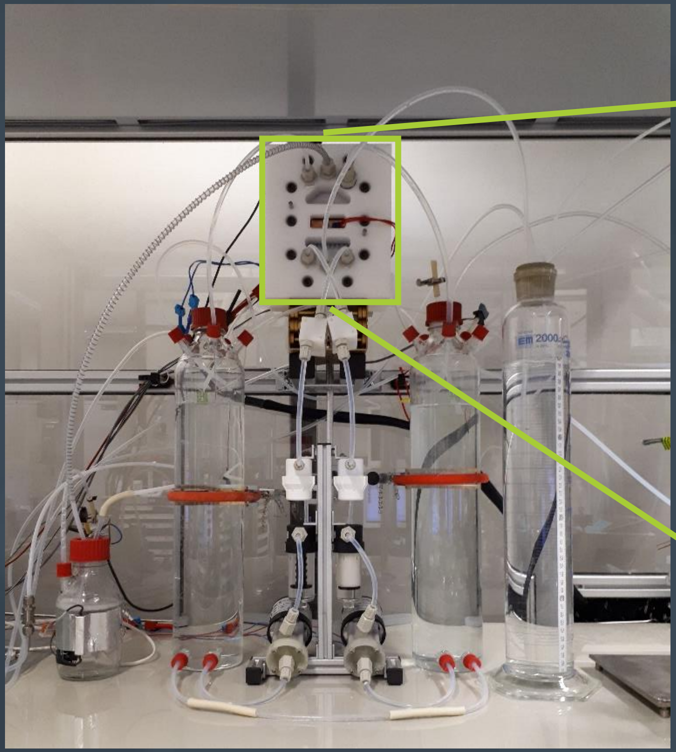
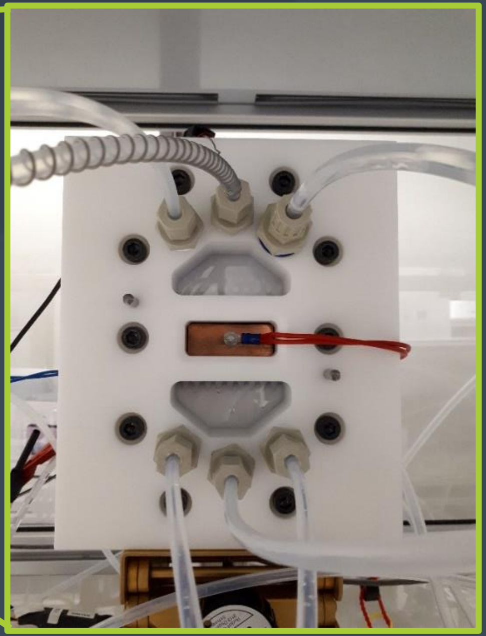
The 25 cm^2 Cell





- More than 10 different anode and cathode catalyst configurations were tested in the 25 cm^2 cell
- No internal leakage during the complete testing procedure was observed

→ Cell design & material choice was evaluated to be suitable

→ Successful 25 cm^2 design was used as base for 300 cm^2 demonstrator unit

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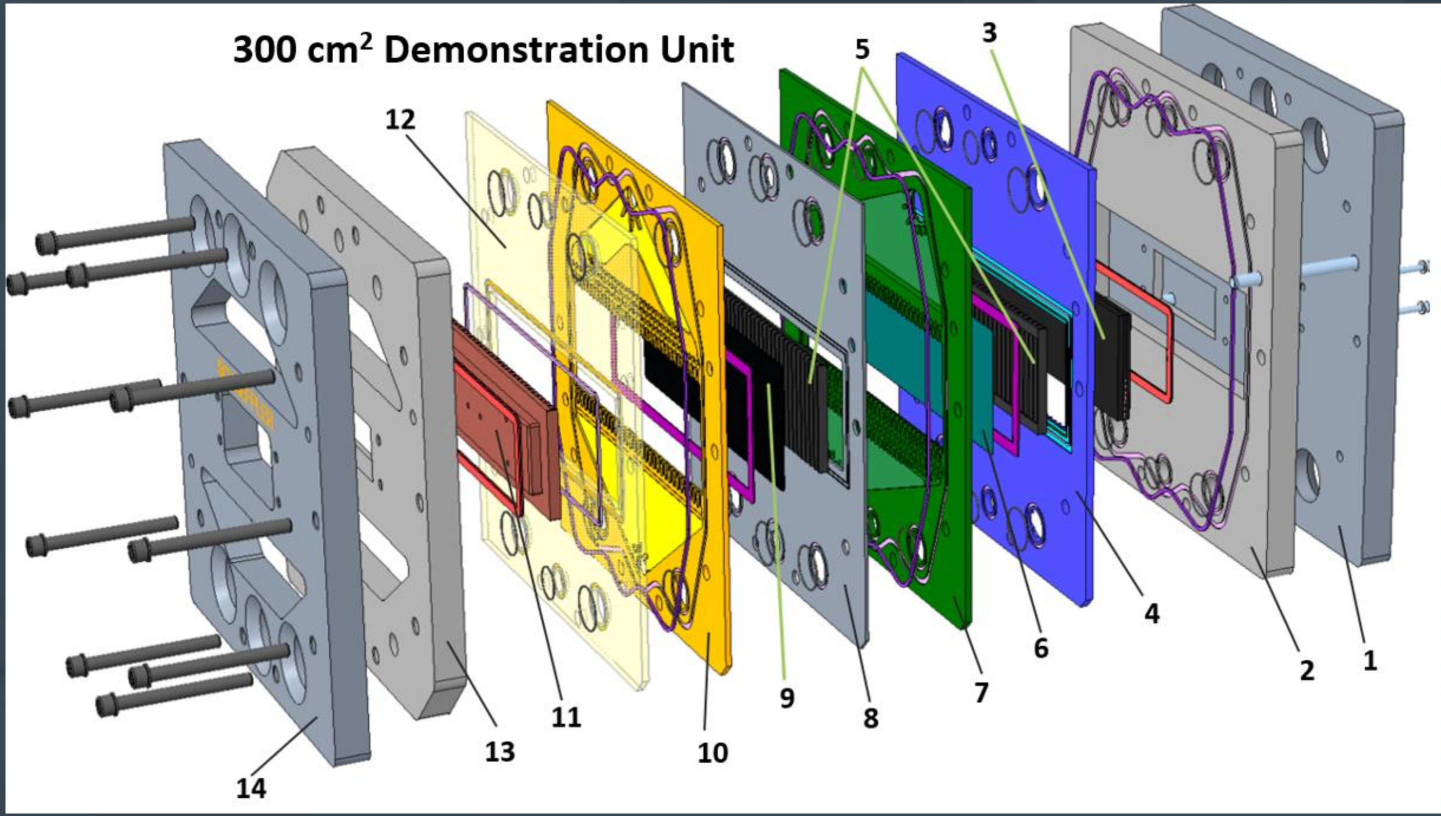
The 300 cm^2 Cell



	Name	Material
1.	Base plate	Aluminium
2.	End plate 1	POM
3.	Anode	Titan (IrO_2 coated) / Boron doped diamond
4.	Anolyt plate	POM
5.	Grid	PEEK
6.	Separator	Nafion 117
7.	Catholyt plate	POM
8.	GDE plate	POM
9.	GDE	H23C2
10.	CO2 plate	POM
11.	Cathode	Copper
12.	Window	PP
13.	End plate 2	POM
14.	Clamping plate	Aluminium

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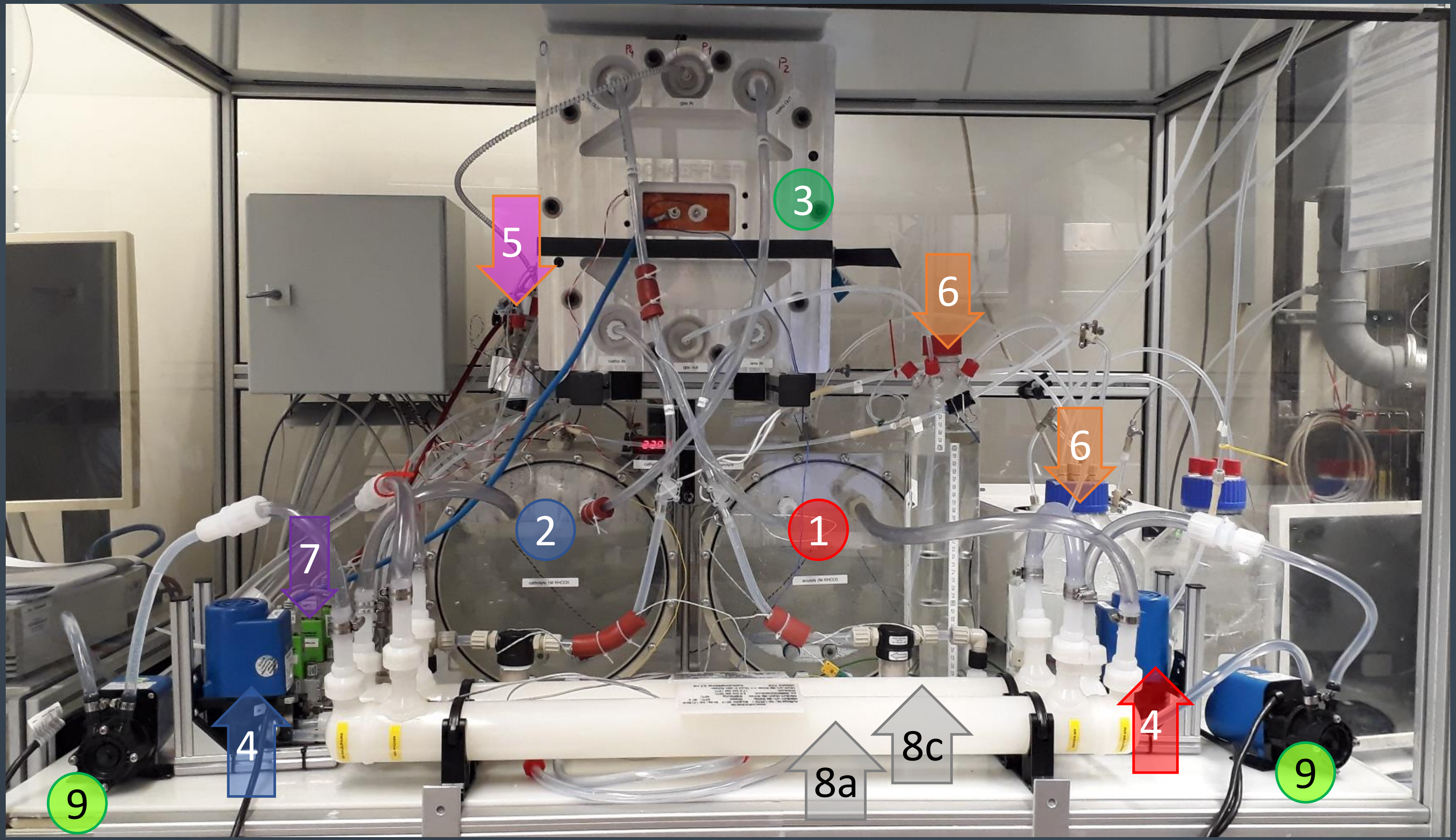
The 300cm² Cell: Test phase in lab



1 anolyte reservoir
4 pump + filter + flow sensor

2 catholyte reservoir
4 pump + filter + flow sensor

3 300cm² flowcell

5 humidification of CO_2 feedgas

6 gas-out differential pressure generation

7 gas-supply for educt and purge (CO_2/N_2)

8c 8a heat exchanger/cooling system for anolyte and catholyte

9 catholyte and anolyte tempering pumps

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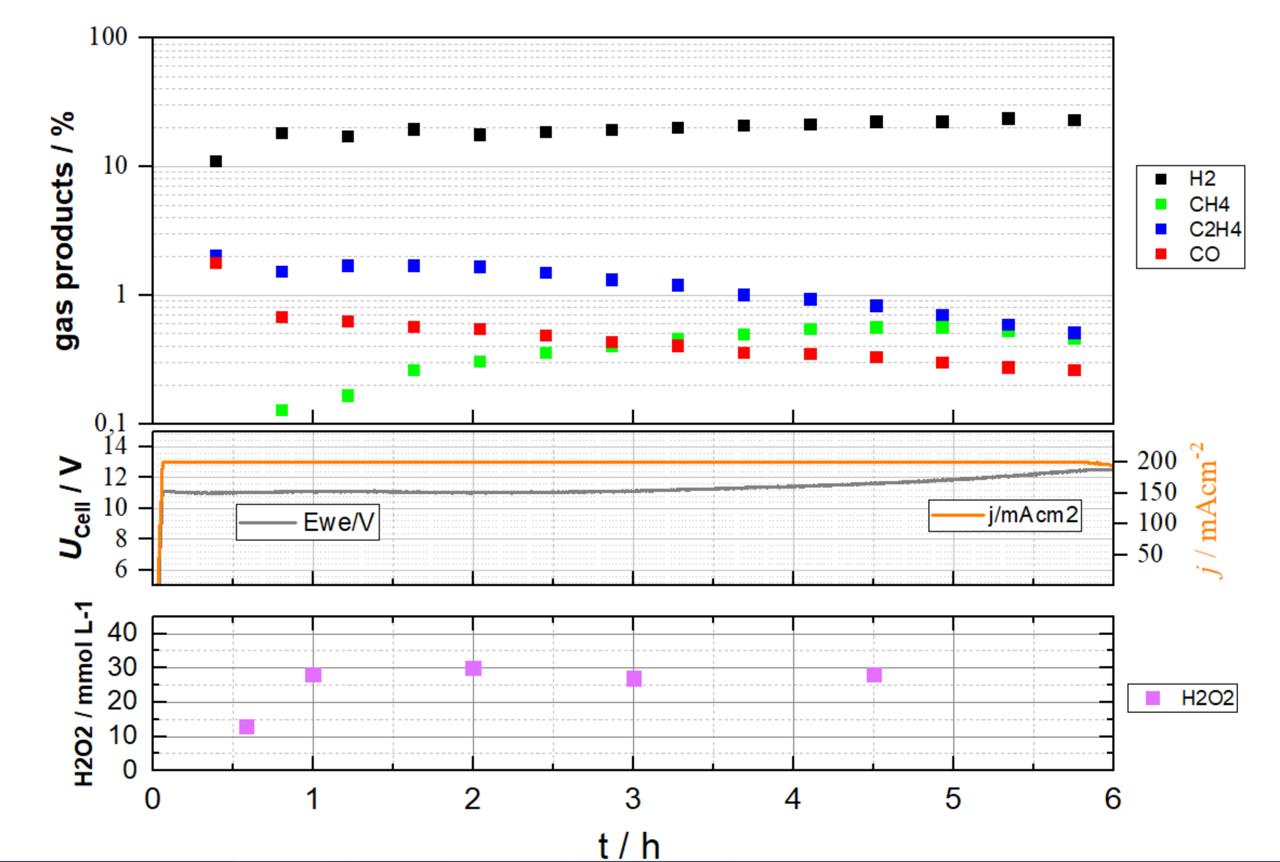
300cm² Cell - simultaneous production of ethylene and hydrogen peroxide



- Cathode: 500 nm Cu sputter deposited on Freudenberg H23C2
- Catholyte: 1M $KHCO_3$
- Anode: BDD/Nb, 2500 ppm boron doping (NeoCoat®)
- Anolyte: 2M $KHCO_3$
- Membrane: Nafion 117
- Current density: 200mA/cm²

- simultaneous production of ethylene at the cathode and hydrogen peroxide at the anode
- Stability ~ 5h
- H_2O_2 concentration in anolyte ~ 30 mmol/L (FE- H_2O_2 30%)
- C_2H_4 in product gas ~1,8% (FE- C_2H_4 25%)

→ Successful testing of scaled electrolyser cell
→ 300 cm² Cell ready for integration in demonstrator set-up

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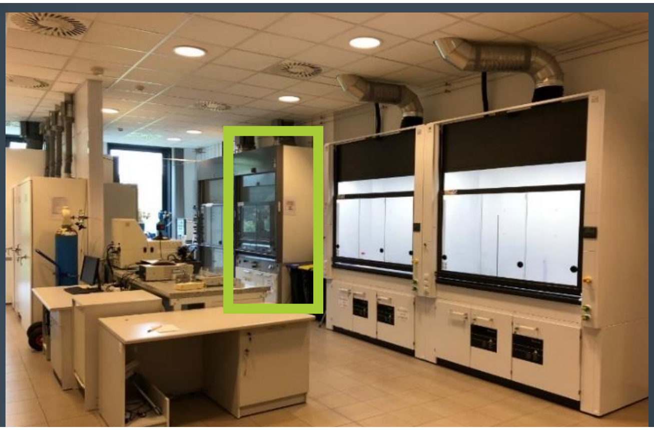
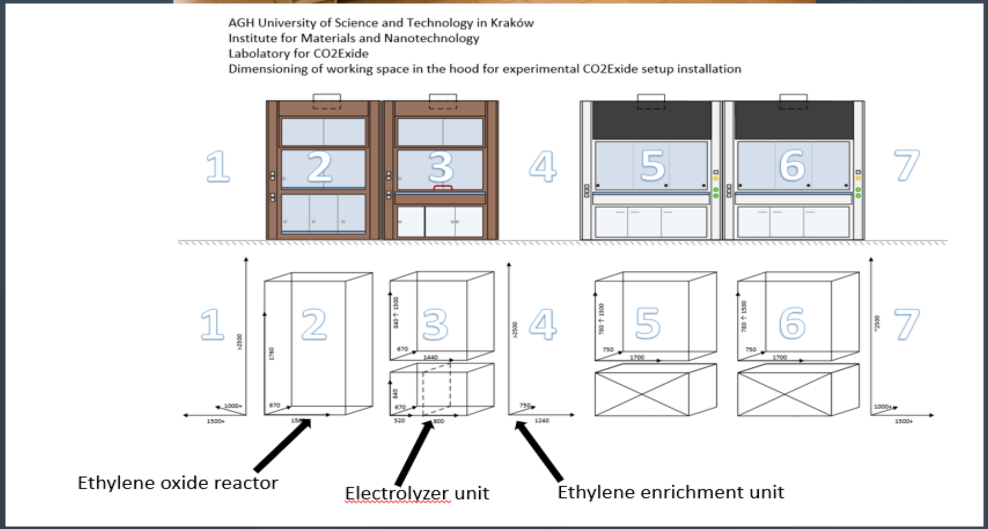
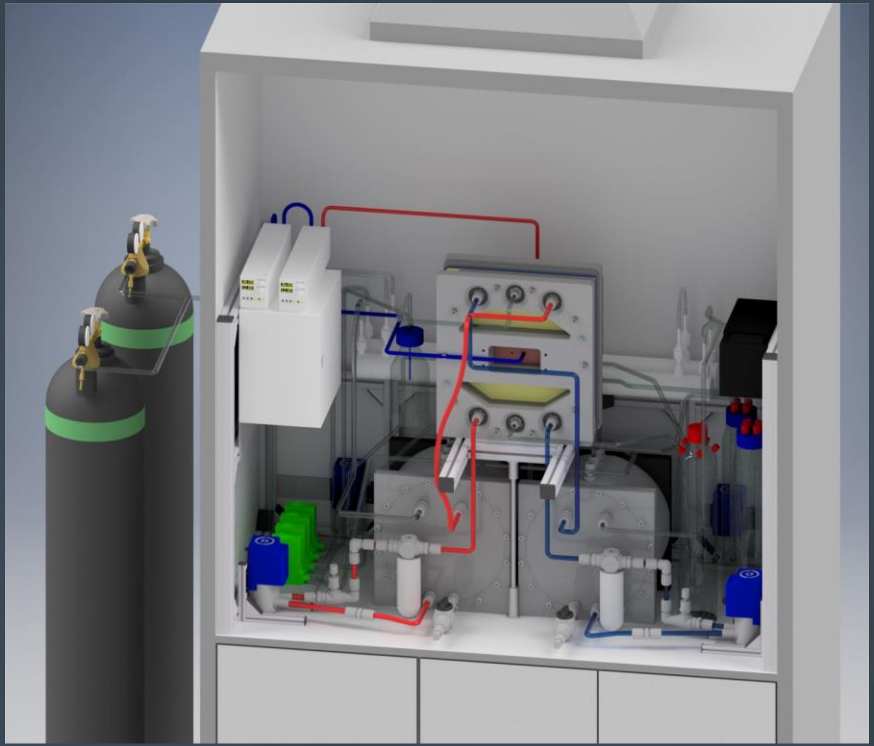
Demonstrator set-up
Planning of installation at AGH, Krakow





CAD-simulated realistic view
of the Electrolysis setup
in the dimensions of fumehood 3
at AGH in Krakow.



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Many thanks for your attention!

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Further Information

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