Negative Emissions based on Photoelectrochemical Methods: Surface Investigation of Potential Catalysts

Daniel Lörch[1], Holger Euchner[1], Aya Mohamed[2], Peter Bogdanoff[2], Matthias M. May[1]

[1]: Institute of Physical and Theoretical Chemistry, Universität Tübingen, 72076 Tübingen, Germany
[2]: Insitute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie, 14109 Berlin, Germany

Biomass production:

~10 Mio. km² [2]

Photoelectrochemical CO_2 reduction:

Up to η = 0.19
= 135000 km² [3]

IPCC:

Active removal of > 10 Gt of CO_2 per year by 2050 [1]

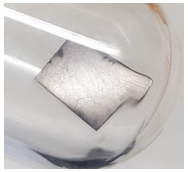
Land-use conflicts:

Need for highly efficient negative emissions technologies

Development of highly efficient photoelectrochemical system for CO_2 conversion to long-term storable products

Investigation of potential Electrocatalysts

Cerium



GaInSn

Cerium Nanoparticles on GaInSn – matrix:

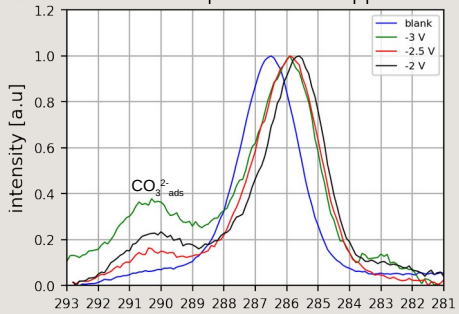
Proclaimed catalytic activity towards graphite [4]

Investigation of both individually as starting point

Cerium:

- Indication of CeO_2 based pathway towards carbonic species via surface carbonates
- Formation of catalyst poisoning species CeF_3

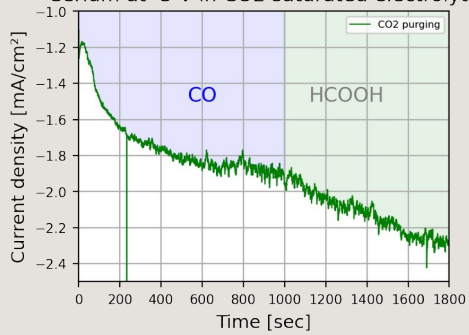
C1s on Cerium in dependence of applied Potential



GaInSn:

- Catalytic activity changes from Carbon Monoxide towards Formic Acid after applying potential for prolonged periods

Cerium at -3 V in CO2 saturated electrolyte



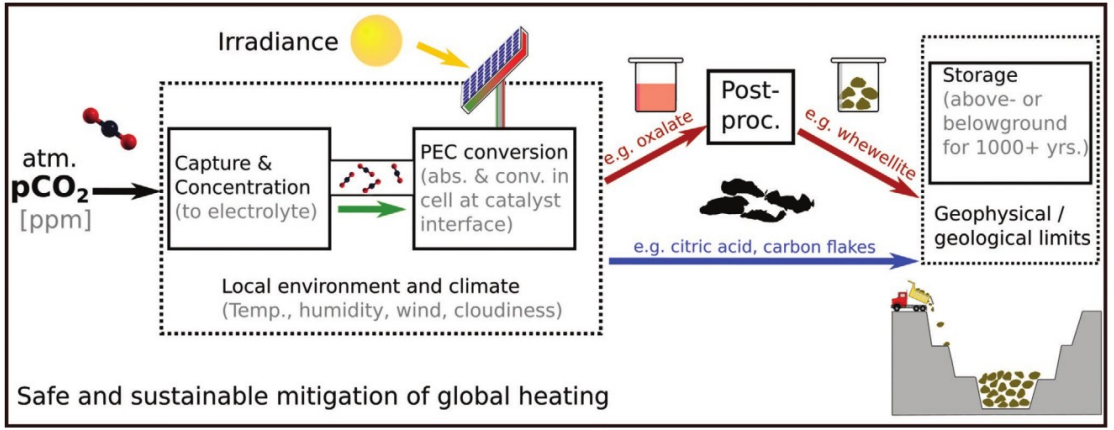
Spectroscopic Operando Analysis of Catalysts

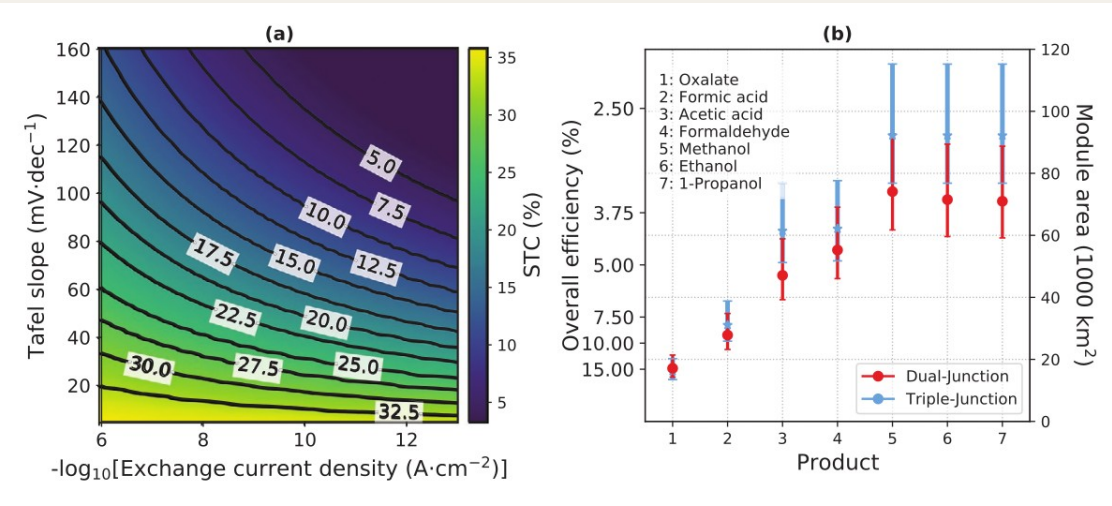
References:
[1] Anderson, K., Peters, G., The trouble with negative emissions.Science354, 182-183(2016).DOI:10.1126/science.aah4567
[2] Smith, P., Davis, S., Creutzig, F. et al. Biophysical and economic limits to negative CO2 emissions. Nature Clim Change 6, 42–50 (2016)
[3] May, M. M. and Rehfeld, K.: ESD Ideas: Photoelectrochemical carbon removal as negative emission technology, Earth Syst. Dynam., 10, 1–7, 2019
[4] Esrafilzadeh, D., Zavabeti, A., Jalili, R. et al. Room temperature CO2 reduction to solid carbon species on liquid metals featuring atomically thin ceria interfaces. Nat Commun 10, 865 (2019).

Motivation

- Remove CO_2 permanently from the carbon cycle at large scale
- Make use of potentially high efficiencies of catalytic Carbon Dioxide reduction
- Combine Electrocatalysis with Photovoltaics for potential synergistic effects

Development of a photoelectrochemical process for CO_2 reduction at high „solar-to-carbon“ efficiencies





Graphs from: M. M. May, K. Rehfeld, Adv. Energy Mater. 2022, 12, 2103801
M. M. May, K., Rehfeld, Earth Syst. Dynam. 2019, 10, 1–7

General Experimental procedure

Experimental Design

Pretreatment for Cerium:

Silicon carbide sandpaper (1000 grid) honing under nitrogen stream (~10 min)

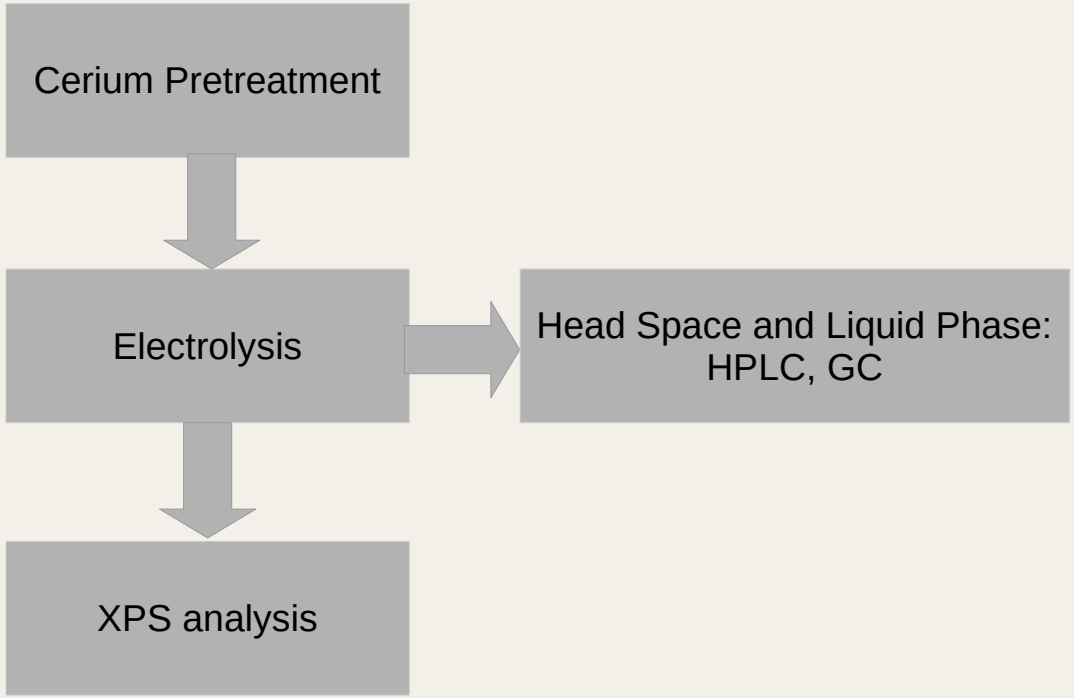
Electrolysis:

WE: Cerium – Foil or GaInSn on Cu
CE: Pt
RE: Ag/AgNO3
Electrolyte: DMF | 2 M H_2O | 0.1M $TBAPF_6$ | CO_2

1. Hold at Open Circuit Potential (3 min)
2. Chronoamperometry (30 min)

XPS analysis for Cerium:

Survey + high resolution scans of C1s, O1s and Ce3d



Investigation: Cerium

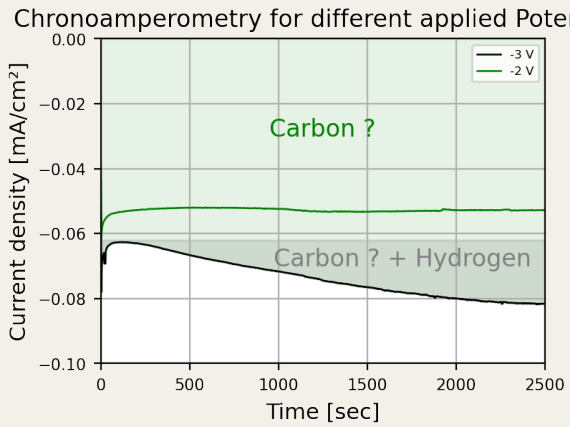
Electrolysis at -3 V vs. $Ag/AgNO_3$:

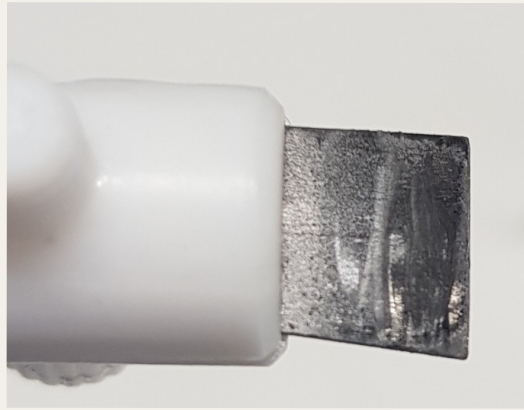
Gaseous product:
- predominantly H_2 formation (GC)

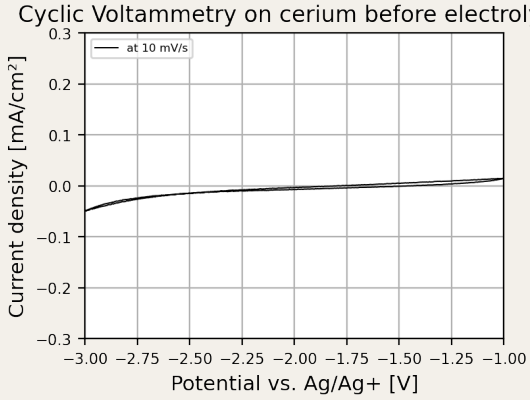
Liquid Product:
- None detectable (HPLC / DAD)

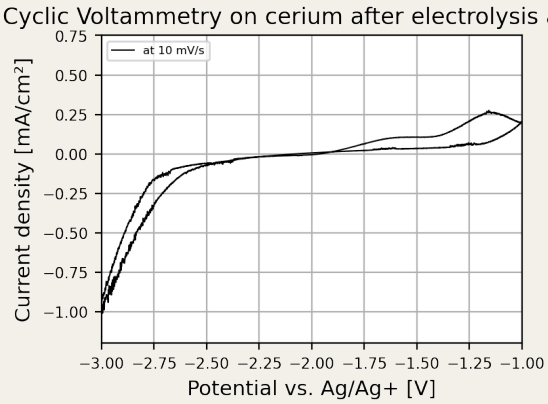
Solid Product:
- blackish surface-bound compound
- oxidated at -1.25 V vs. $Ag/AgNO_3$

What is formed and can we deduce the reaction pathway?



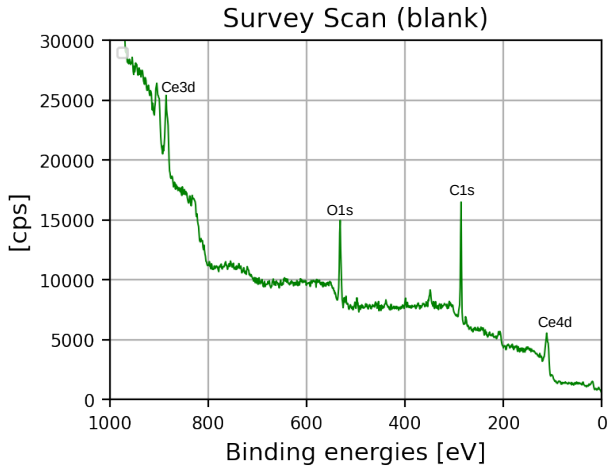






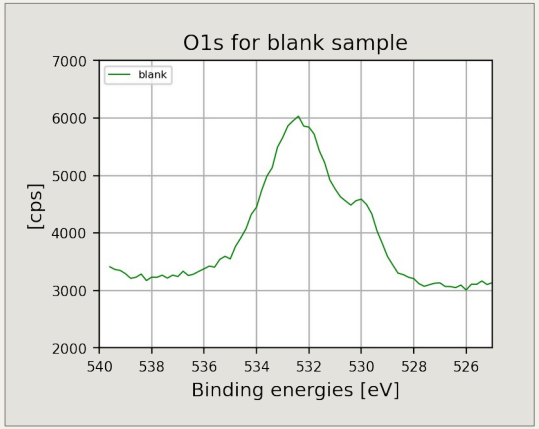
Investigation: Cerium

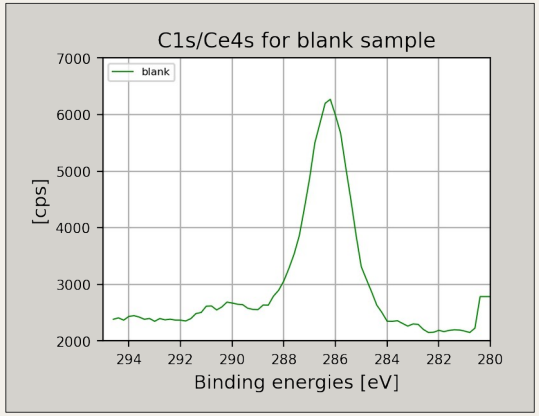
Characterization of Cerium before electrochemical experiments by XPS analysis

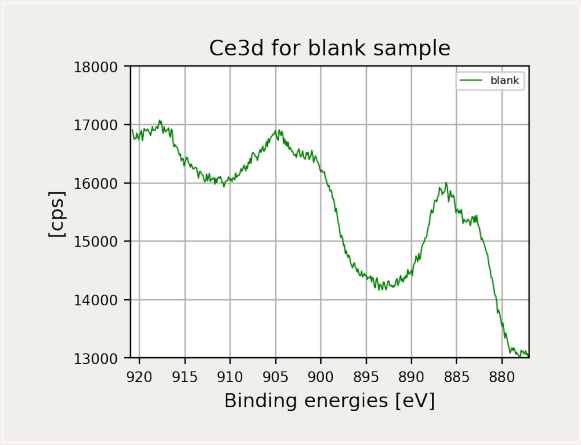


O1s	(Ce(III))	(Ce(IV))
Area	9327	2096
Ratio	Ce(III) / (Ce(IV)+Ce(III)) = 0.817	

"Blank cerium" → ~82 % Ce_2O_3 and 18 % CeO_2







BE [eV]	O1s	Ce3d 5/2	Ce3d 3/2
Ce(III)	532.5	885.8	907.1
Ce (IV)	530	881.9	916.7

Binding energy reference values:
NIST X-ray Photoelectron Spectroscopy Database, last access: 20th April 2023

Investigation: Cerium

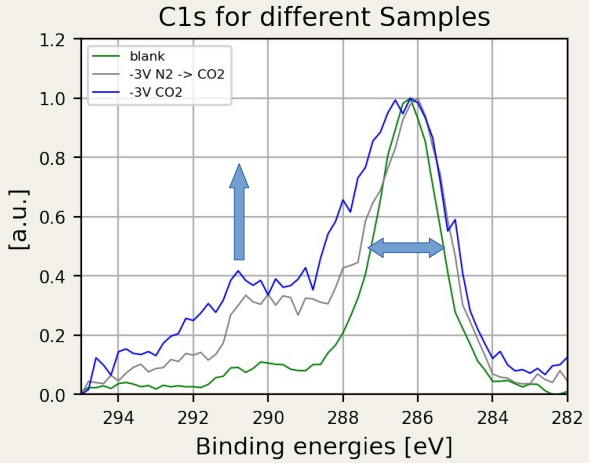
Electrolysis in the presence of different dissolved gases and subsequent investigation of surface changes by XPS Scans

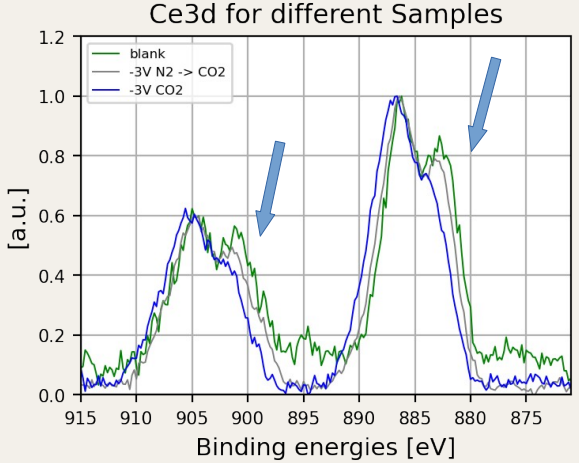
	Experimental Series
1.	Just honing (blank)
2.	Electrolysis at -3V (N2 → CO2)
3.	Electrolysis at -3V (CO2)

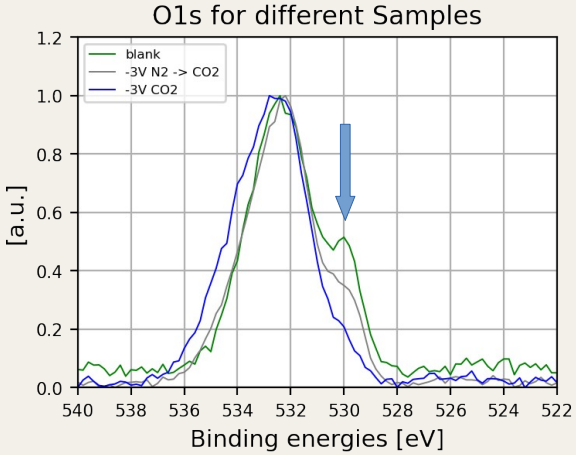
Observations:

In the presence of CO_2:

- C1s at 291 eV increases while the width of 286 eV increases asymmetrically
- O1s at 530 eV *[Ce(IV)]* decreases
- Ce3d – satellites decrease in intensity
- Ce3d slightly shifts to higher energies







Interpretation:

The changes of Ce3d might be explained by an increase of the oxidation state of cerium or a change in the chemical environment by e.g. the formation of a carbon species.

Observations for C1s and especially O1s support latter interpretation

Investigation: Cerium

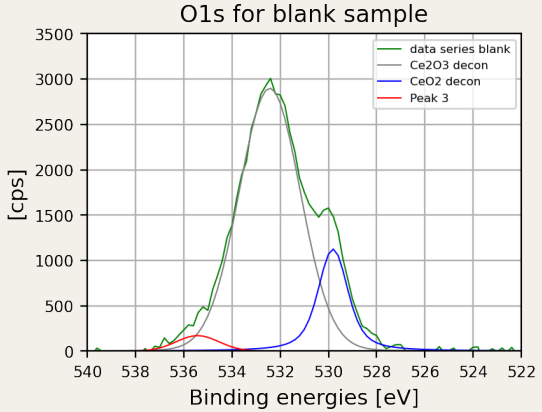
Deconvolution of O1s - Peaks

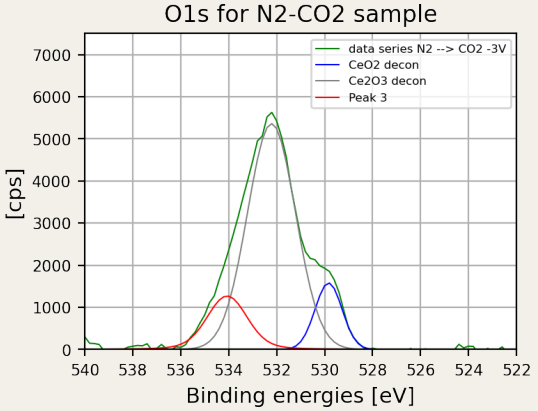
- Relative amount of Ce(IV) compared to Ce(III) decreases

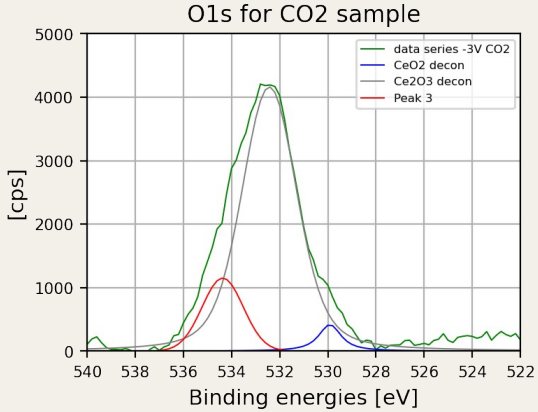
  → supports the interpretation of a species forming at the expense of Ce(IV).

- Additional O1s Peak around 535 eV shifts to lower binding energies after electrolysis.

  → O1s of adsorbed CO_2 on Ce(III): 535.1 eV
  → O1s of adsorbed CO_3^{2-} on Ce(III): 533 eV







O1s	532.5 eV (Ce(III))	530 eV (Ce(IV))	Ratio
Area “blank”	9327	2096	0.82
Area ¨N2-CO2”	13457	2223	0.85
Area “CO2”	13210	673	0.95

O1s references: Chengwu Yang et al., ChemPhysChem 2017, 18, 1874 – 1880

Investigation: Cerium

Electrolysis at different Potentials and subsequent investigation of surface changes by XPS Scans

Observations:

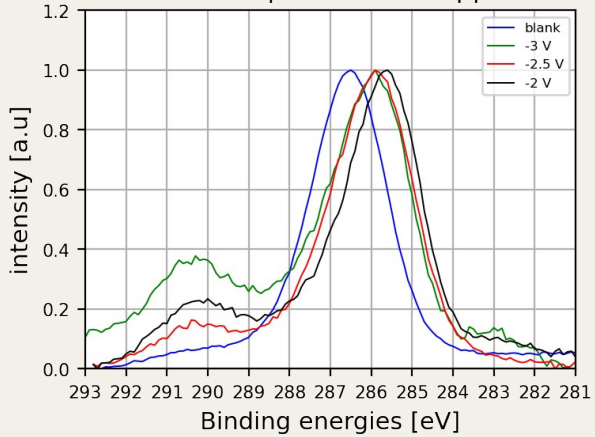
- C1s at 290.5 eV (CO_3^{2-}) increases in dependence of applied potential and the 286 eV Peak is shifted to lower binding energies

Interpretation:

1. Partial reduction of surface oxides due to applied potential leads to decrease in charge displacement of C1s - Peak (blank vs. electrolysis samples)

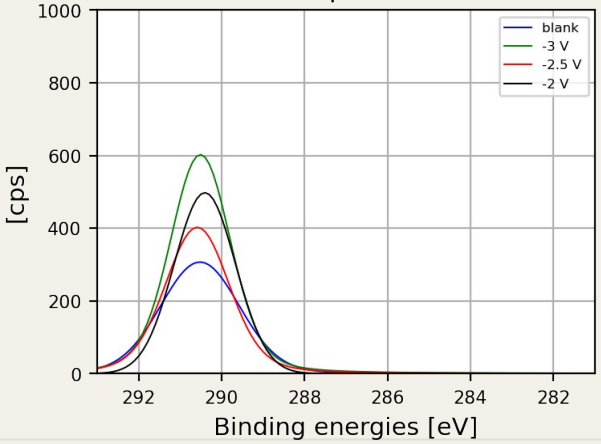
2. Competing processes:
   - H_2 formation at higher potentials (-3 V)
   - Reducton of CO_3^{2-} at lower potentials (-2V)
     → Shift to lower binding energies in dependence of applied Potential

C1s on Cerium in dependence of applied Potential

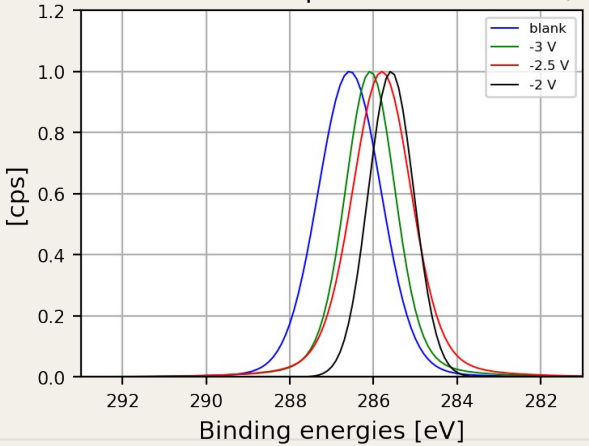


	Experimental Series
1.	Electrolysis at -3 V
2.	Electrolysis at -2.5 V
3.	Electrolysis at -2 V

C1s for different Samples deconvoluted (4th)



C1s for different Samples deconvoluted (Main)



C1s reference: Chengwu Yang et al., ChemPhysChem 2017, 18, 1874 – 1880

Investigation: Cerium

Formation of potentially catalysis-inhibiting surface species **Cerium Fluoride**

Experimental:

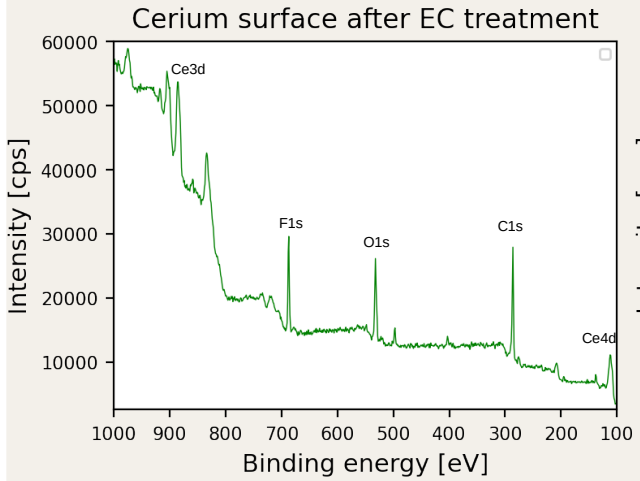
- Conducting Electrolysis in the absence of H_2O

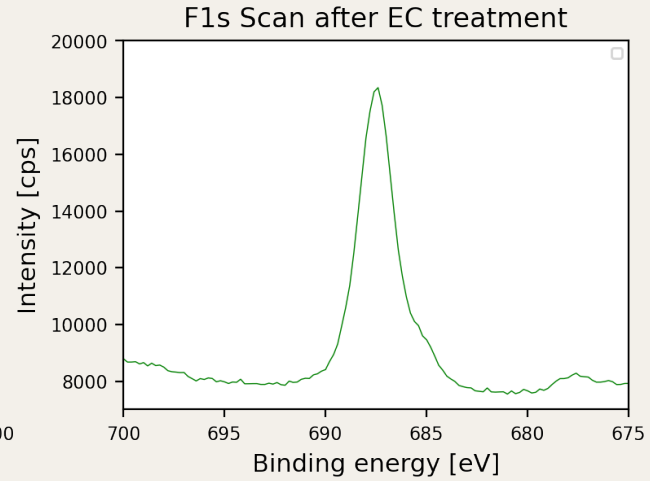
Additionally:

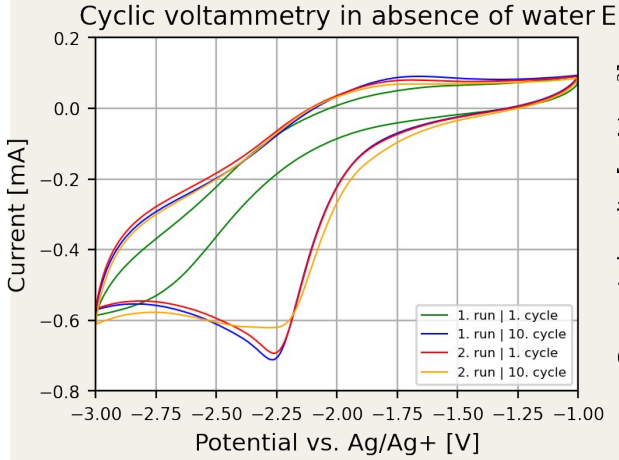
Conducting Cyclic Voltammetry in absence of H2O

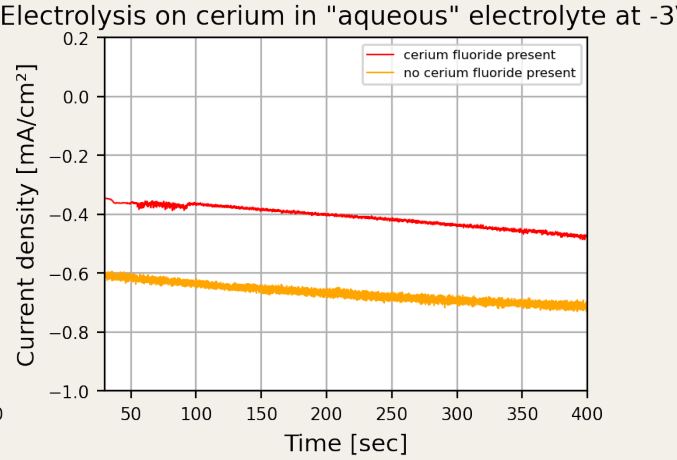
Observations:

- F1s peak at 685 eV which can be assigned to CeF_3
- F1s Peak at 687.3 eV, which might be assigned to a precursor (degradation of PF_{6-} anion)
- Lower current density for CeF_3 surface









F1s references: Davide Barreca et al., Surface Science Spectra 13, 87 (2006)

Investigation: GaInSn

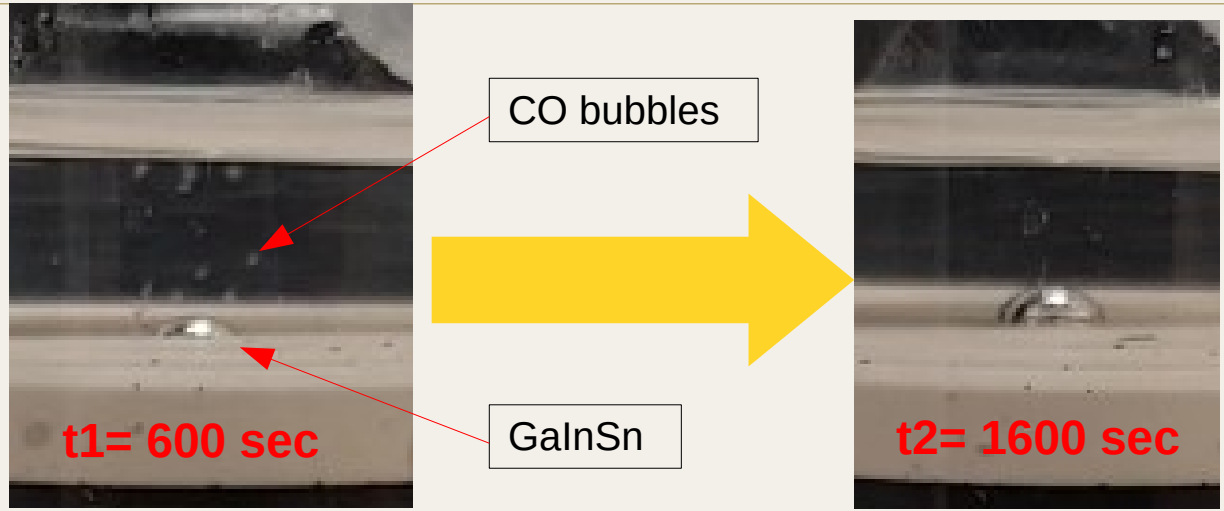
Change in Product Formation with GaInSn as Working Electrode

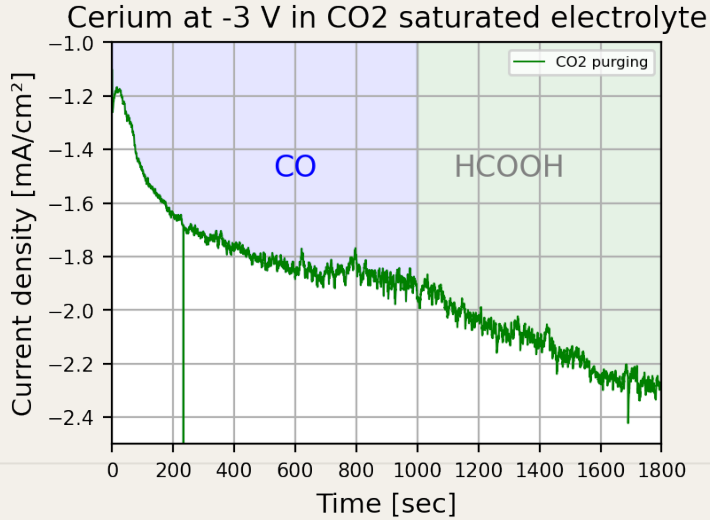
Observations:

- After ~1000 sec of Electrolysis at -3 V a gradual decrease in bubbles (CO) forming on the GaInSn surface can be observed
- At the same time the current density does not decrease but even increases

Interpretation:

- Surface restructuring induces a change in catalytic activity, preferring a different reaction pathway towards dissolved product (Formic Acid)





Spectroscopic Operando Investigation

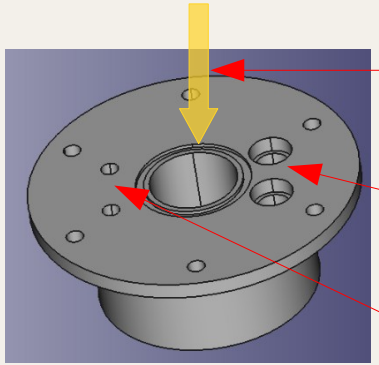
Operando Raman and RAS measurements to verify reaction pathway

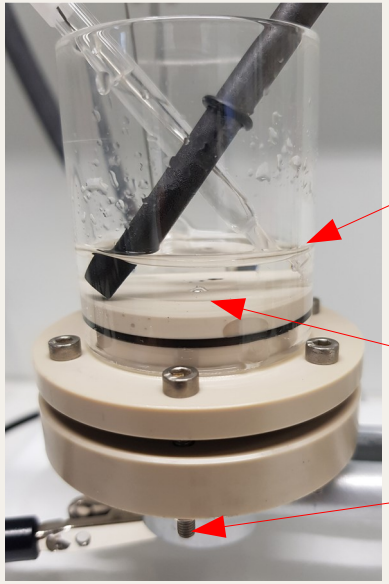
Motivation:

The shift of adsorbed CO_2 to CO_3^{2-} to reduced carbon species as well as the reason for the product shift with GaInSn, might be clarified by monitoring the catalytic reaction mechanism under operating conditions (operando Raman, RAS)

Currently:

Design of Cell, capable to conduct Electrochemistry while the catalyst surface is spectroscopically investigated





Light Path

Reference and Counter Electrode Mounts

2x Gas In- and Outlet

Electrolyte Volume

Working Electrode (Catalyst)

Back Contacting