CO_2SimO - Photoelectrochemical CO_2-reduction with simultaneous oxidative raw material production

1st CO_2 WIN Conference
8-9 June 2021

JX Metals Group

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Project target CO_2SimO

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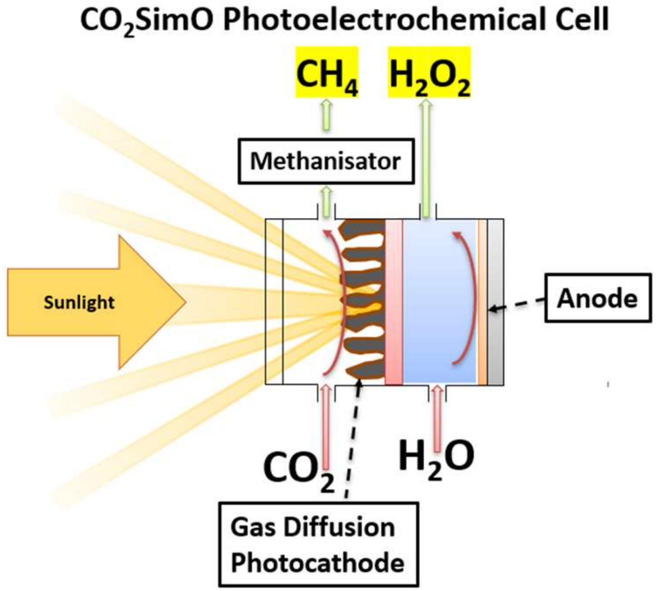
- Development of a solar driven photoelectrochemical cell (PEC) for the simultaneous
  - reduction of CO_2 to CO/CH_4 with newly developed photocatalysts using a gas diffusion electrode at the cathode and a methanisator
  - oxidation of H_2O to H_2O_2 or peroxides at the anode



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CO_2SimO project team & work packages

- **University Bayreuth, Prof. Marschall, M. Weiß:** development and characterisation of new photocatalysts (p-type Cu-Niobates/- Tantalates)
- **TANIOBIS GmbH (formerly H.C. Starck Ta&Nb GmbH), Dr. Albrecht, B. Spyra, S. Barnick:** Upscaling, process optimization, supply for photocatalysts
- **DECHEMA´s Research Institute, Dr. Bloh, T. Schanz:** manufacturing of gas diffusion electrodes using photocatalysts; development of electrocatalysts for the anode; supply of electrodes
- **Leibniz University Hanover, Prof. Bahnemann, Dr. Dillert:** photochemical and spectroscopic characterization, mechanistic studies for optimization of CO_2-reduction
- **neoxid GmbH, Dr. Ostermann, H. Müller, S. Puthenkalam:** construction of photoelectrochemical cell based on electrodes from DECHEMA; development of methanisator, measurement of solar efficiencies
- **Karlsruhe Institute of Technology, Institute for Technology Assessment and Systems Analysis, Dr. Patyk, L. Lazar:** LCA and Cycle Costing (LCC)

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Leibniz Universität Hannover

neoxid research for nanoenergy

KIT Karlsruher Institut für Technologie

Development of photocatalysts

- Cu-Niobates / -Tantalates: p-type semiconductors with low bandgaps
- higher chemical stability compared to Cu_2O and CuO

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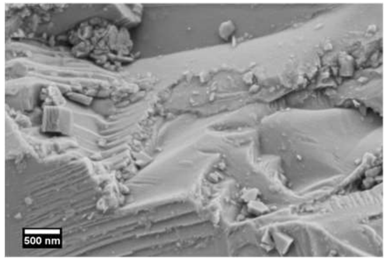
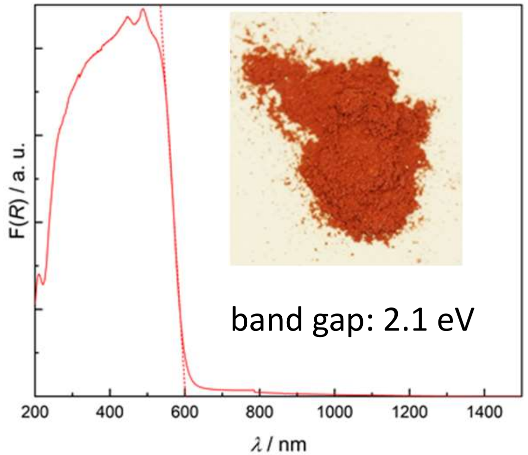
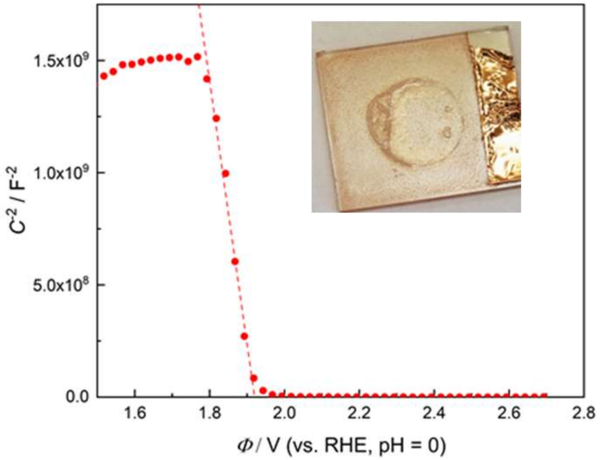
$CuNbO_3$

- Successful preparation of spin coating electrodes
- flat band potential 1,9V vs. RHE

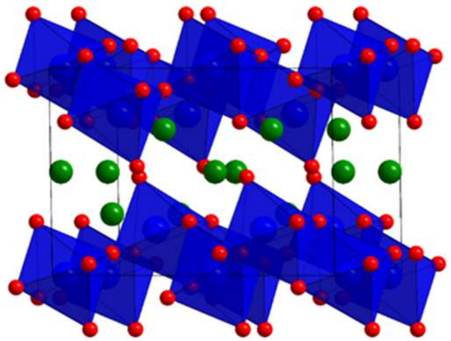




UV Vis band gap



Mott Schottky flat band potential



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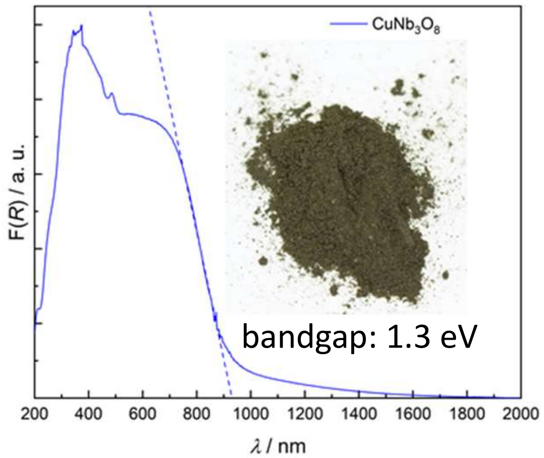
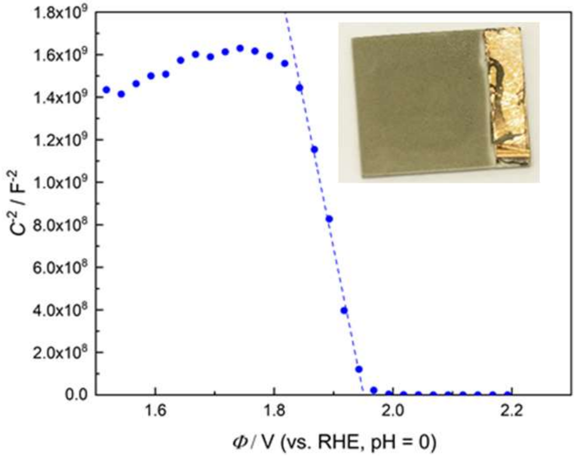
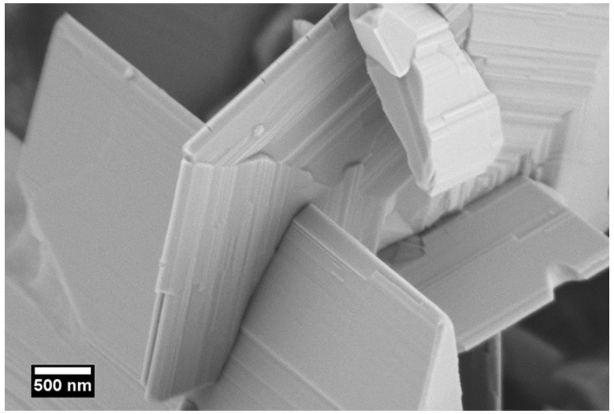
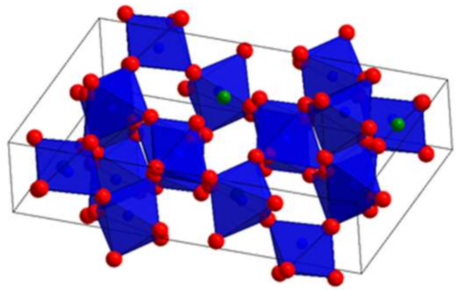
Development of photocatalysts: $CuNb_3O_8$





- low bandgap of 1,3eV
- Flat band potential at 1,95V





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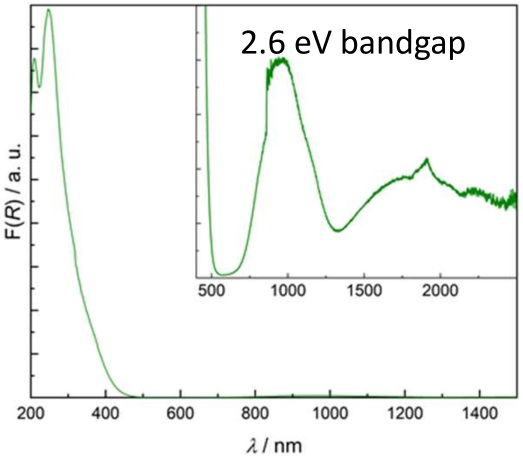
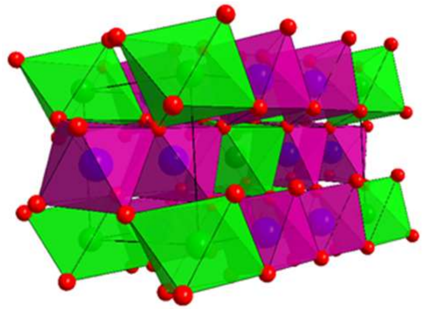
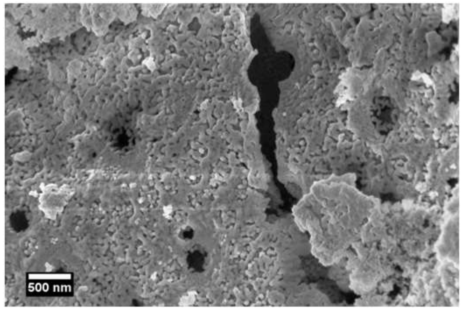
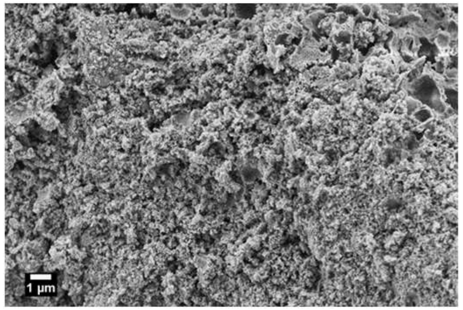
Development of photocatalysts: $CuTa_2O_6$

- sponge-like morphology
- nanoparticles with high surface area (42 $m^2\ g^{-1}$)
- electrophoretic electrode preparation









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Development of photocatalysts: Cu_2O reference materials

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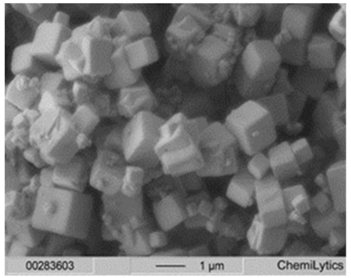
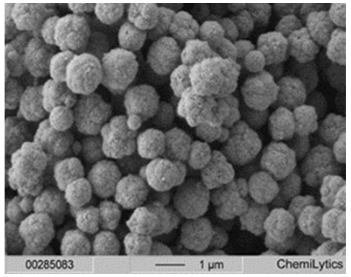
- Precipitation with different molar ratios gives variable particle characteristics

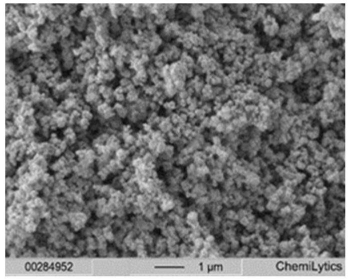
BET 1,2 m^2/g

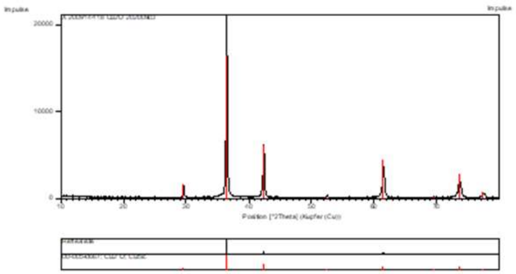


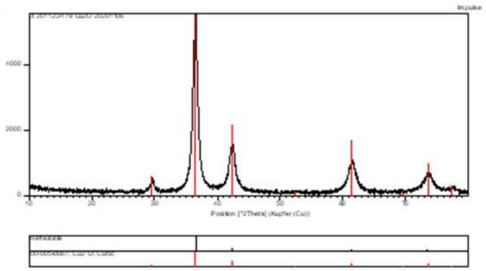
BET 16,0 m^2/g

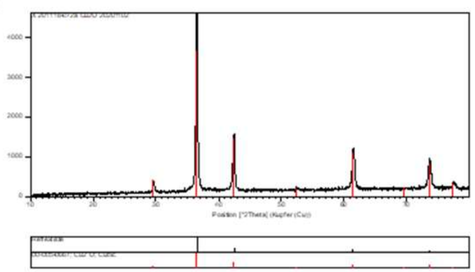


BET 5,36 m^2/g









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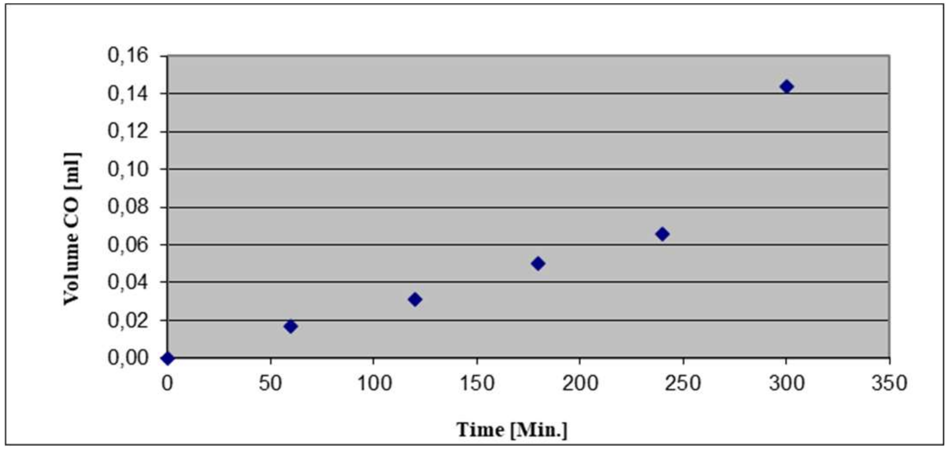
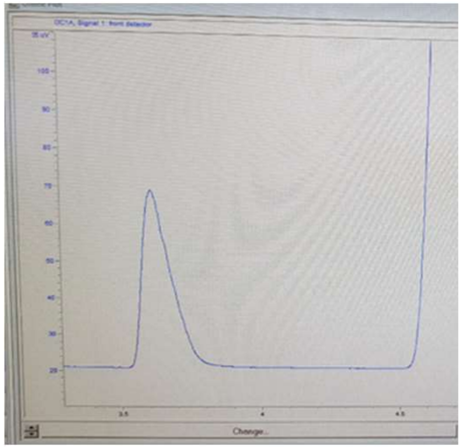
Development of photocatalysts: Reduction to CO

- 300W Xe lamp
- electrolyte 0,5M NaHCO3
- Cu_2O reference material; appr. 1µmol/h CO



CO GC-signal



Anode reactions

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- Typically, the water oxidation to molecular oxygen serves as the anode reaction in electrolysis processes
- Unfortunately, this reaction is kinetically demanding, requiring high overpotentials and expensive catalysts
- The generated product oxygen is also of only little commercial value
- The idea of this project is therefore to employ an alternative anode reaction that generates a more valuable product

Product	Chemical formula	Molar mass [g/mol]	Value [€/t]	Value [cent/mol]	n	Value per transferred electron [cent]
Methane	CH_4	16	400	0,64	8	0,08
Oxygen	O_2	32	30	0,10	4	0,02
Chlorine	Cl_2	71	80	0,57	2	0,28
Sulfur	S	32	200	0,64	2	0,32
Hydrogen peroxide	H_2O_2	34	700	2,38	2	1,19

Peroxides as product of the anode reaction

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- Peroxides such as H_2O_2 but also other technical peroxides such as peracetic acid have a wide-spread use in a variety of industries as chemical reagent, bleach or disinfectant but their storage and transportation is often difficult making on-site production particularly interesting
- This diverse and decentralized demand matches well with a decentralized generation using solar light
- Economic value is much higher than traditional anode products such as oxygen and even higher than many products of the reduction reaction (such as methane)
- The resulting process may therefore become economically feasible far earlier than processes employing anodic oxygen production

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Anodic peroxide generation

- The electrochemical oxidation of water can produce different products depending on the potential and the selectivity of the electrode material
- Some metal oxides such as $BiVO_4$ are able to selectively oxidize water to hydrogen peroxide
- Depending on the electrolyte, it may be possible to directly synthesize other technical peroxides such as peracetic acid

$$2\,H_2O \longrightarrow H_2O_2 + 2\,H^+ + 2\,e^- \qquad E° = 1.76\ V$$

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- \qquad E° = 1.23\ V$$

$$H_2O \longrightarrow OH^\bullet + H^+ + e^- \qquad E° = 2.38\ V$$

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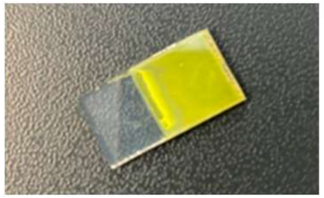
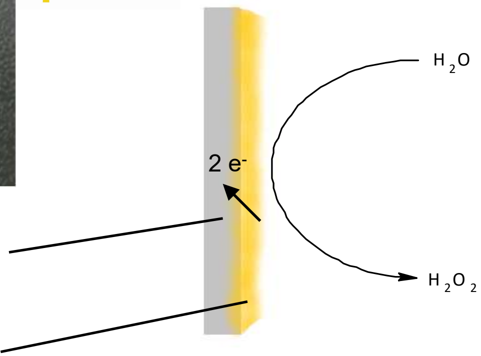
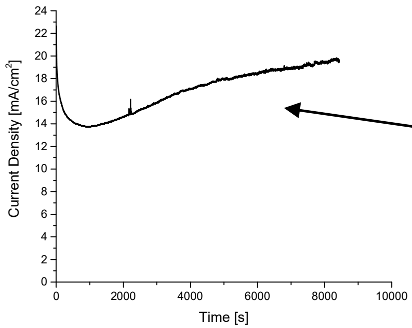




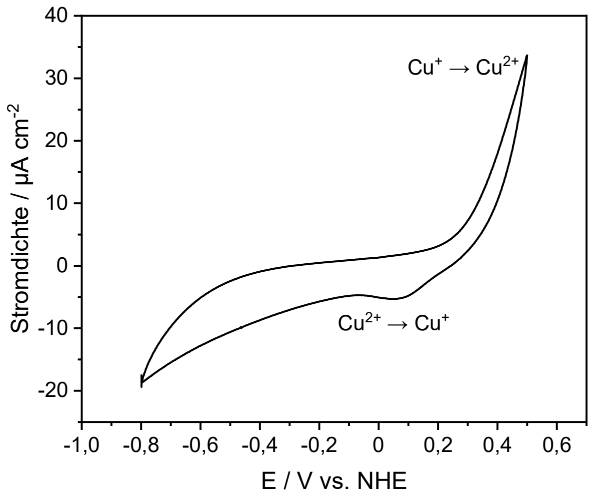


Exemplary chrono-amperometric experiment at 2.8 V vs. Ag/AgCl in 2M $KHCO_3$ electrolyte.

-> 1.9 mM H_2O_2 generated

Photoelectrochemical CO_2 reduction: Cyclic voltammetric potentials for Cu_2O

- Oxidation of Cu_2O to CuO at anodic potentials
- Appropriate potential range for photoelectrochemical CO2-reduction < 0 V vs. NHE (-0,2 V vs. Ag/AgCl)



- Working electrode: Cu_2O on FTO
- Counter electrode: Pt, Reference: Ag/AgCl
- Electrolyte: 0,5 M $NaHCO_3$ saturated with CO_2

Laser flash photolysis

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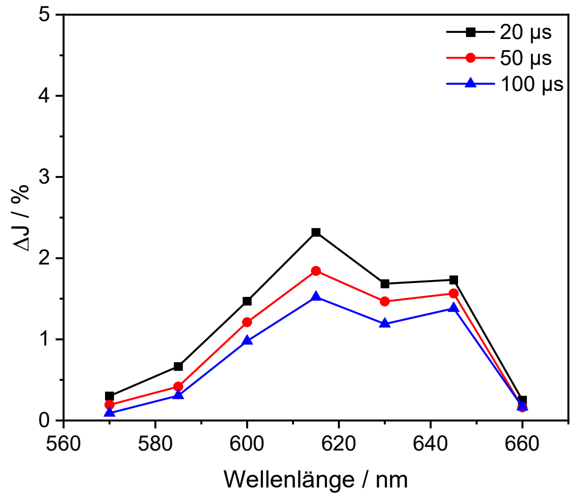
- Excitation of Cu_2O with 355 nm leads to photogenerated charge carriers
- Peak @ 615 nm possibly due to intermediate Cu^0 formation



- Cu_2O-Pulver in N_2 atmosphere
- Excitation: 3 mJ 355 nm

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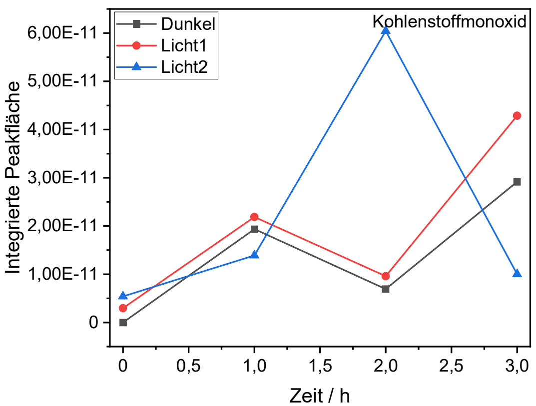
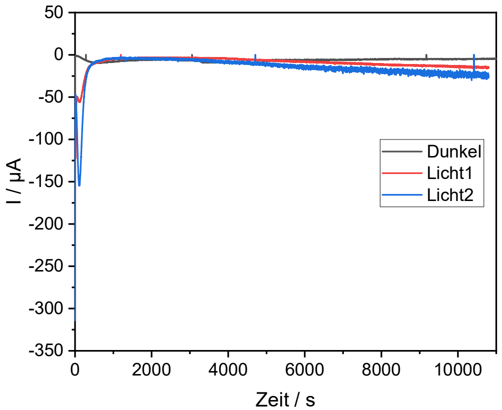
Photoelectrochemical CO_2 reduction products

- mass spectrometry of Cu_2O reduction products under simulated sunlight in photoelectrochemical reactor





Dark coulored electrode after measurement due to Cu^0

- Formation of CO (and formic acid) detected
- Further experiments ongoing with other applied potentials

- Working electrode: electrochemically dep. Cu_2O on FTO
- Counter electrode: Pt, Reference: Ag/AgCl
- Electrolyte: 0,5 M $NaHCO_3$ saturated with CO_2
- Potential: -0,5 V vs. Ag/AgCl (-0,3 V vs. NHE)

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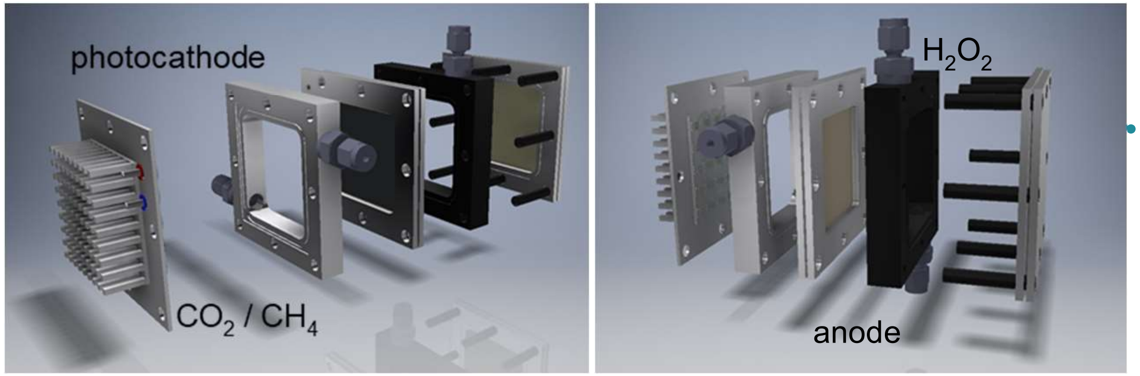
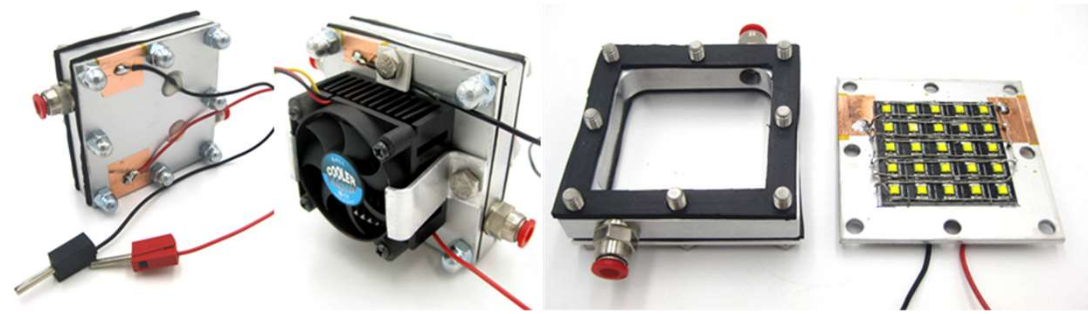
Construction of photoelectrochemical cell

Prototype reaction cell for CO_2SimO





- Analyzed light sources:
  - UV LED panel: 365nm; 3,7W
  - xenon short arc lamp, total 300W; <390nm; 6,6W
  - LED panel 6000k; 400–750nm, 25W

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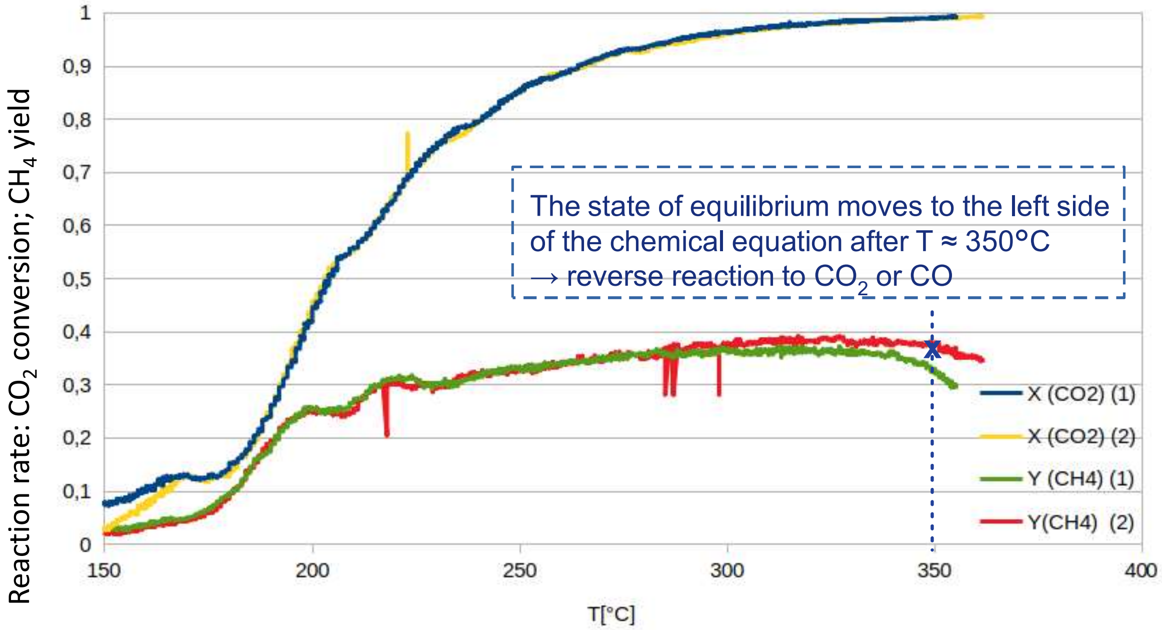
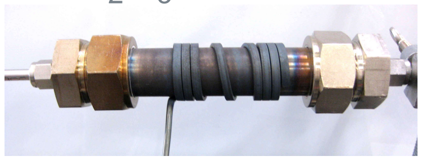
Development of methanisator

Post-cell catalysis with fixed bed reactor: CO_2 methanisation

$CO_2 + 4H_2 \longleftrightarrow CH_4 + 2H_2O$



Fixed bed reactor with Ni/Al_2O_3 catalyst:



- Highest CO_2 conversion: T > 300°C
- Highest CH4 yield: 300°C < T < 350°C
- Highest CH_4 selectivity T ≈ 180°C

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Sustainability Assessment: Goal & Scope

LCA & LCC: Goal definition, Functional unit

- **Environmental and economic performance** of hydrogen peroxide + methane in the future (**2030**, **2050, OPTIMUM**) with a solar-driven photoelectrochemical cell in **Germany / EU**, by oxidising water and reducing CO_2 to CO and CH_4

- Conventional production
  - H_2O_2 anthraquinone process
  - CH_4 from natural gas

- Support of micro-level decision-making, chosen method → **attributional LCA**

- Assessment of emerging technologies in future→ **ex-ante / prospective LCA / LCC** based on lab data, process simulations, **scalings** and **scenarios**

- **Functional unit and reference flow**
  I. y kg H_2O_2 + z kg CH_4
  II. 1 kg CO_2

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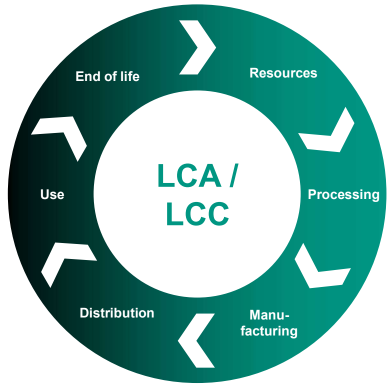
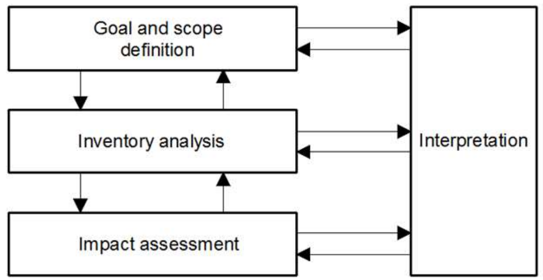


Norm LCA (DIN EN ISO 14040/44)



Sustainability Assessment: Start of LCA Model Development

Reference product system, 0.89 kg H_2O_2 and 0.11 kg CH_4 : LCIA

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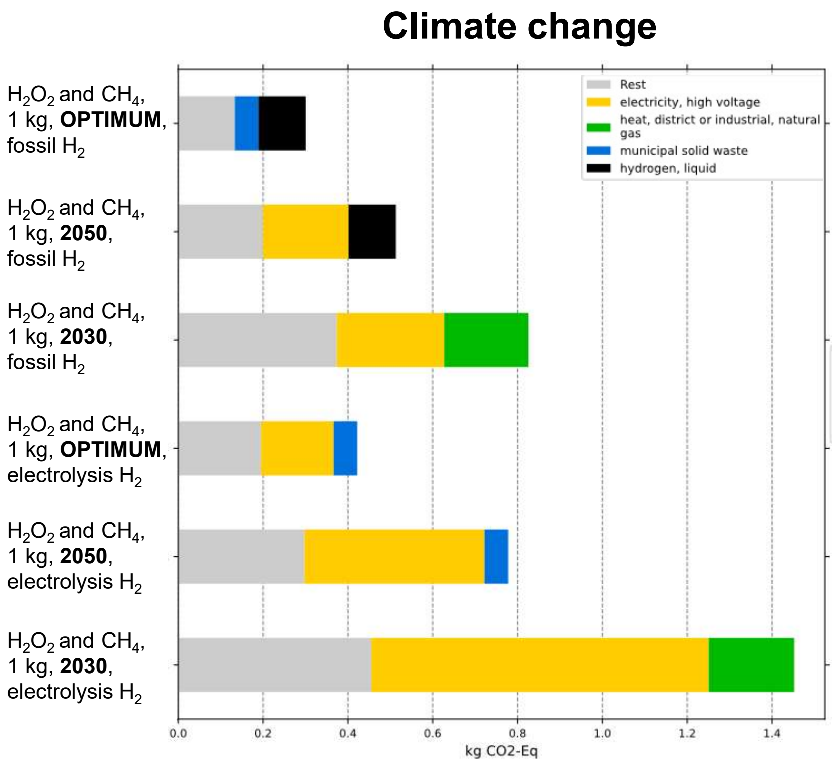

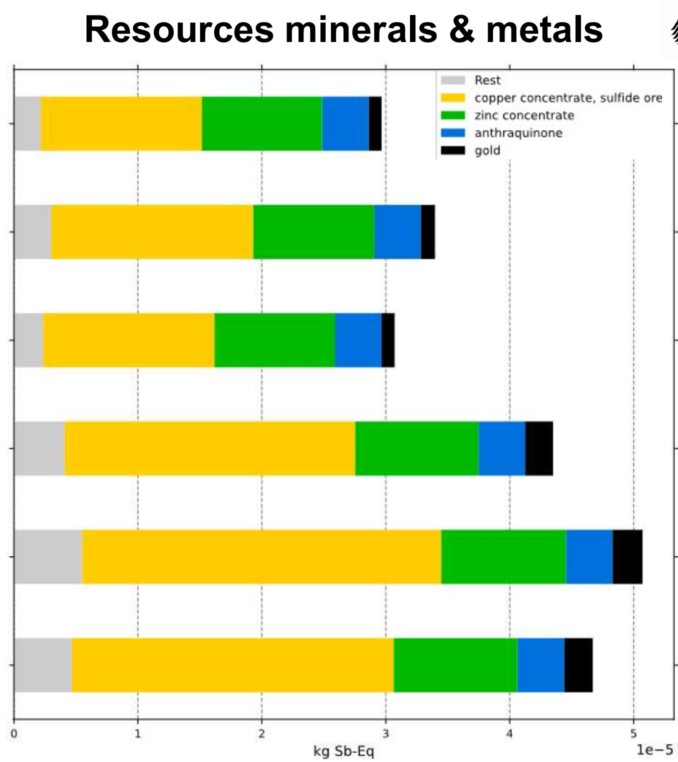

Summary

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- Several Cu Niobates / Tantalates with promising band positions were prepared, characterisation ongoing
- CO_2 reduction to CO could be proven with Cu_2O reference materials
- Stable H_2O_2 generation with BiVO4 electrodes
- Construction of 1st prototype for photoelectrochemical cell finished, several catalysts for methanisation reaction tested
- LCA: environmental sustainibility assessment of the reference product systems done

Next steps

- Improvement of BET surface areas and measurement of CO_2 reduction for Cu Niobates / Tantalates
- Characterisation of oxidation products at anode
- Preparation of gas diffusion electrode for photocathode
- Optimization of photoelectrochemical cell and methanisator
- LCA: Data exchange of energy in the whole background database for all activities for the prospective technology assessment