CO_2SimO – Photoelectrochemical CO_2 reduction with Simultaneous Oxidative raw material production

Final Conference CO2-WIN – Berlin, Sep 28/29 2023

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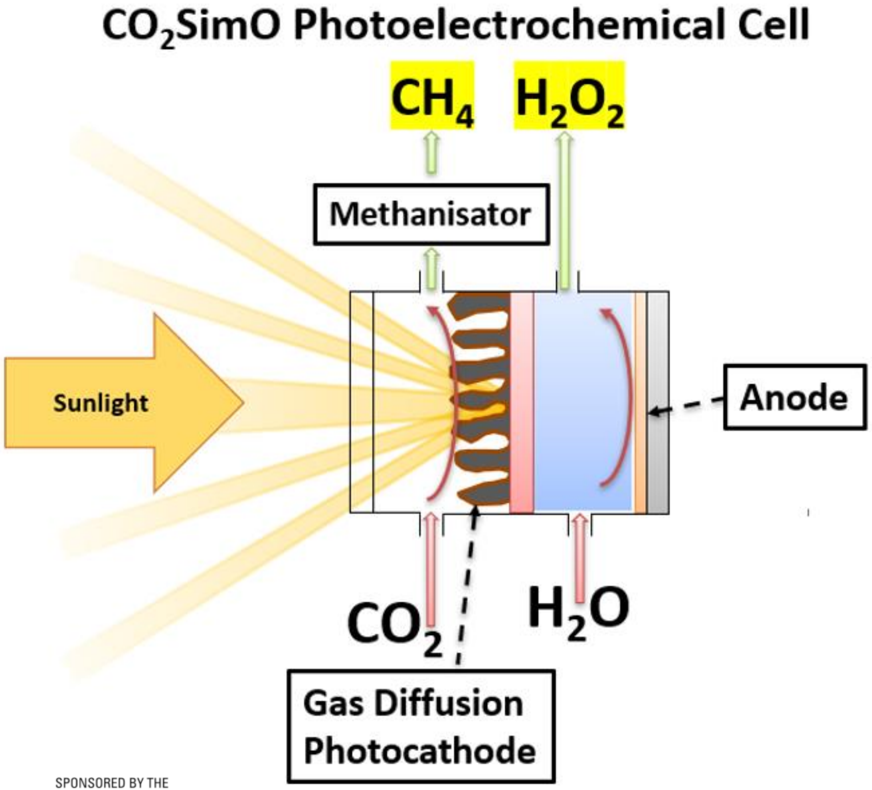
Project Targets:

- Development of a solar-powered photoelectrochemical reaction cell
- simultaneous oxidation of water to usable peroxides (e.g. H_2O_2) at the anode + reduction of CO_2 to CO and methane with the help of suitable photocatalysts at the cathode
- Development of a gas diffusion photoelectrode for the reaction at the photocatalyst/water/CO_2 gas three-phase boundary



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Development of photocathode materials: Synthesis of 11 different Cu niobates and tantalates and their comprehensive spectroscopic investigation carried out

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	$CuNbO_3$ (m)	$CuNb_3O_8$ (m)	$CuNb_{13}O_{33}$ (m)	$CuNb_2O_6$ (o)	$CuNb_2O_6$ (m)	$Cu_3Nb_2O_8$	($Cu_2Ta_4O_{11}$)	($Cu_3Ta_7O_{19}$)	$Cu_5Ta_{11}O_{30}$	$CuTa_2O_6$ (o)	$CuTa_2O_6$ (t)
Synthesis Method	SSR	Molten Salt	SSR	SSR (Sol-Gel)	Sol-Gel	Sol-Gel	Molten Salt +SSR	Molten Salt +SSR	Molten Salt	SSR (Sol-Gel)	Sol-Gel
Temp. / °C	900-950	750	900	1000	800	900/950	680-800	700-800	900-1100	1000	700
Time / h	24	1	10	20	10	10	10-24	10-24	10/24	10	1
Color	red	black	yellow	brown	yellow	brown	yellow	yellow	yellow	green	yellow
Band Gap / eV	1.9	1.1	2.3	1.9	2.4	1.8	~ 2.5	~ 2.5	2.5	2.4	2.6
BET / $m^2 g^{-1}$	0.27	0.7	0.7	0.2	2.5	0.23		1.3	0.09	1.2	42
Morphology	large particles	platelets	rods	sponge-like	agglo-merated	Large voids		sponge-like	large particles	sponge-like	sponge-like
Stability, H_2O							Unstable in air over longer period				
H_2O_2 30%											
2M HCl											
2M NaOH											
Photochemically											

Development of photocathode materials: Photocurrents detected on electrodes with $CuNb_{13}O_{33}$ (with NiO layer)

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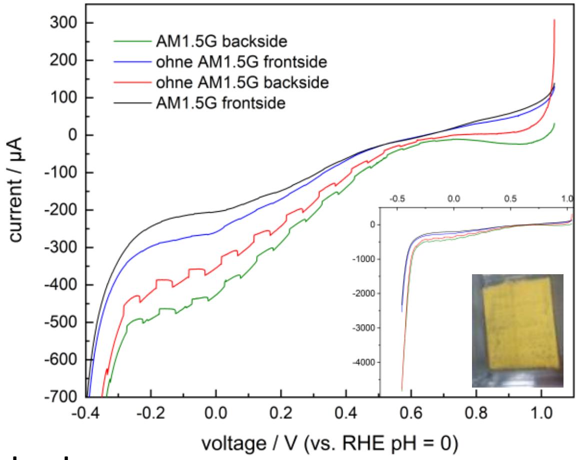
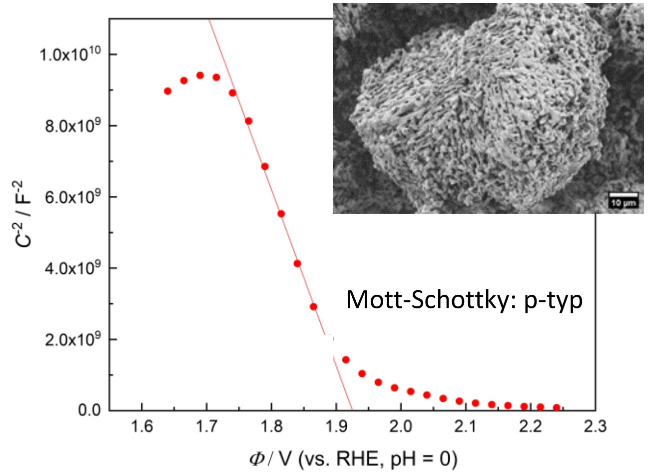
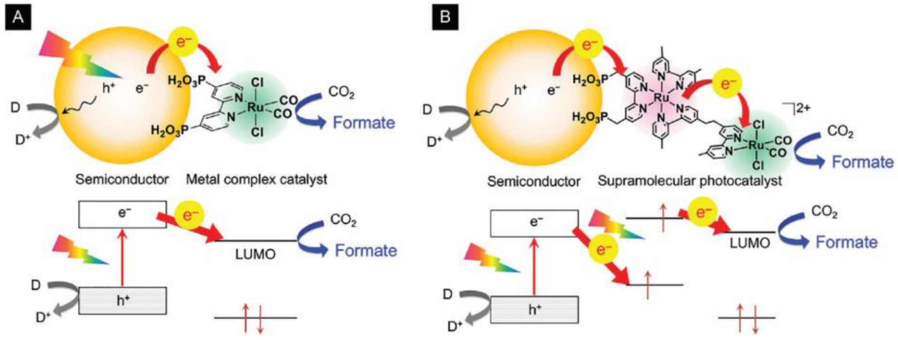




Outlook



Adv. Mater. **2019**, *31*, 1808205

- Collaboration between University Bayreuth and Prof. K. Maeda on $CuNb_{13}O_{33}$ planned
- Modification of p-type niobates with molecular catalysts for CO_2 reduction

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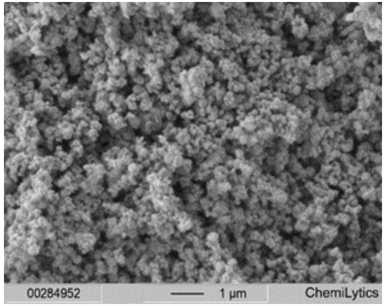
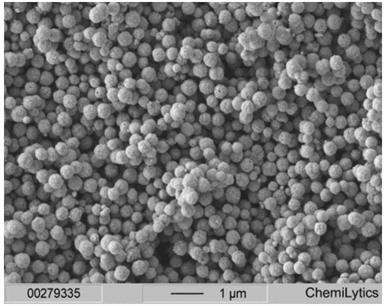
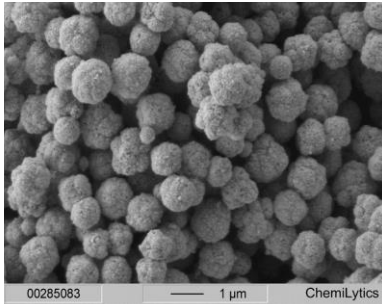
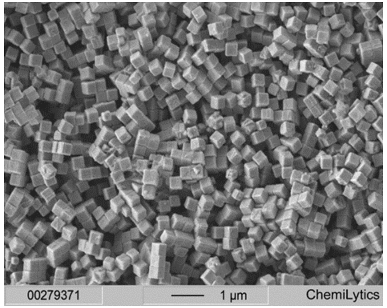
Optimization and upscaling of photocathode materials

- Varying the parameters of the Cu_2O reference material creation led to powders with different morphologies and BET surfaces between 5 and $16 m^2/g$



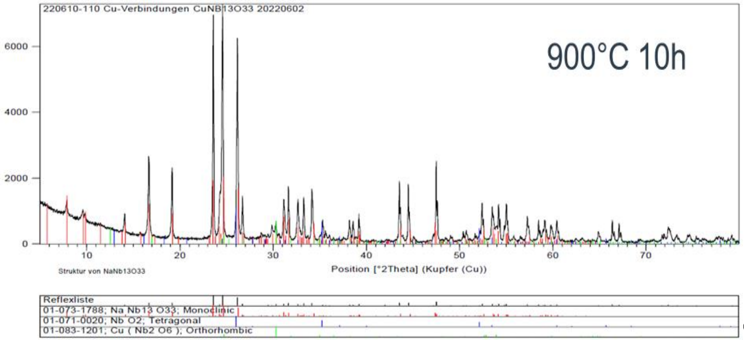






- **intended reference material Cu_2O is not stable, contrary to literature information**

- Scalable processes to produce multiple Cu niobates optimized
- Attempts to increase the BET surface area of $CuNb_{13}O_{33}$ resulted in reduced phase purity



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Peroxide synthesis in 2M $KHCO_3$ electrolytes

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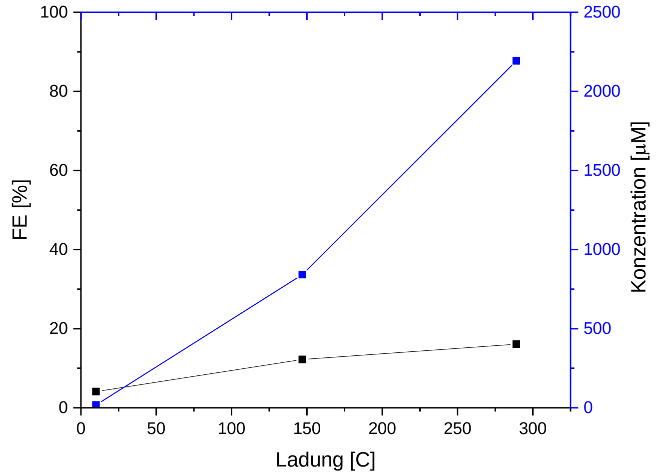
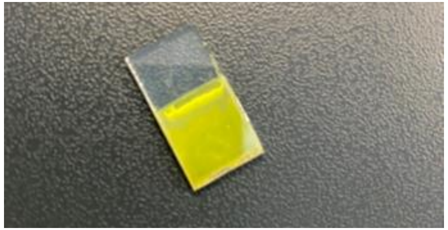
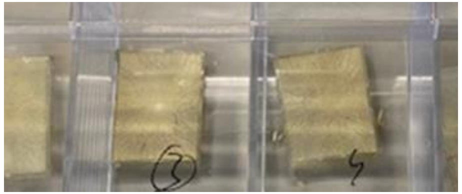
- At different potentials (here 2.9 V vs. Ag/AgCl), current efficiencies (FE) between 10-20% are achieved (Electrolyte: 2M $KHCO_3$ (pH 8.3))
- $BiVO_4$ electrodes as anode and carbon gas diffusion electrode (GDE) as cathode Fabrication of the $BiVO_4$ electrodes via organometallic decomposition (MOD) on FTO
- $BiVO_4$ is doped with gadolinium and molybdenum to achieve higher oxidation stability and increased conductivity
- Experiments show lower efficiencies for anodic H_2O_2 production, but unusually strong oxidation power
- Generation of additional peroxo species such as percarbonate







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Peroxide synthesis in advanced electrolytes

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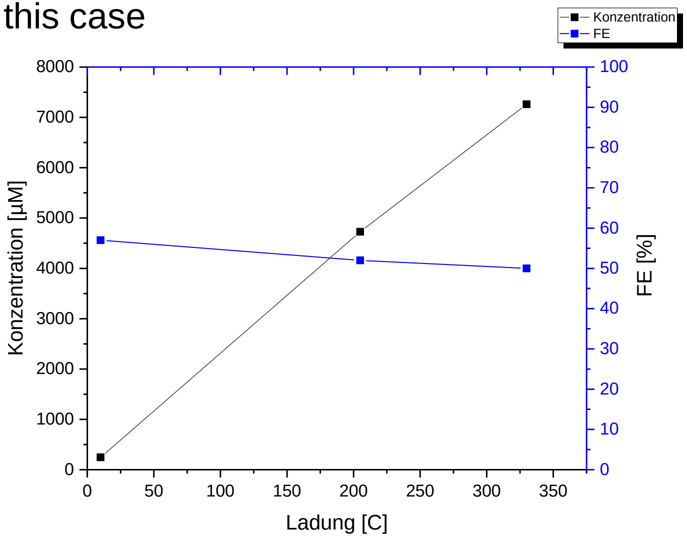
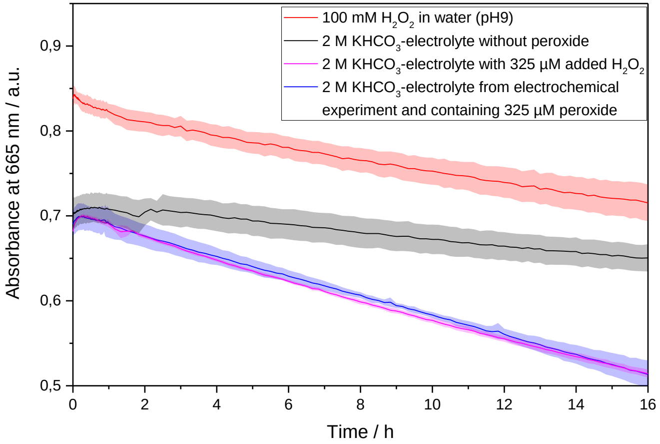
- The electrochemically generated oxidative species in 2M KHCO3 is highly reactive and can decolorize methylene blue and oxidize other small molecules even in low concentrations
- With a further developed electrolyte (0.5M KHCO3 + 3.5M K2CO3) efficiencies between 40-50% and peroxide concentrations >10 mM can be achieved
- here too, an increased oxidation power can be observed, so other peroxide compounds are probably also present in this case





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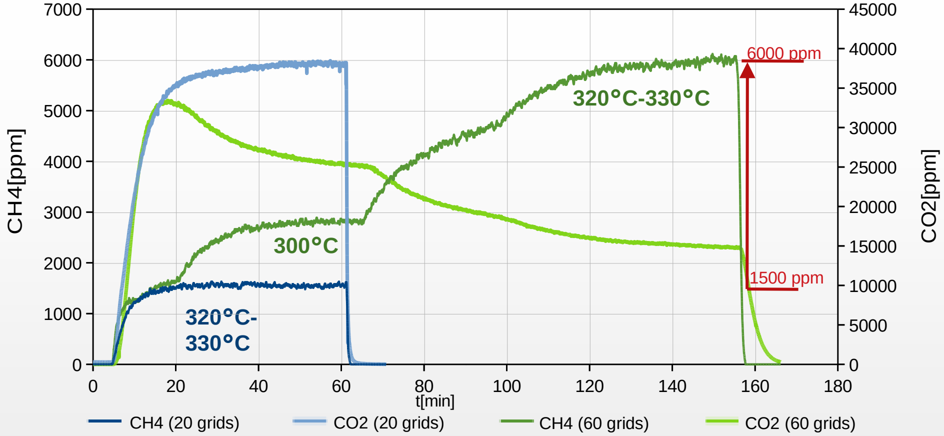
- **Development of high efficiency $BiVO_4$ anodes; Formation of additional peroxo species with high oxidizing power**

Development of methanizer

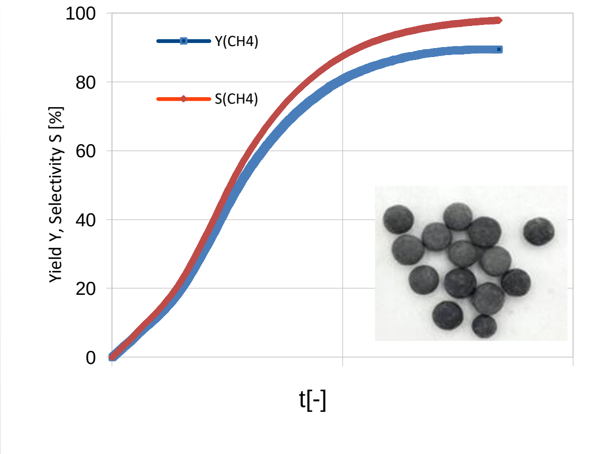
Thermal catalyst for product stream refining

- Inlet: 5 vol.-% CO_2 in H_2 $v = 0{,}013\ m\ s^{-1}$; $f_{ges.in} = 250$ sccm

  Quantity of catalyst grids installed : 20 piece vs. 60 piece



Ni/Al_2O_3 - Pellets; $CO_2:H_2=20:80$; T = 320°C - 330°C; GHSV = 390 h^-
$v_{in} = 0{,}013\ m\ s^{-1}$; $f_{ges.in} = 250$ sccm



Higher spec. surface of the pellets favors the catalytic reaction of CO_2 to CH_4

Ni/Al_2O_3cat grids

CO_2, CH_4IR-sensors

CH_4-H_2 dualsensor

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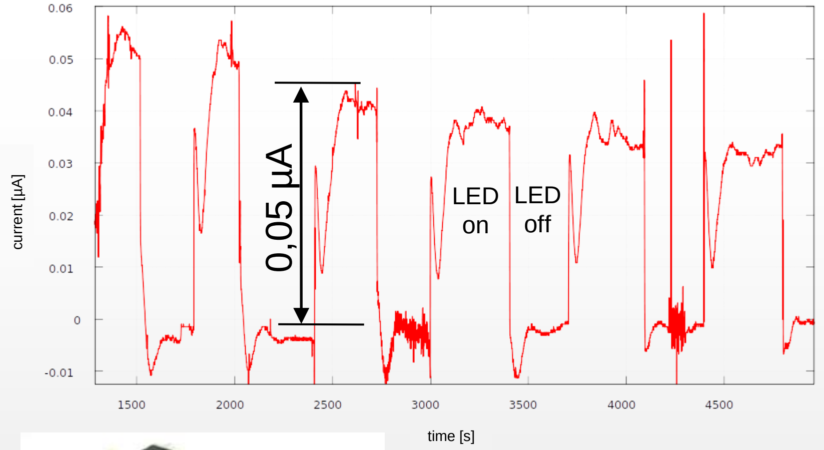
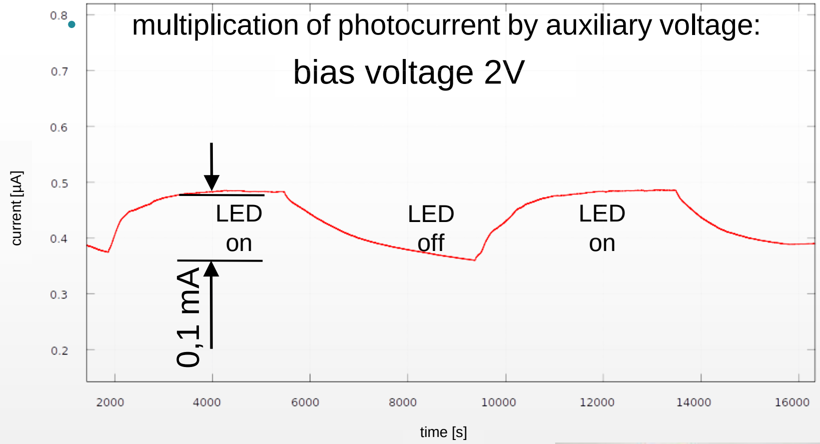
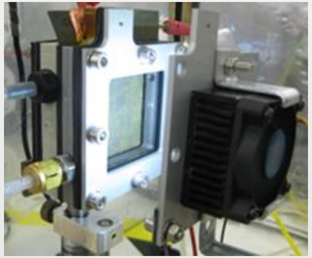
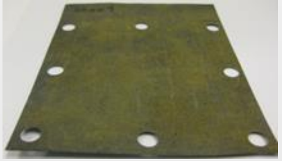
Development and construction of the reaction cell

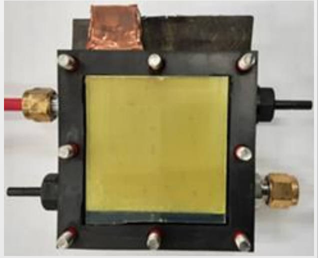
illumination test results show clear photocurrents under visible light











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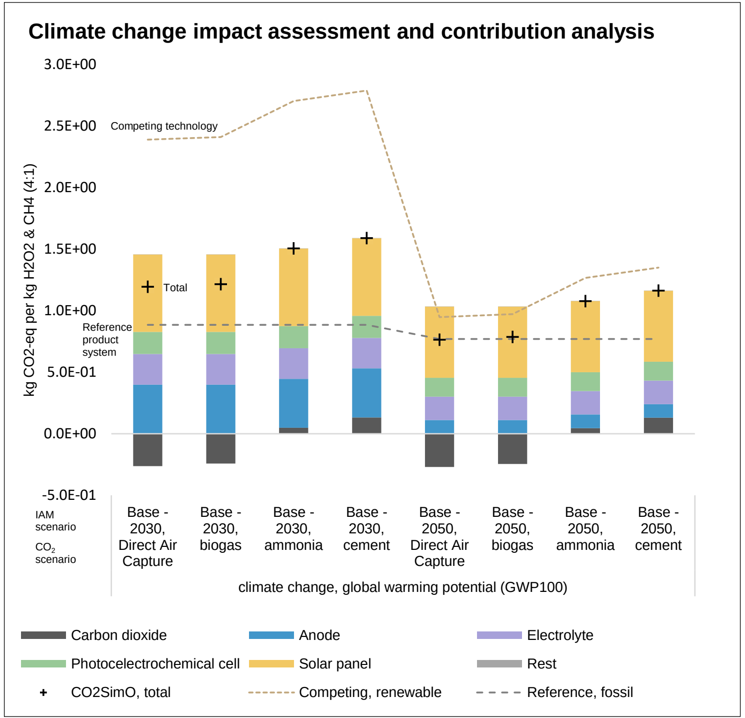
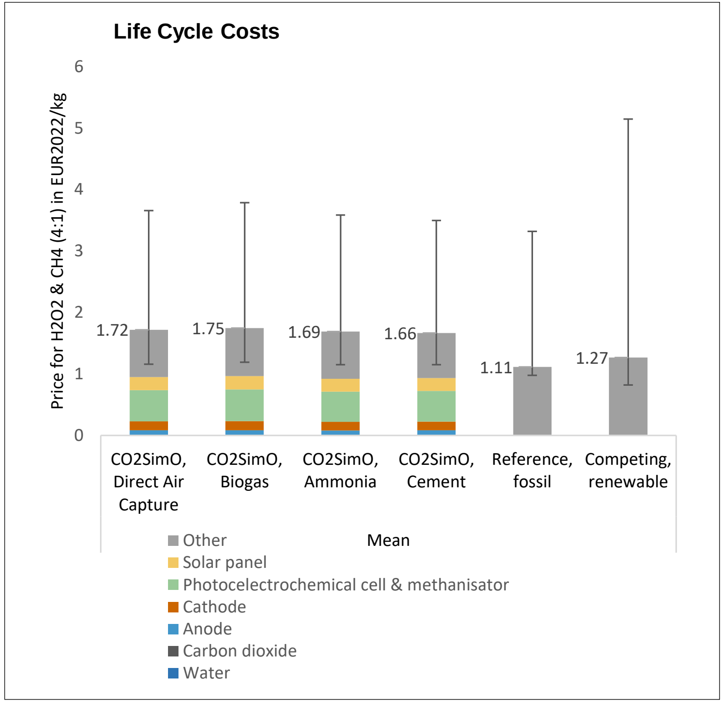
Environmental Life Cycle Assessment
Partial results of the Life Cycle Impact Assessment

Economic sustainability assessment
Life Cycle Costs and eco-efficiency

Karlsruhe Institute of Technology





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- **CO_2SimO concept could reach a similar environmental performance to the fossil reference product system in the impact category climate change; for other categories CO_2SimO overall efficiency has to be improved**

Summary

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Which innovations have been achieved or can be created in the future?

→ New syntheses and properties of a variety of copper tantalates and niobates were researched

→ Future work on combinations with molecular catalysts for CO2 reduction is being planned

→ innovative concept of a gas diffusion photoelectrode was experimentally demonstrated for the first time

→ combination of photoelectrochemical CO2 reduction with value-adding peroxide production at the anode was also shown for the first time, which can enable economically viable processes in the future

→ anode process has also been further developed to directly produce percarbonate as technical peroxide, which has a much higher oxidizing power than hydrogen peroxide. The photoelectrochemical reaction cell developed in the project showed clear activity under sunlight

→ methanizer was developed to upgrade the product stream.

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Summary

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What is needed for your technology to generate a successful business case?

→ functionality of the photoelectrochemical COSimo cell was demonstrated on a demonstrator under sunlight

→ increase in efficiency is necessary for a business case

→ in principle an economically viable process is possible due to the high added value of the anode reaction

Which research areas have particularly benefited from your technologies?

→ For the first time, the concept of a gas diffusion photocathode was demonstrated experimentally

→ This fundamental work is very valuable for the further development of photoelectrochemistry

→ results achieved in the project have improved the fundamental understanding of electrochemical anodic peroxide production. The results clearly showed that when appropriate electrolytes are used, technical peroxides such as percarbonate are formed directly and are also stable.

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