KOPERNIKUS P2X PROJEKTE
Die Zukunft unserer Energie

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Ingenuity for life

Technical Photosynthesis, employing Single Step Direct Electrocatalytic Reduction of CO_2 Toward CO and Hydrocarbons

Günter Schmid, Ralf Krause and Team

Definition of Technical Photosynthesis

Technical photosynthesis is a **process** or **process sequence**, that converts **renewable energy**, **CO_2** and/or **water** into **chemical feedstock**, **chemicals** or **fuels** in a **doable**, **profitable** and **efficient** way.

Renewable energy "electrons as feedstock"

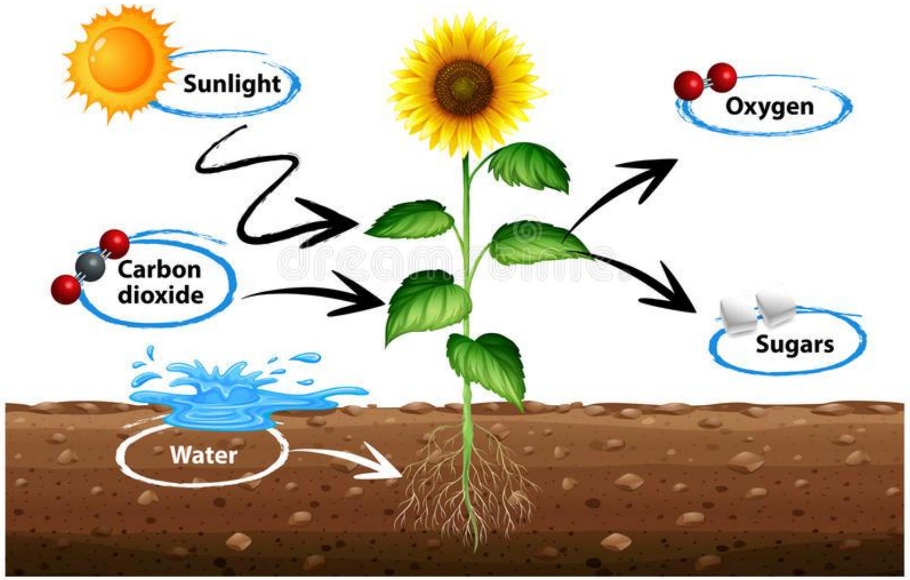
- solar
- wind
- geothermal
- …

Processes

- photo catalysis
- electro catalysis
- sequences *i.e* electrolysis (up-stream) & fermentation (down-stream)

electrolysis & classical thermal chemistry (*i.e.*Fischer Tropsch)

Natural Photosynthesis



… but, we don't copy nature

Outlook

- Industrial perspective
- What is CO_2 electrolysis ?
- Market considerations: CO_2 & electricity ➡ chemical feedstock
- Electro reduction of CO_2 to CO (use case & results)
- *Perspectives* Electro reduction of CO_2 to C_2H_4; Electro refineries
- Conclusions

Prerequisites for Electrons *as* Feedstock

Conversion / Storage of ELECTRONS in chemical COMPOUNDs leads to different ECONOMY scenarios

Electrification of process industry

➔ **Decoupling of oil and electricity prices**
(1.78 US cent/kWh lowest bid Oct. 2017 in Saudi Arabia 300 MW plant)

➔ **Coupling of energy sector and chemistry sector**

➔ **Electrochemical feedstock production vs. traditional petro chemistry**

Chemistry follows energy market

Radical new production processes for chemicals

- Production of intermediates such as H_2, CO and Ethylene via electrolysis out of electricity, water, and CO_2

Future scenario of the chemical industry

- Independence from chemical parks allows **decentralization** of the chemical production locations
- New technology developments of electrolysis are pushing these process solutions into the existing chemical parks – it will be **common to see electrolyzers in chemical plants**

https://www.pv-magazine.com/2017/10/04/saudi-arabias-300-mw-solar-tender-may-conclude-with-lowest-bid-ever/

CO_2 Reduction on Metal Electrodes in aqueous Electrolytes

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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

CO_2- Reduction product formation is strongly dependent on the electrode / electro catalyst material

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

Electrode Processes in Electrochemical CO_2 Reduction (Simplest Case)

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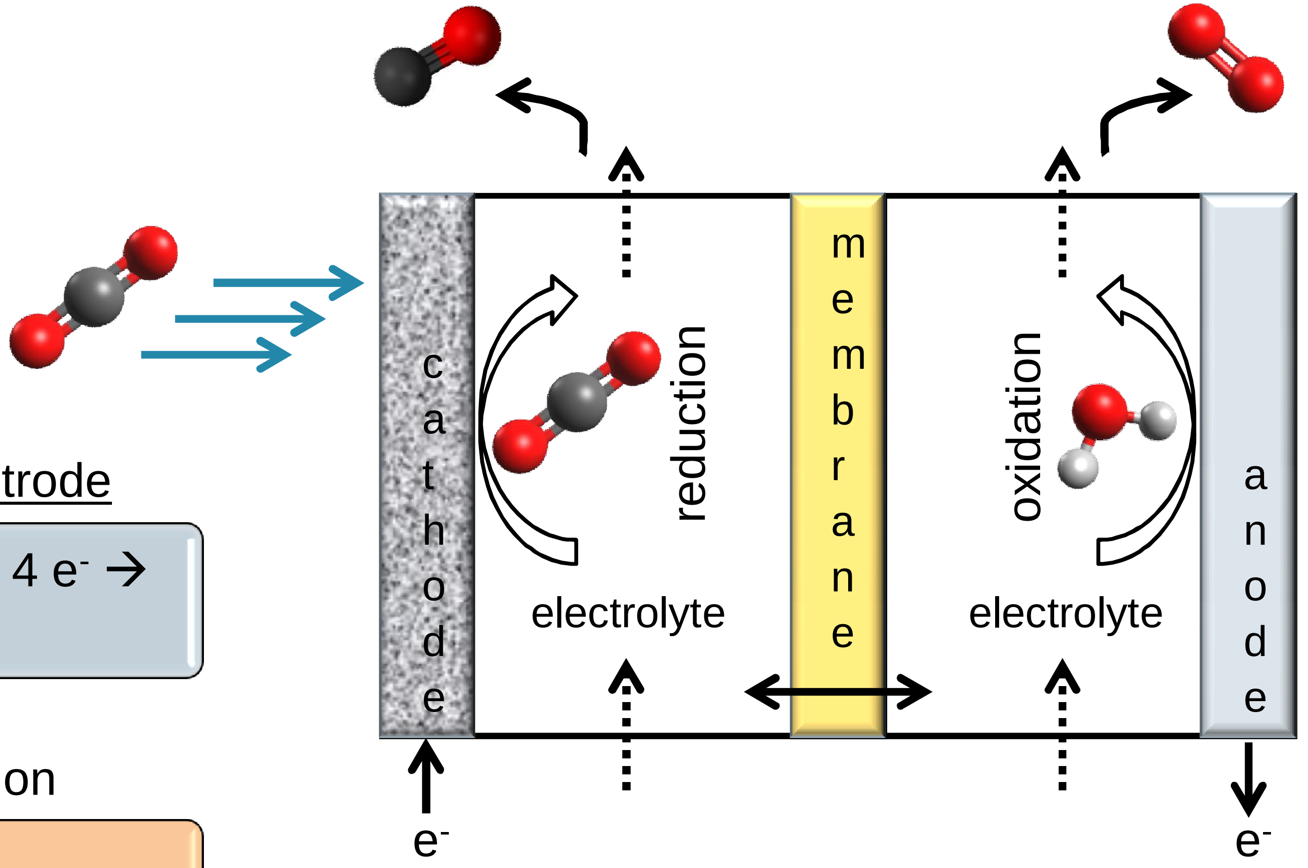


Cathode (Ag)

gas diffusion electrode

$2\ CO_2 + 2\ H_2O + 4\ e^- \rightarrow$
$2\ CO + 4\ OH^-$

competing reduction

$2\ H_2O + 4\ e^- \rightarrow$
$2\ H_2 + 4\ OH^-$

Anode (IrO_2 on Ti)

$2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$

charge neutralization

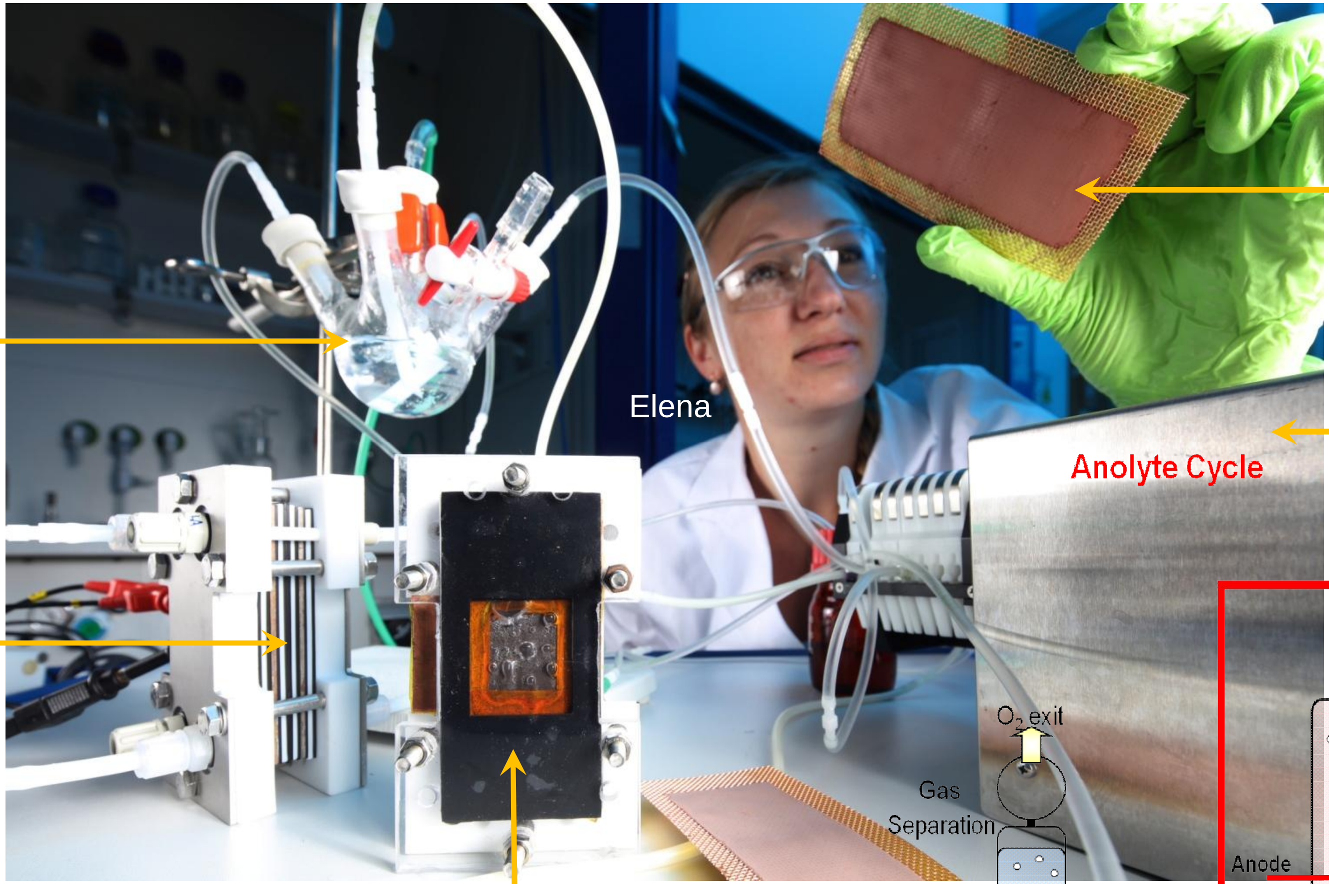
$4\ OH^- + 4\ H^+ \rightarrow 4\ H_2O$

overall reaction: $CO_2 \rightarrow CO + ½\ O_2$

CO_2-Electrolysis in the Laboratory

Electrolyte-reservior

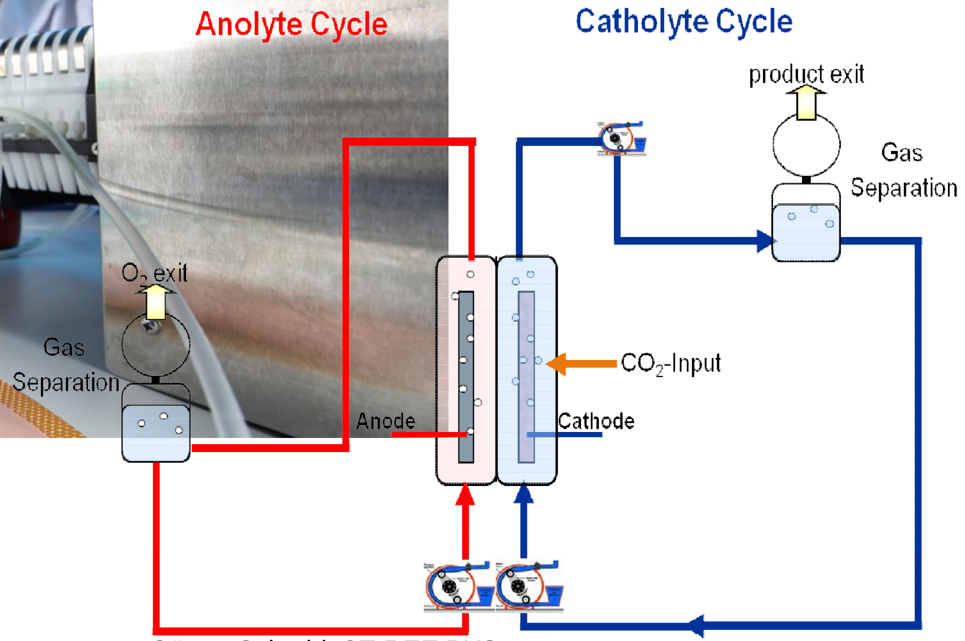
Flow Cell



Gas Diffusion Electrode

Electrolyte-pump

Gas Diffusion Electrode



CO_2 To Value

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Renewable Electricity “unabsorbed by the net”

Storage of volatile energy in chemical bonds

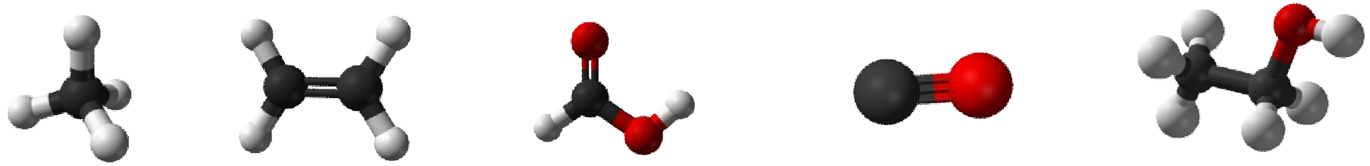
Electrocatalysis

CO_2 from any Source

Maximize economical value of available stranded energy

Synthetic fuels or chemical feedstock

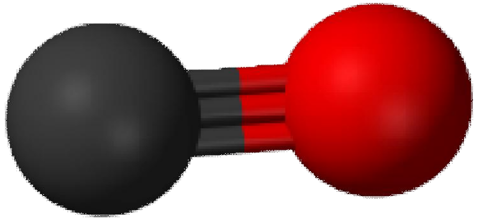
	Methane (CH_4)	**Ethylene** (C_2H_4)	**Formic acid** (HCOOH)	**Carbon monoxide** (CO)	**Alcohols** C_2 , C_3
Market price:	100 -150 EUR/t	1,000 EUR/t		650 EUR/t (+H_2 > gasoline)	
Market volume:	>2,400 Mt/y	141 Mt/y	0.7 Mt/y	>300 Mt/y	



Electroreduction of CO_2 to CO

Targets

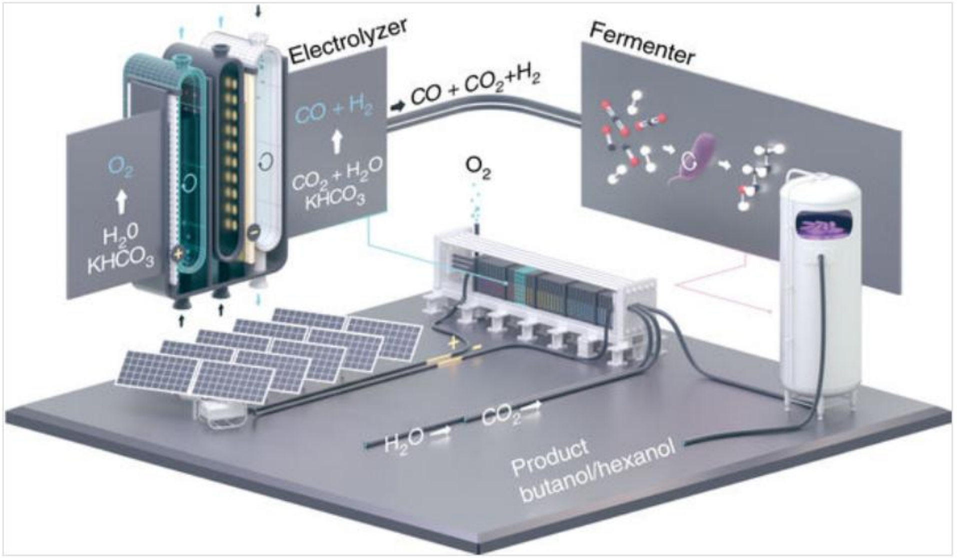
- Upscaling,
- Lifetime
- Application Development



$$\begin{array}{lll} \text{Cathode:} & CO_2 + H_2O + 2\,e^- & \rightarrow CO + 2\,HO^- \\ \text{Anode:} & H_2O & \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \\ \hline & CO2 & \rightarrow CO + \tfrac{1}{2}\,O_2 \end{array}$$

https://www.nature.com/natcatal/videos/photosynthesis

https://www.youtube.com/watch?v=VK-dULEK-rc&feature=youtu.be



Article | 08 January 2018

Technical photosynthesis involving CO_2 electrolysis and fermentation

The generation of useful chemicals from CO_2 and renewable energy is an attractive–but challenging–endeavour. This work reports on the long-term operation of commercial electrodes for efficient CO_2 reduction, with subsequent fermentation of the syngas product completing the technical photosynthesis of alcohols.

Thomas Haas, Ralf Krause [...] & Guenter Schmid

Nature Catalysis , Vol 1, Jan. 9, 018, 32–39

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KOPERNIKUS PROJEKTE P2X
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eChemical/eFuel production
A joint industrial effort out of Kopernikus P2X

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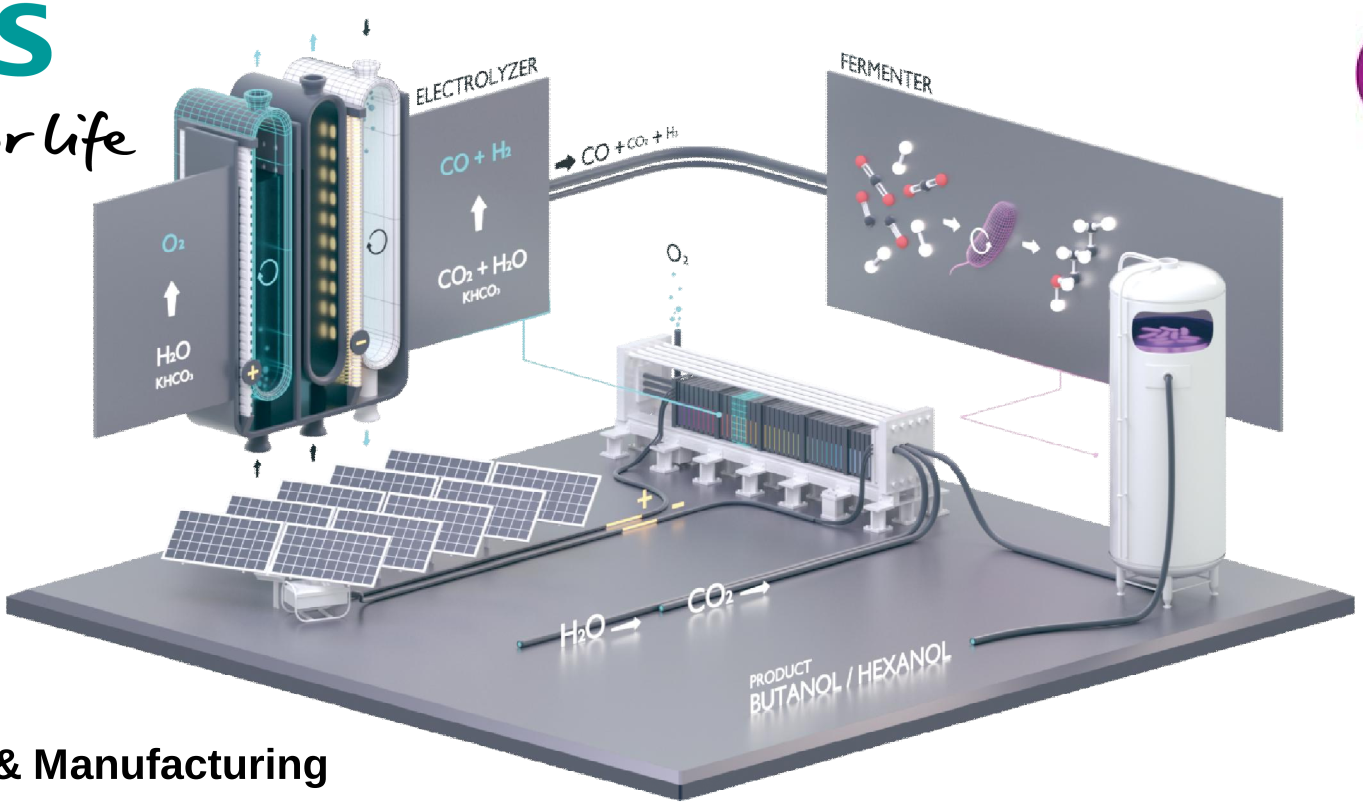
Developing & Building Electrolyzers

- H_2O to H_2
- CO_2 to CO



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POWER TO CREATE

Developing & Operate Fermentation Processes

covestro

Developing & Manufacturing Gas Diffusion Electrodes

Rheticus

To date, ~ 8% Solar-to-Chemical total system efficiency is possible at industrial relevant conversion rates

How to get into a renewable economy ?
Scaling

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Implementation strategy for an electrolyzer business

Specialty chemicals	*Bulk chemicals*	*Green fuels*
• Small market sizes • High product prices • << 1 Mio t/a, MW/System	• Medium market sizes • Medium product prices • 1 – 100 Mio t/a, two-digit MW/System	• Large market sizes • Low product prices • >> 10 Mio. t/a, GW/System

Short term

- To be realized under existing conditions
- Learn about markets, customers, and business models
- Learn about technology and processes
- Select further specialty chemicals for business

Mid term

- Addressable with more mature technology and higher scales
- Industrialize technology and business processes and setup

Long term

- Market entry into large scale plants with green fuels
- Production plants may include own power production
- Need of favorable market condition

Today: Butanol market is between Speciality & Bulk

Tomorrow: Butanol is a more preferred fuel compared to Methanol / Ethanol (see ARAL Website: http://www.aral.de/de/forschung/zukunft/ottokraftstoff/butanol.html)

A ramp up starting today leads to new business opportunities tomorrow

Down-Stream Fermenation Process

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- Anaerobic bacteria from black smokers can built complex molecules from H_2, CO, H_2O and CO_2 while gaining their energy to reproduce and live
- Carbon selectivity is very high avoiding large amounts of side products (different to thermo chemical synthesis)
- Products are of very high economical value
- H_2, CO, CO_2 concentrations can vary in a wide range

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1. *C. autoethanogenum* ("the reducer / C-H – bond former")

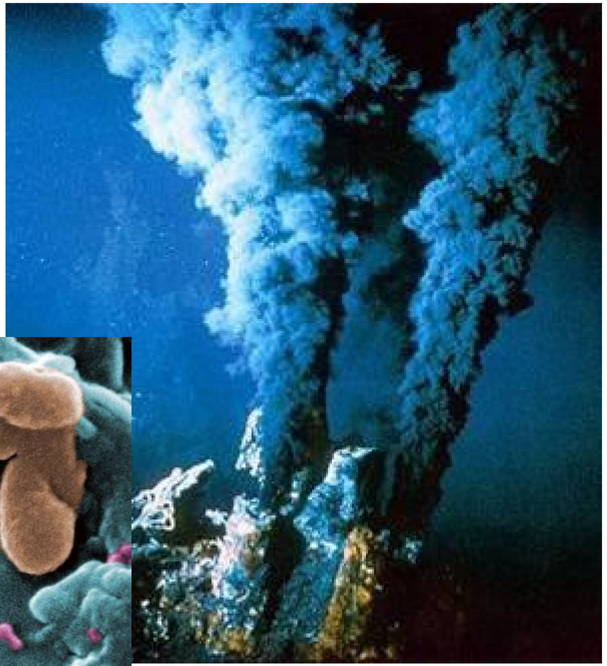
$$2\,CO + 2\,H_2 \rightarrow CH_3COOH$$
$$CH_3COOH + H_2 + CO \rightarrow C_2H_5OH + CO_2$$

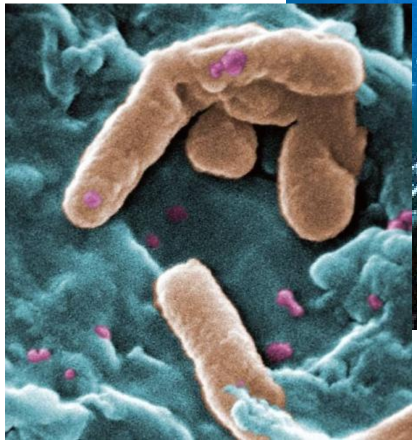
2. *C. kluyveri* ("the condenser / C-C – bond former")

$$CH_3COO^- + C_2H_5OH \rightarrow C_3H_7COO^- + H_2O \quad \text{(butyrate)}$$
$$C_3H_7COO^- + C_2H_5OH \rightarrow C_5H_{11}COO^- + H_2O \quad \text{(hexanoate)}$$

3. *C. autoethanogenum*

$$C_3H_7COOH + H_2 + CO \rightarrow C_4H_9OH + CO_2 \quad \text{(butanol)}$$
$$C_5H_{11}COOH + H_2 + CO \rightarrow C_6H_{13}OH + CO_2 \quad \text{(hexanol)}$$





https://oceanography101.wikispaces.com/Black+Smoker

Up-Stream Electrolysis Process

- Conversion of volatile electrical energy in materialized energy carriers
- Energy storage in CO and H_2
- Electrochemistry is almost isothermal (no losses in „Entropy")
- CO is preferred due to higher thermodynamic potential and carbon content
- Potential use of commercial electrodes for CO_2-to-CO electrolyzer
- Upstream processes have efficiencies << 100% (Thermodynamics)

1. Silyzer 200 (product)

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

2. CO_2-to-CO Electrolzer (under development)

$$CO_2 \rightarrow CO + \frac{1}{2} O_2$$

Towards Continuous Operation of a CO_2-to-CO Electrolyzer

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Continuos operation requires managment of all charge carriers / ions, their ion concentration and pH

Cathode: $CO_2 + H_2O + 2\ e^- \rightarrow CO + 2\ HO^-$

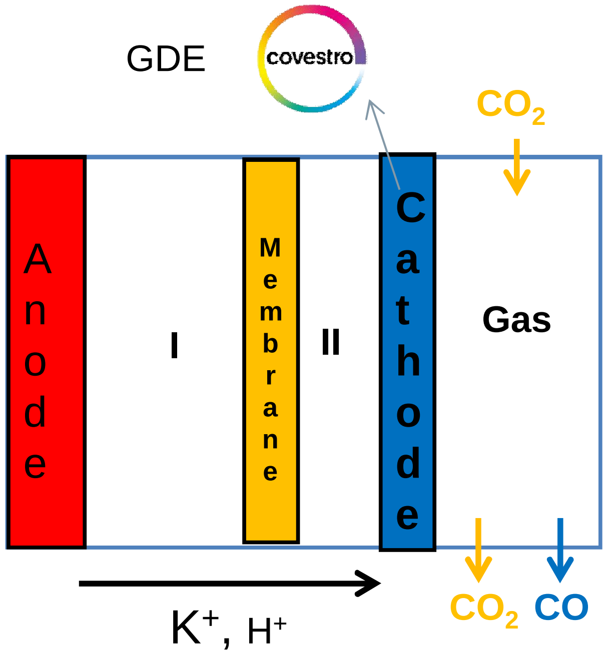
Anode: $H_2O \rightarrow \frac{1}{2}\ O_2 + 2\ H^+ + 2\ e^-$

$$CO_2 \rightarrow CO + \frac{1}{2}\ O_2$$

Buffer reaction: $2\ OH^- + 2\ CO_2 \rightarrow 2\ HCO_3^-$

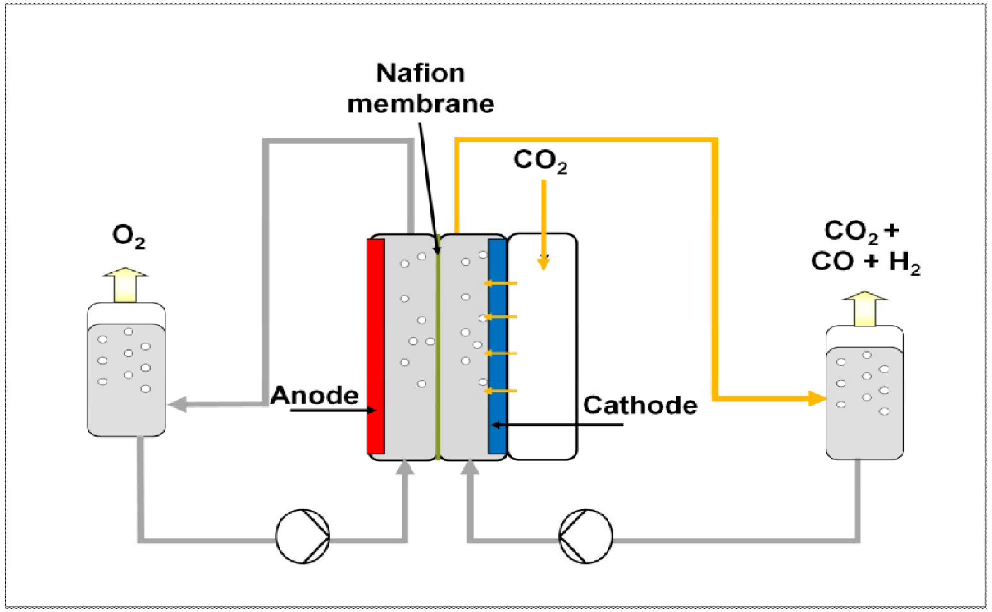
Buffer reaction: $2\ HCO_3^- + 2\ H^+ \rightarrow 2\ H_2O + 2\ CO_2$

- Ion transport within the cell is accomplished not only by protons but also other cations such as potassium, even if membranes like Nafion are used
- Stable continuous operation requires active equilibration of ions
- Two methods are discussed in the following
  - Mode 1: Separate electrolytes, charge equilibration by protons
  - Mode 2: Mixing of catholyte and anolyte

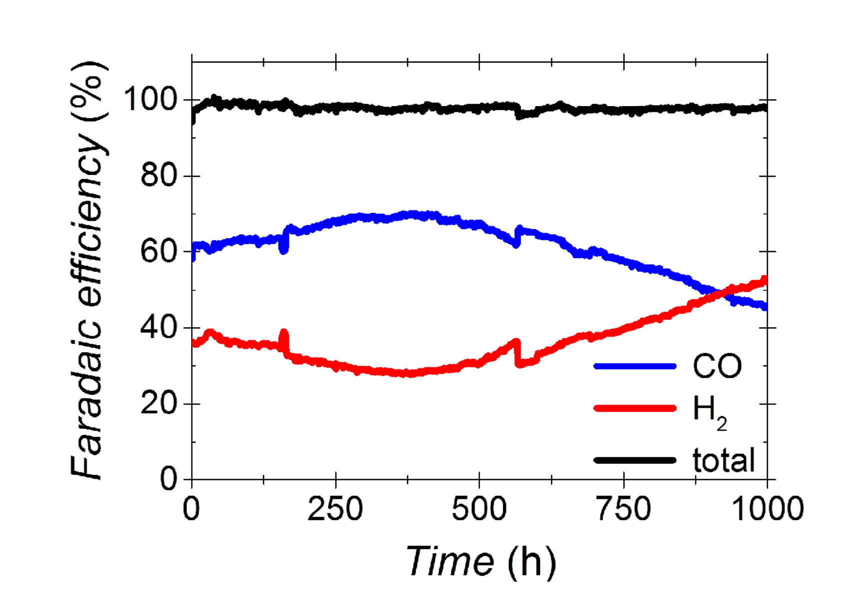


Mode 1: Separated electrolytes, Charge equilibration by protons

Setup



Result



- *Anolyte and Catholyte are fully separated*
- Catholyte: 0.4M K_2SO_4 + 1M $KHCO_3$
- Anolyte: ***1M H_2SO_4***
- Electrode area: 10 cm²
- Cathode Ag-GDE, Anode IrO_x
- Membrane: Nafion (cation conductor)
- Current density: 50mA/cm²

- The ion transport in the cell is driven by protons from the anolyte to the catholyte through the cation selective Nafion membrane
- Protons are stoichiometrically produced at the anode, and neutralized by OH^- from the cathode
- Electrolyis is running for 1000 h, however some changes are visible
- Protons pull also H_2O molecules through the membrane (anolyte gets concentrated, catholyte get diluted)

Mode 2: Mixing of catholyte and anolyte

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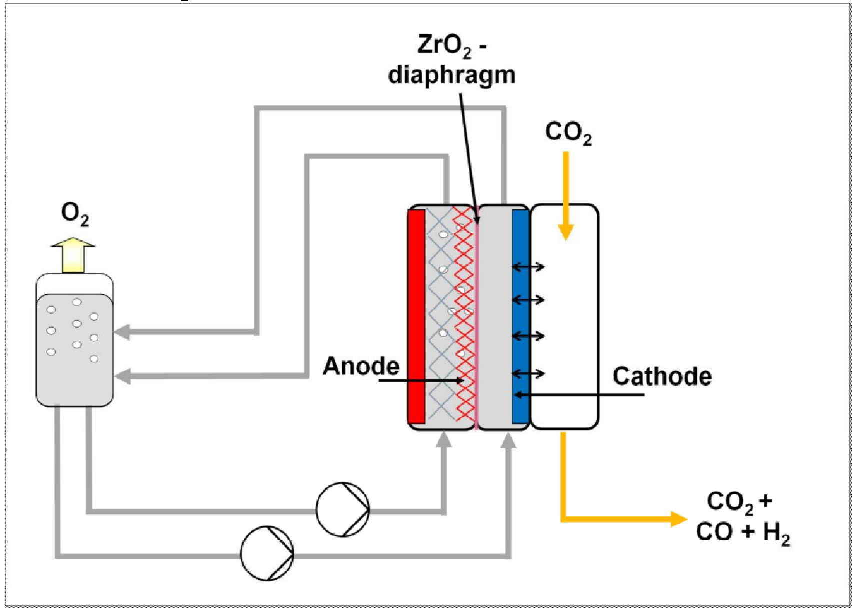
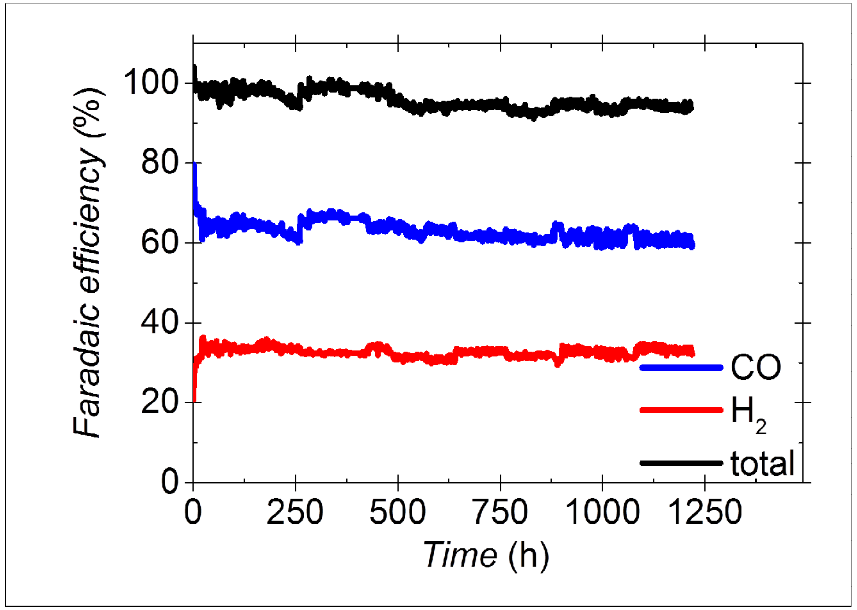
Setup



Result



- *Anolyte and Catholyte are continuosly mixed*
- Electrolyte: 0.1M K_2SO_4 + 1.5M $KHCO_3$
- Electrode area: 10 cm²
- Cathode Ag-GDE, Anode IrO_x
- Membrane: Diaphragm seperator
- Stromdichte: 300mA/cm²

- Charge transport is mainly accomplished by potassium cations (proven by experiment)
- Changes in concentration are equilibrated by continous mixing
- The electrolysis process is running stable
- Current densities up to 300 mA/cm²
- Industrial application is feasible

Mode 2: Energy Efficiencies

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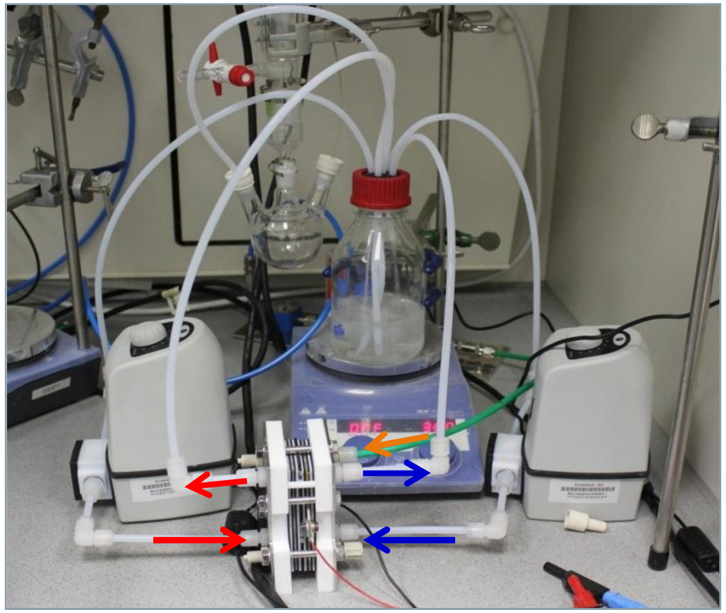
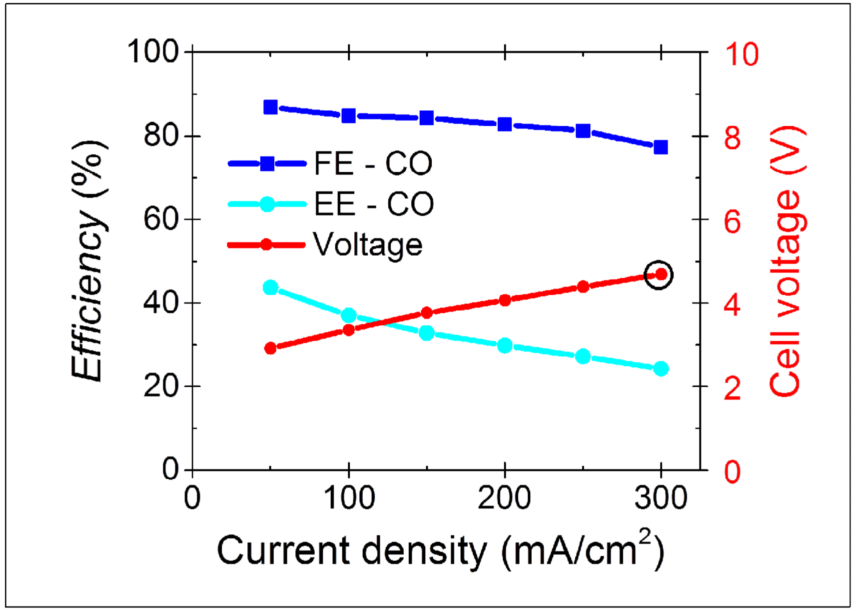
Setup

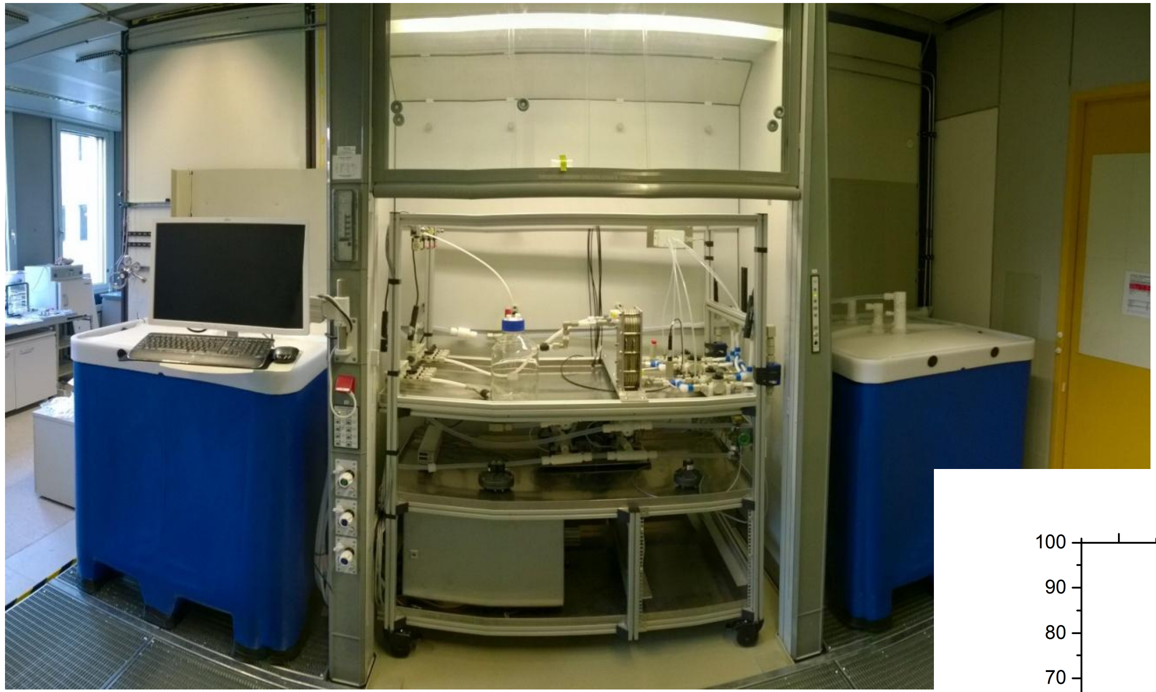


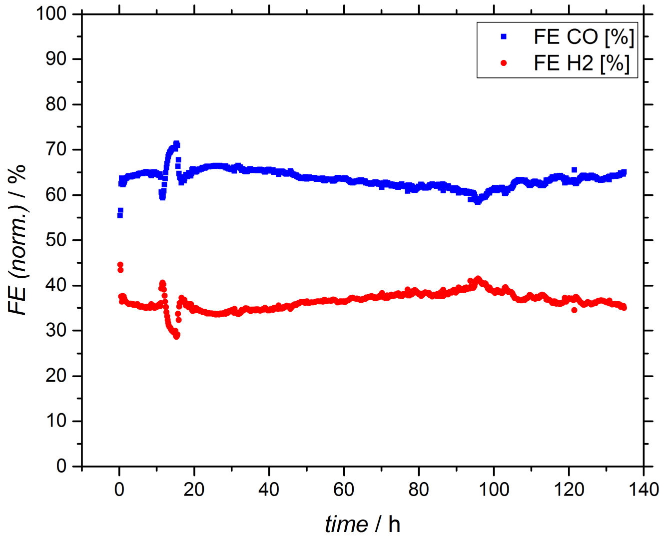


- Two continuous operation modes on lab scale identified (10cm²)
- Mixing of catholyte and anolyte has significant advantages over separated electrolytes (concentration management and accessible current density)
- The non-optimized cell design (distance between cathode & anode) requires at a current density of 300mA/cm² cell potentials of 4.8V. At FE_{CO} of ~80%, an energy efficiency of 25% for CO were achieved (incl. H_2 28%).
- Increasing temperature from 30°C to 60°C will decrease ohmic losses and increase energy efficiency

Next step: Scaling

- Up to 8 x 100 cm² electrode area
- Up to 3 l/min CO
- Power consumption total <1 kW
- Electrolyte volume up to 1,000 l
- Gas separation
- Online gas analysis
- Temperature controlled
- Automated operation for long life term measurements



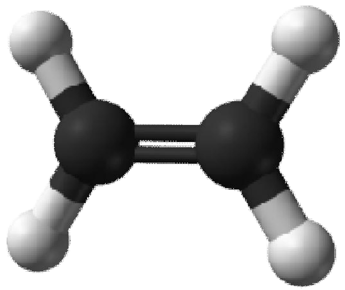


Current density 150 mA/cm²
Single cell

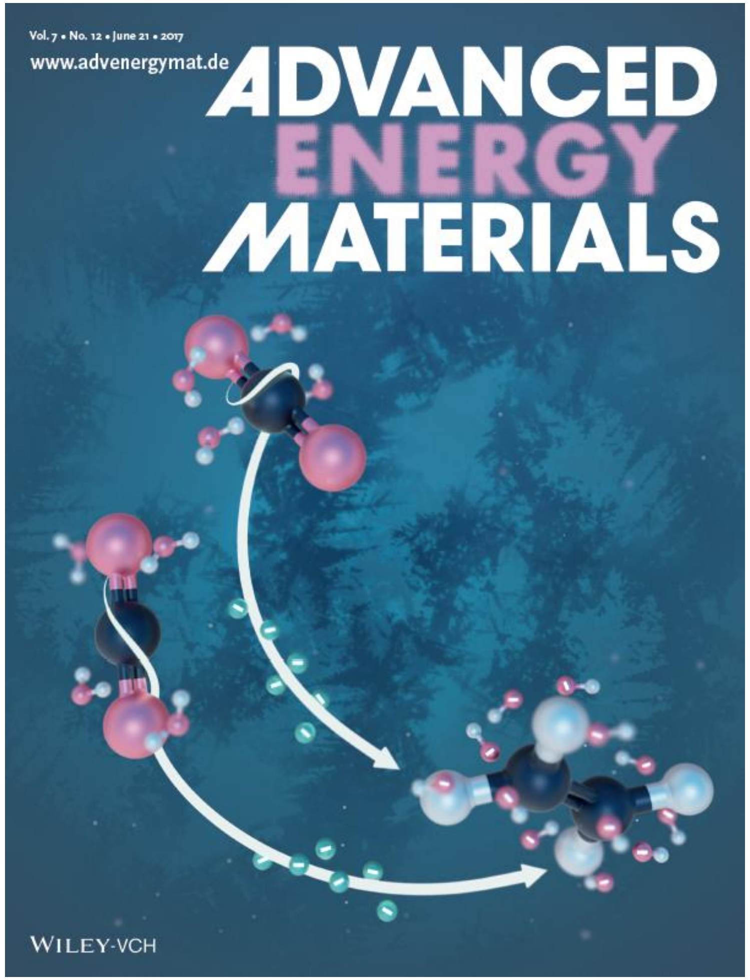
Electroreduction of CO_2 to C_2H_4

Target

Development of a selective ethylene electro catalyst



Cathode:	$2\ CO_2 + 12\ H^+ + 12\ e^-$	$\longrightarrow$	$C_2H_4 + 4\ H_2O$
Anode:	$6\ H_2O$	$\longrightarrow$	$3\ O_2 + 12\ H^+ + 12\ e^-$
	$2\ CO_2 + 2\ H_2O$	$\longrightarrow$	$3\ O_2 + C_2H_4$



DOI: 10.1002/aenm.201602114
C. Reller et. al. ***Adv. Energy Mater.*** *2017, 1602114*

eEthylen: the Vision

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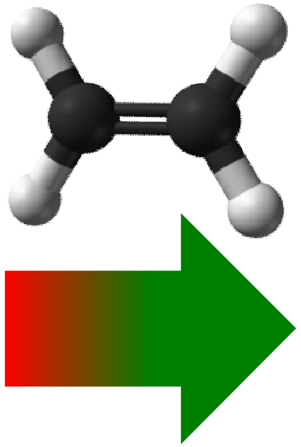
Substitution of a Steam-Cracker by a CO_2-to-Ethylene electrolyser in a 140 Mio. t/year ~ 140 Bill. €/year market



What product should we produce – Profitability- ? (*Rule of Thumb*)

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Ratio between the **Economical Value** and the **Heating Value** for a given point in time

Burning Processes

Methane $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + 15{,}4$ MWh/t

Ethylene $C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O + 13{,}9$ MWh/t

Synthesis by Single Step Electrochemical CO_2 Reduction

Methane $CO_2 + 2\,H_2O + \text{min. } 15{,}4 \text{ MWh/t} \rightarrow CH_4 + 2\,O_2$

Ethylene $2\,CO_2 + 2\,H_2O + \text{min. } 13{,}9 \text{ MWh/t} \rightarrow C_2H_4 + 3\,O_2$

Thermodynamic considerations with 100 % efficiency assumption

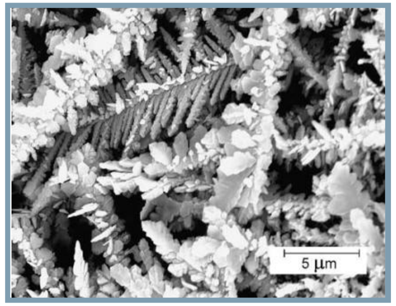
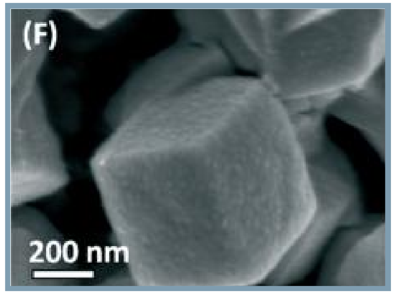
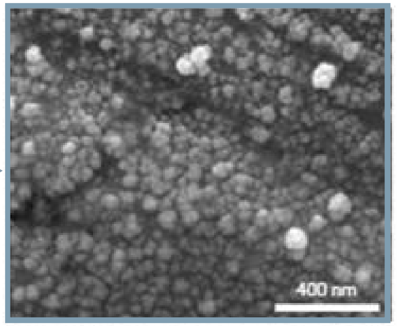
A factor of 4 – 6 might be enough to compensate for all losses

	Energy Demand	Min. Energy Cost [1]	Product Value	Cost Covering min. System Efficiency
	MWh / t	€ / t	€ / t	%
Methane	15,4	463 - 694	150	308 - 463
Ethylene	13,9	419 - 629	1000	42 - 63

[1] electricity cost 30 €/MWh; tax & net use 15 €/MWh (there is no excess energy)

Data taken from BMBF-Project eEthylen

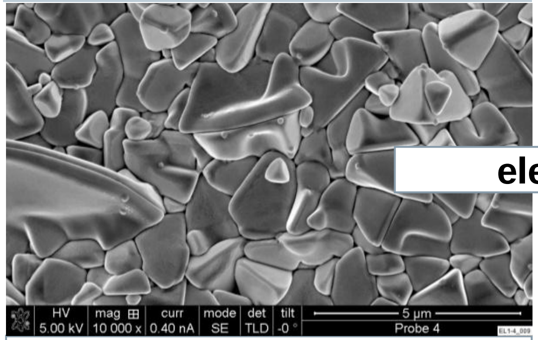
Ethylene Catalysts Described in Literature

preparation	morphology	results	interpretation
CuBr Film K. Ogura et al. Catalysis Today, 2004, 98, 515–521		65% FE (Ethylene) 30 mA/cm² duration 30 min	catalyst ?
in-situ reduced CuCl film Boon Siang Yeo et al. Catal. Sci. Technol., 2015, 5, 161–168		25% FE (Ethylene) 25 mA/cm² duration 6 h	
in-situ Cu nano deposition Chorkendorff et al. Phys. Chem. Chem. Phys., 2012, 14, 76–81		35% FE (Ethylene)	

Evaluation of the Selective Cu-Electrocatalyst for Ethylene Formation – CuBr Film

Hypothesis: **CuBr is the active species for selective ethylen formation (K. Ogura et al.)**

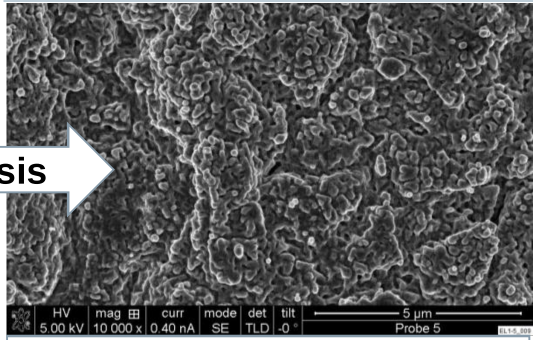
SEM image CuBr before El.



anodic bromination of a Cu ETP sheet in 3M KBr

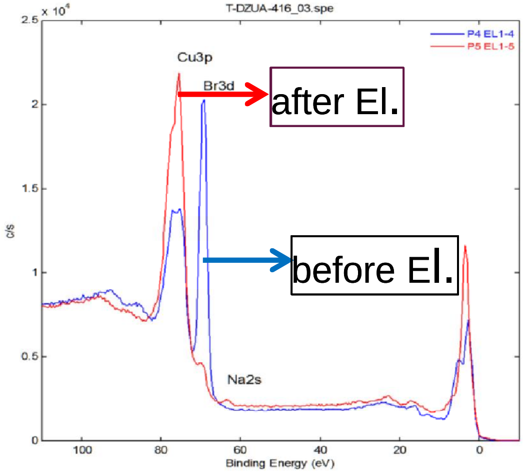
electrolysis

SEM image CuBr after El.



after 1h electrolysis @ -1.3V vs. Ag/AgCl

XPS analysis



Results

- CuBr -film is not stable against reduction, only residuals were identified after electrolysis
- Cu ^{0} deposites were identified after reduction
- ➢ **CuBr film is not solely the active species**

Solid Cu Electrode Modification
-Addition of Oxidizing Agents (Br_2) to the Electrolyte

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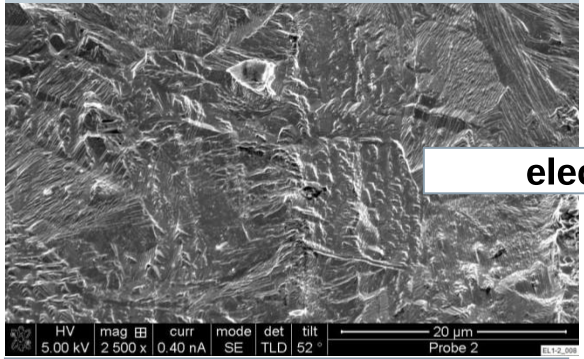
<u>Hypothesis:</u> Copper corrosion is enhanced by bromine

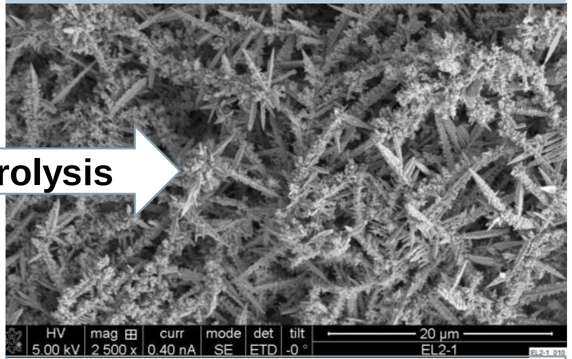
SEM image of copper surface



Cu ETP sheet before electrolysis

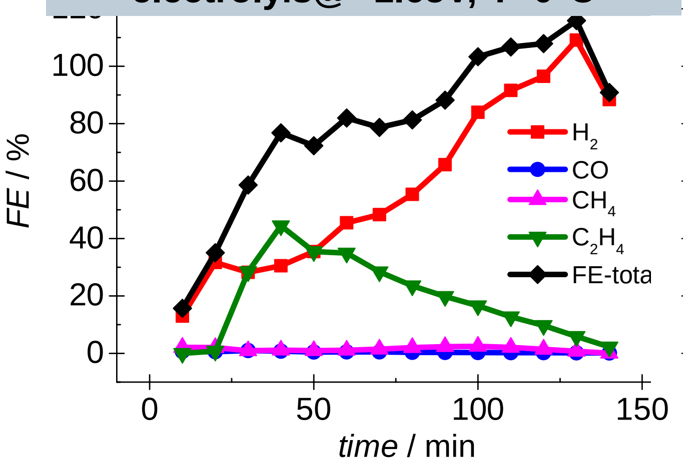
electrolysis

SEM image after electrolysis



after 1h electrolysis @ -1.65V vs. Ag/AgCl

electrolyis@ -1.65V, T=0°C



Results

- addition of bromine leads to massive copper corrosion (Cu dissolution followed by re-deposition)
- 40% FE were observed for ethylene after 50 min
- comparable results were obtained using O_2, H_2O_2, $S_2O_8^{2-}$
- ➢ bulk composition: Cu_2O, CuBr species were identified after El.

In-Situ Copper Nano-Deposition
-Copper on Silver Substrate

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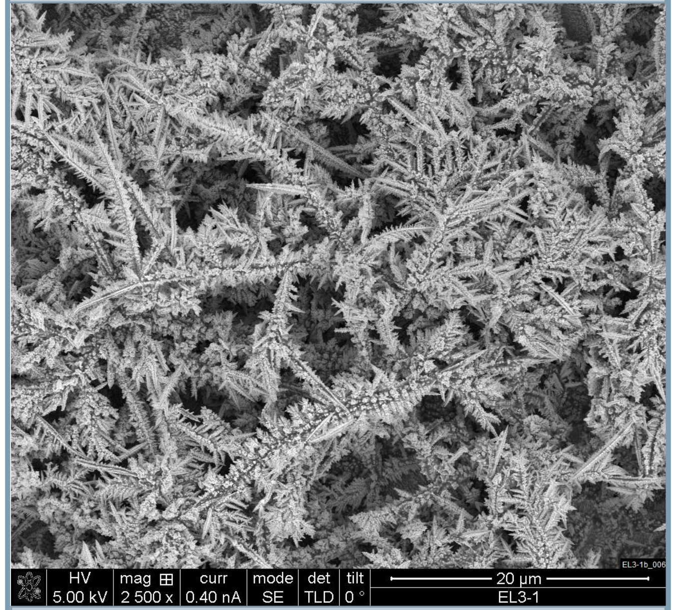
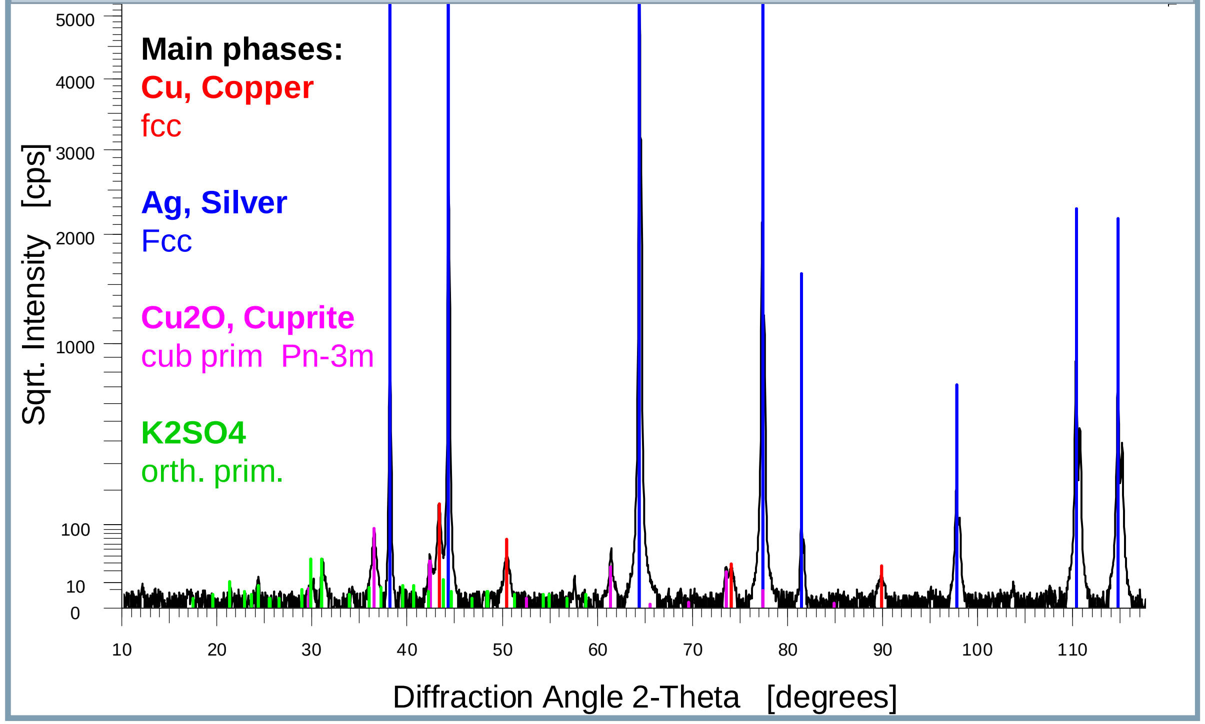
SEM image of electrode surface



in-situ nano Cu on Ag electrode electrolysis 150min @ -1.65V

Powder pattern of the decorated Ag electrode



Conclusion

- Cu nano-deposites were identified on the Ag electrode surface
- Cu_2O phase was present after electrolysis
- ethylene production on silver substrate (FE~20%)
- CO production was completely suppressed

Transfer of Catalyst to a Gas Diffusion Layer
In-Situ Copper Deposition

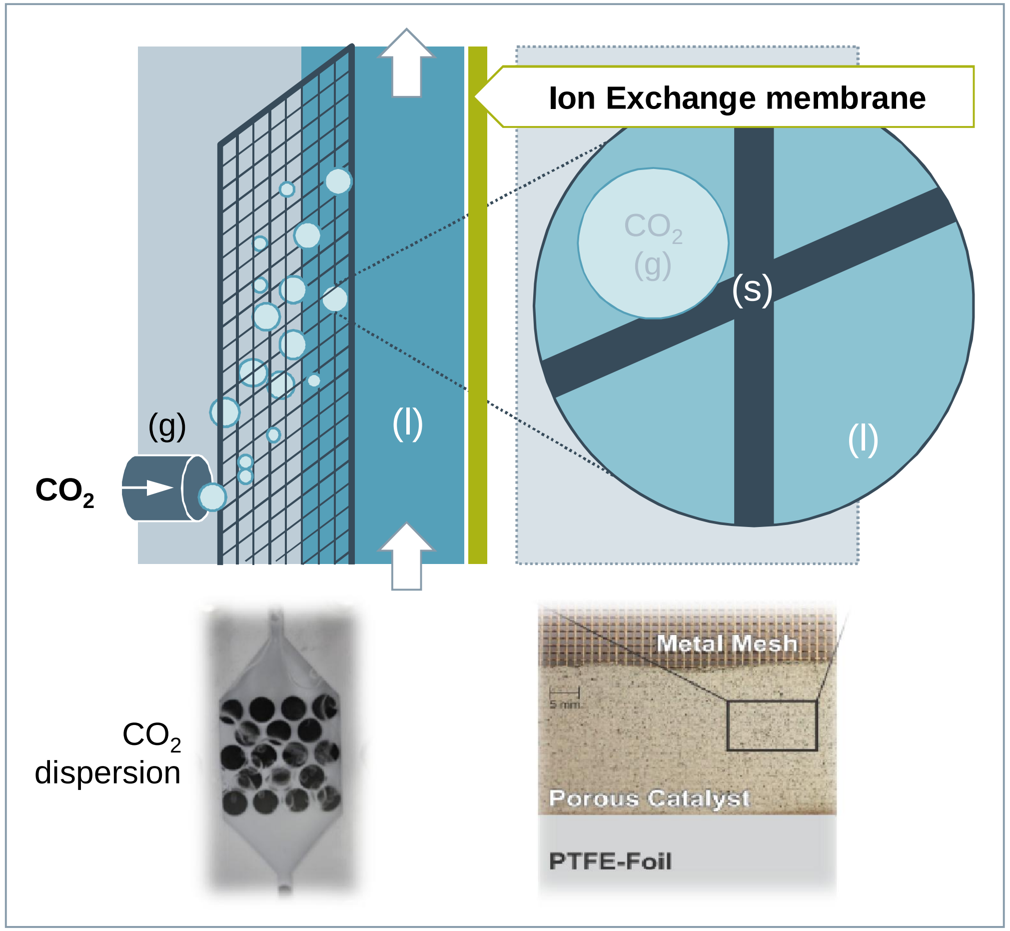
Benefits of the GDE:

- no mass transport limitation (due to bad CO_2 solubility in water)
- higher active surface area
- material costs
- in-situ deposition could be applied onto the substrate

Key component: Gas Diffusion Electrode (GDE) to overcome the low solubility of CO_2 in water

- Only CO_2 can be electrochemically reduced not HCO_3^- or other chemically dissolved species
- 3-Phase interface ensures high CO_2 concentration at the electrode (gas-liquid-solid)

  → Key challenge to achieve industrial relevant current densities >> 100 mA/cm²
- CO_2 is absorbed on the electro catalytic electrode
- Gas separation may be needed in subsequent processes



Electrochemical characterization
GDE with In-Situ Grown Copper-NP-Catalyst

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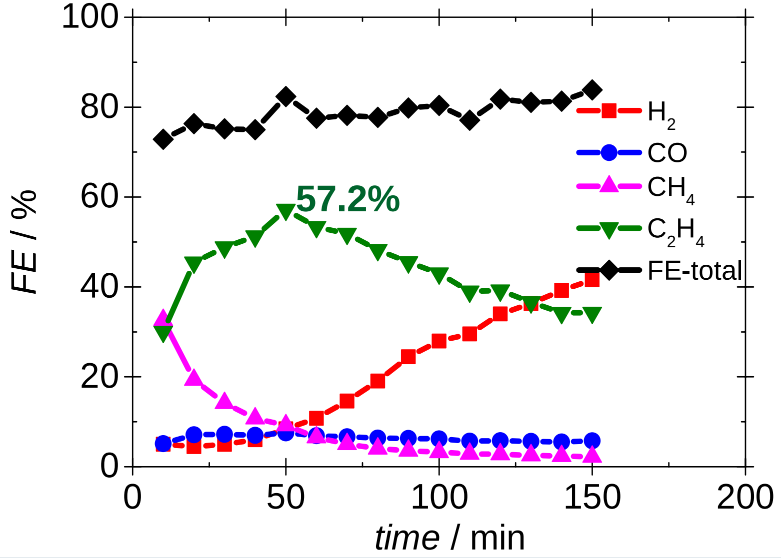
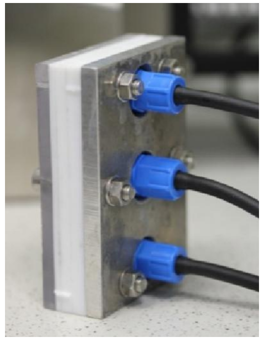
Faradic Efficiency over time



Experimental



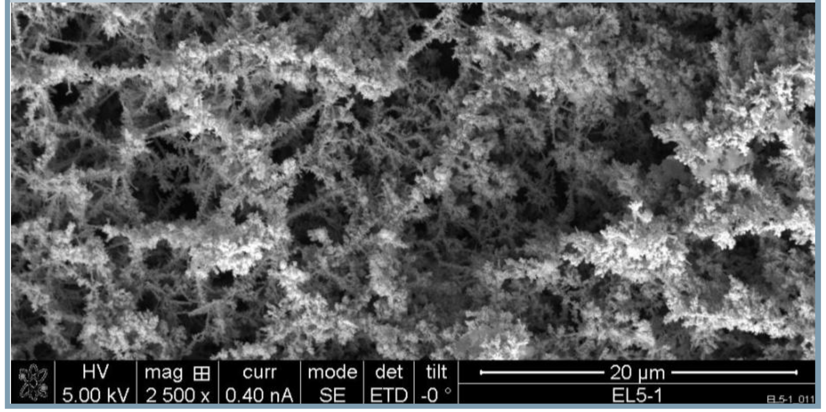
- Flow cell with GDE setup
- copper NP-catalyst is formed from Cu^{2+} ions
- pH value of the catholyte increases pH 3 to 7.5

Results

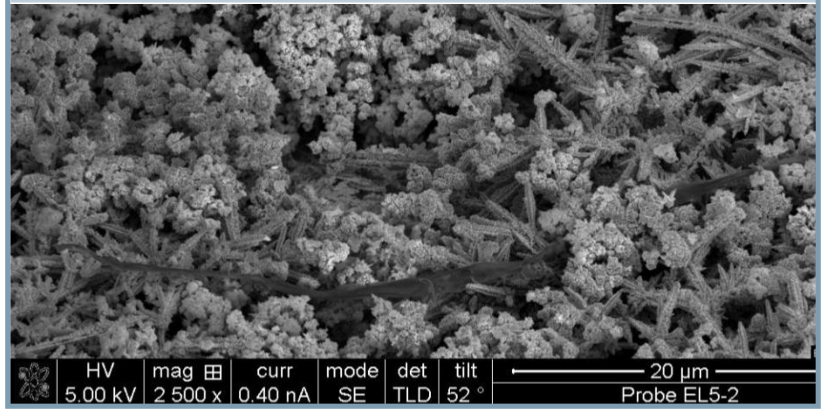
- the maximum FE for ethylene (57%) is reached after 50 min
- current density of 170 mA/cm² was achieved for ethylene
- system efficiency (SE=20% @ 10 mm cathode – anode distance) (electrical energy to chemical energy)

Degradation of In-Situ Deposited Nano Structured Catalysts

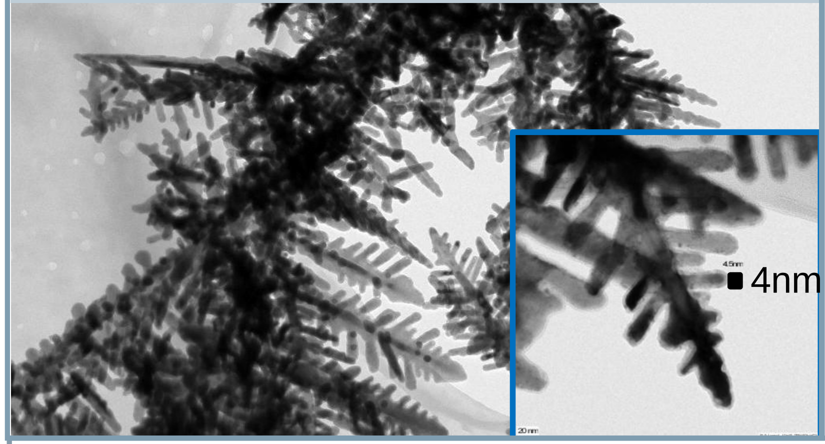
SEM image after deposition



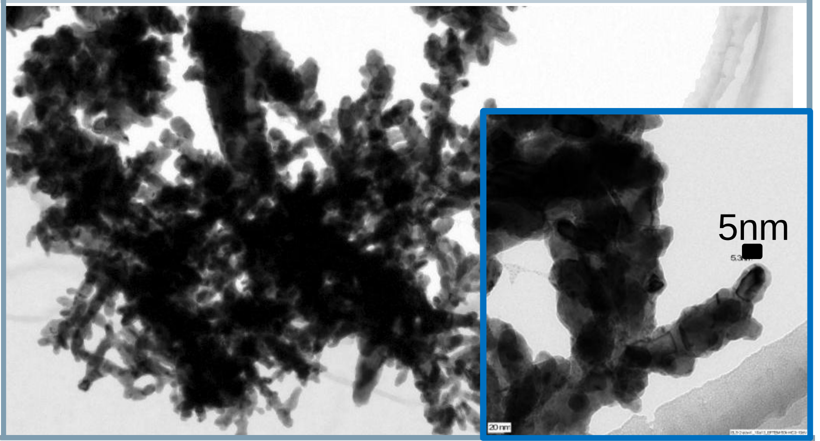
SEM image after 150 min El. time



TEM image after deposition



TEM image after 150 min El. time



- structural changes of the nano catalyst layer were identified by REM and TEM measurements
- coarsening of the nano dendritic structure was observed
- dendrites consist mainly of Cu and Cu_2O

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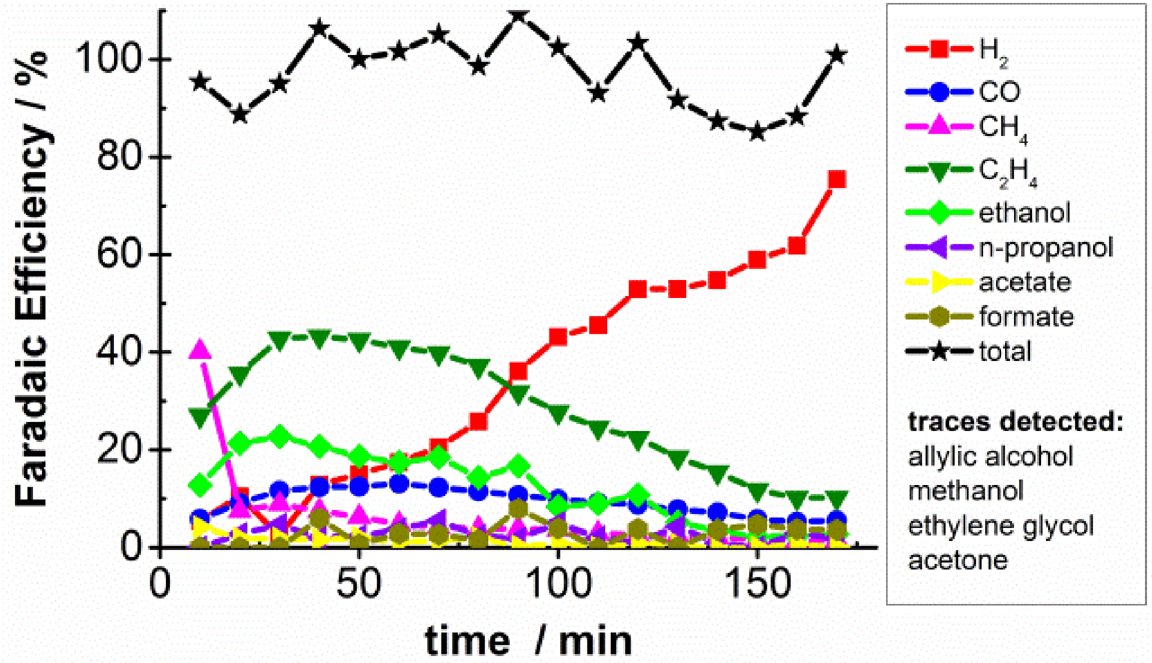
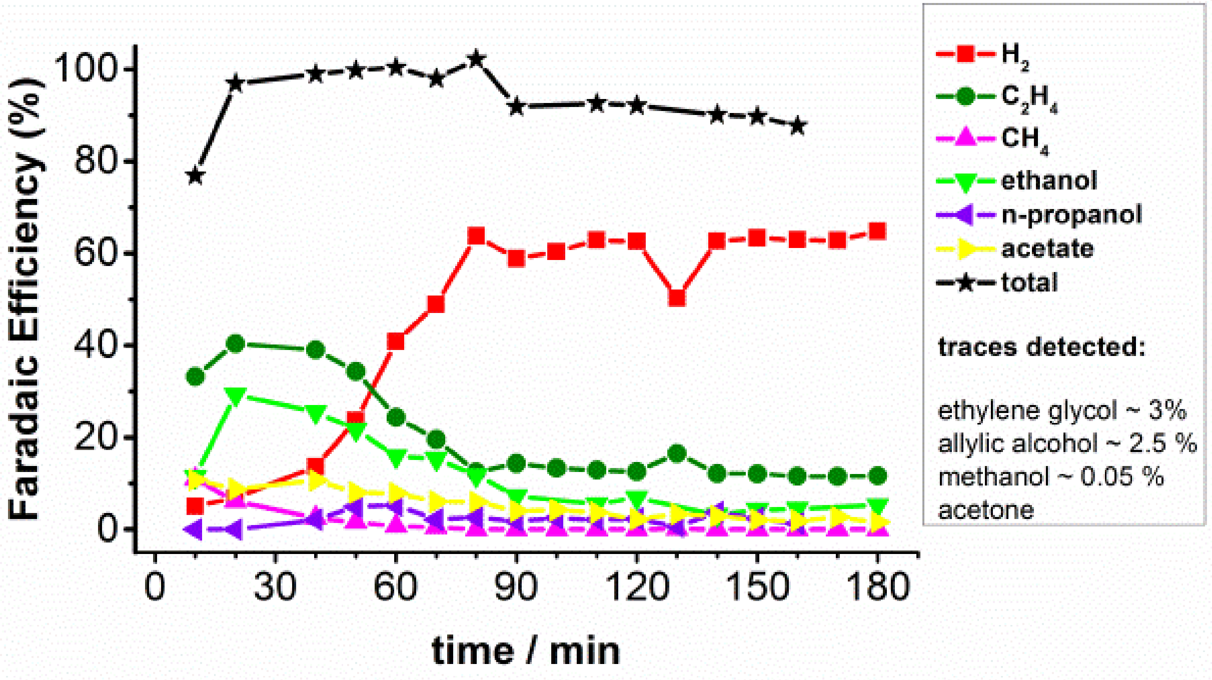
Other substrates ? CO_2 *vs.* CO

FE *vs.* time for major products of bulk electrolysis at 170 mAcm^{-2}.

Substrate CO_2



Substrate CO



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In the high current density regime CO_2 and CO substrates yield similar results upon reduction with the dendritic *in-situ* grown copper catalyst

Observed production: **carboxylates, conjugated alcohols, alkenes, conjugated alkanes, ketones** ?

Paving the way to a new electrochemical petro chemistry
Conversion of *C-X* bonding motives with the in-situ deposited copper catalyst

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Reagent	Product	Faradaic Efficiency	Selectivity
C≡C tipple bonds	C=C double bonds	> 60 - 90 %	> 95%
C=C double bonds	C-C single bonds	< 20% (high, if substituents are electron withdrawing)	> 99 %
C=O double bonds (aldehydes, ketones)	C-O single bonds (alcohols)	Aldehydes > 95 % Ketones < 10 %	> 99% (successive reactions to be considered)
C-O single bonds	no reaction		
carboylates	no reaction		

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Conclusions

- Technical photosynthesis start to become an industrially feasible approach to a green economy
- Electro catalysis is able to convert CO_2 in a single step into viable carbon based feedstock
- CO_2 to CO approaches industrial applicability
- The combination of CO_2-electrolysis and anaerobic fermentation enables a selective and efficient pathway toward green chemicals
- CO_2 to Ethylen still requires deeper understanding with respect to catalyst stability

…. We started

https://www.siemens.com/press/de/pressemitteilungen/?press=/de/pressemitteilungen/2018/corporate/pr2018010135code.htm

http://www.ssu.edu/academics/courses/finance/

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Ingenuity for life

Team

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  - **eEthylen** (electro catalyst development)
  - **Kopernikus Power-To-X Technologies** (operation modes CO_2-to-CO)
  - **Rethicus** (platform of electrolysis & fermentation, scaling)
  - **Re-Future** (…. which made this talk possible)

GEFÖRDERT VOM

Bundesministerium
für Bildung
und Forschung

….. thanks for your kind attention

Backup

CO_2 Sources in Europe and Germany

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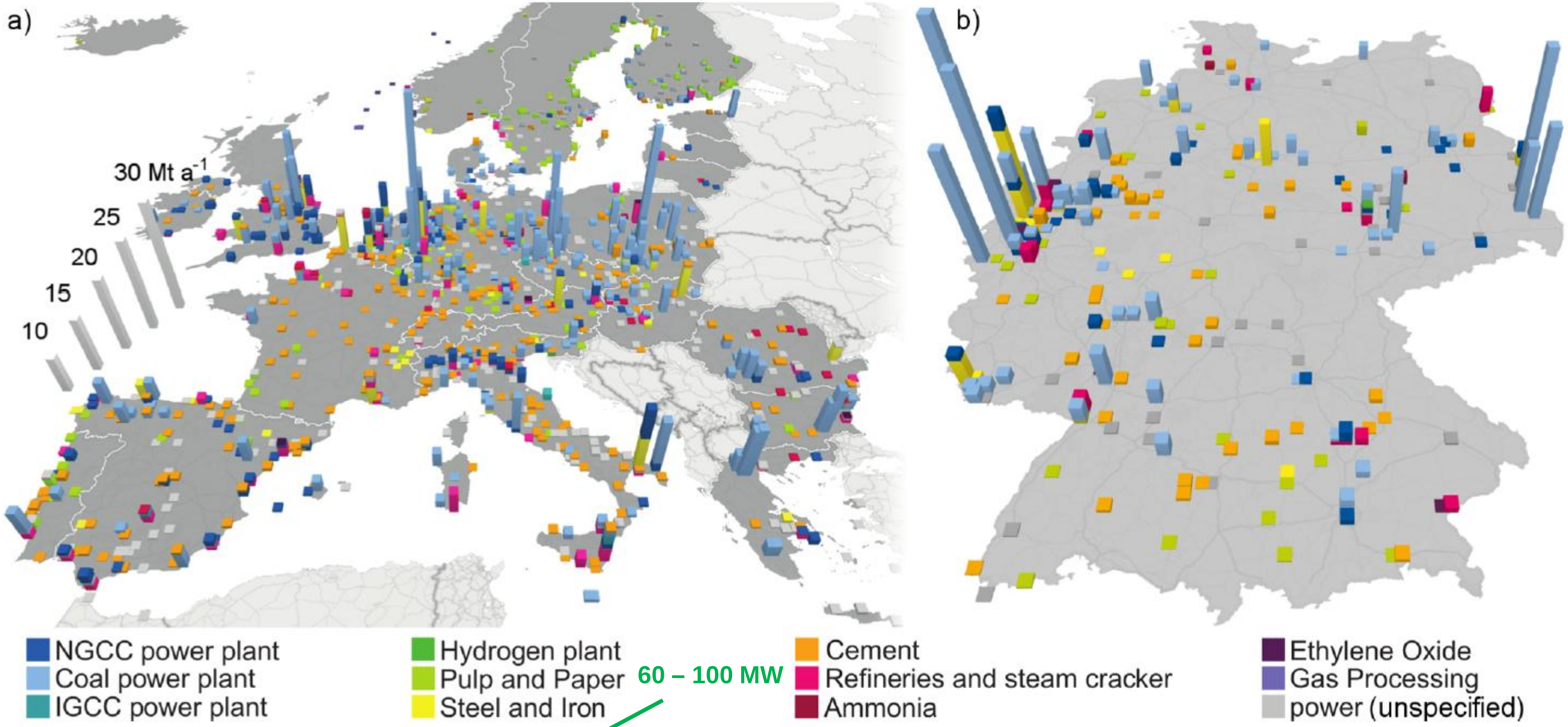
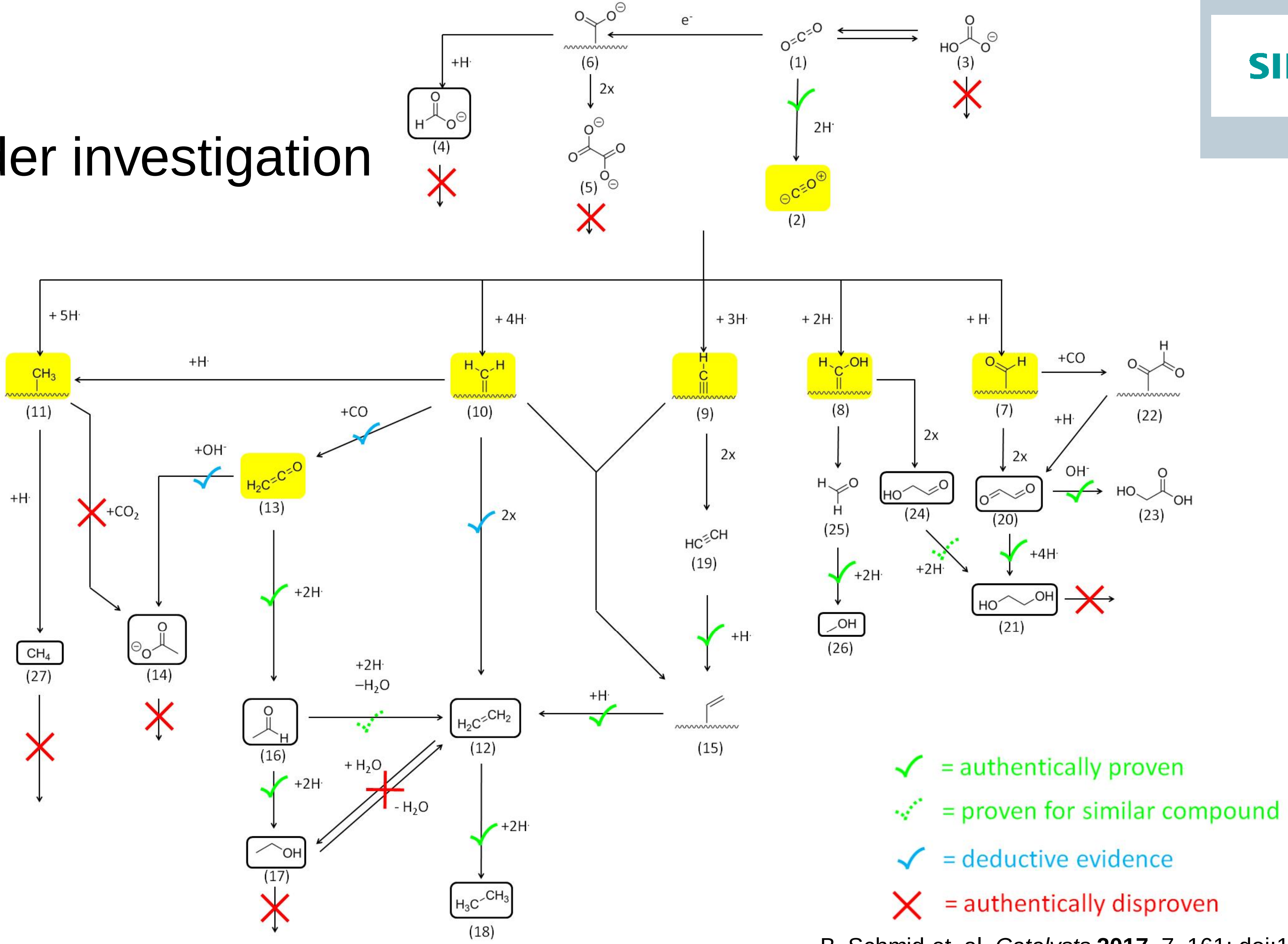


Figure 2. Distribution of CO_2 point sources (>0.1 Mt a^{-1}) in 2011 in a) Europe and b) Germany as exemplary country. The CO_2 emissions map has been created using the PowerMap Preview Plugin for Microsoft Excel 2013.[59] Color online.

http://pubs.acs.org/doi/abs/10.1021/acs.est.5b03474
Environ. Sci. Technol., 2016, 50 (3), pp 1093–1101

Routes under investigation



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