

Anodic peroxide production with different metal oxides in carbonate-containing electrolytes

Tobias Schanz, Jonathan Z. Bloh*

DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany

* Corresponding author, jonathan.bloh@dechema.de

Supporting Information

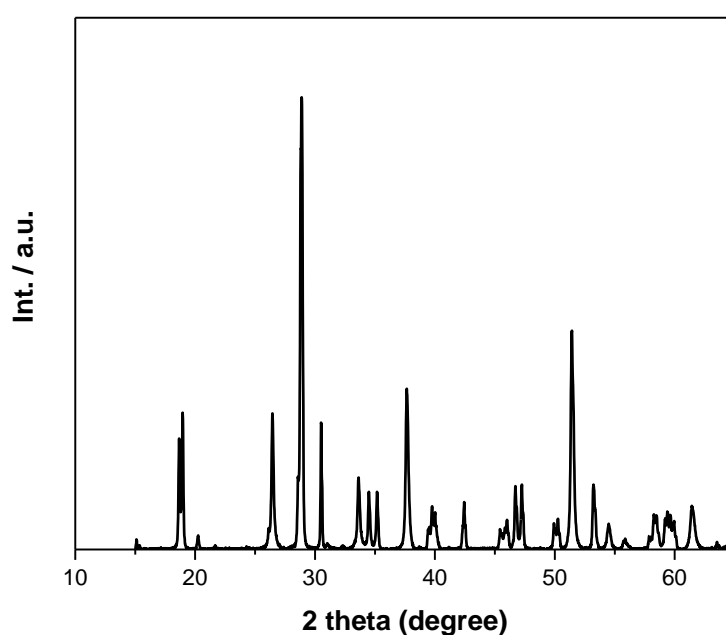


Figure S1: XRD spectra BiVO₄ working electrode with Mo and Gd doping. The data show a more than 70% monoclinic clinobisvanite crystal structure. Further peaks can be seen due to the doping with molybdenum and gadolinium and the resulting crystal structure. The radiation source was a Mg-K α 0.1591 nm.

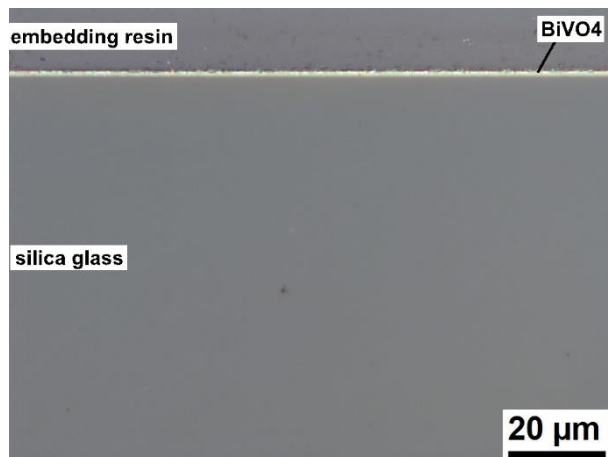
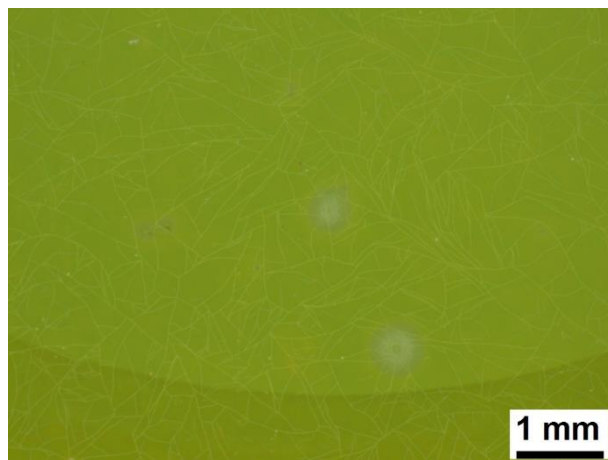
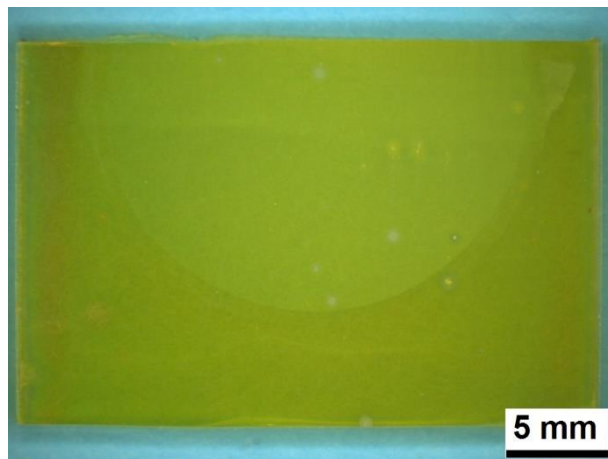


Figure S2: Images and cross-section of a BiVO₄ electrode with a drawing speed of 700 mm min⁻¹. The cross-section shows that the coating is very even and approx. 1 μm thick.

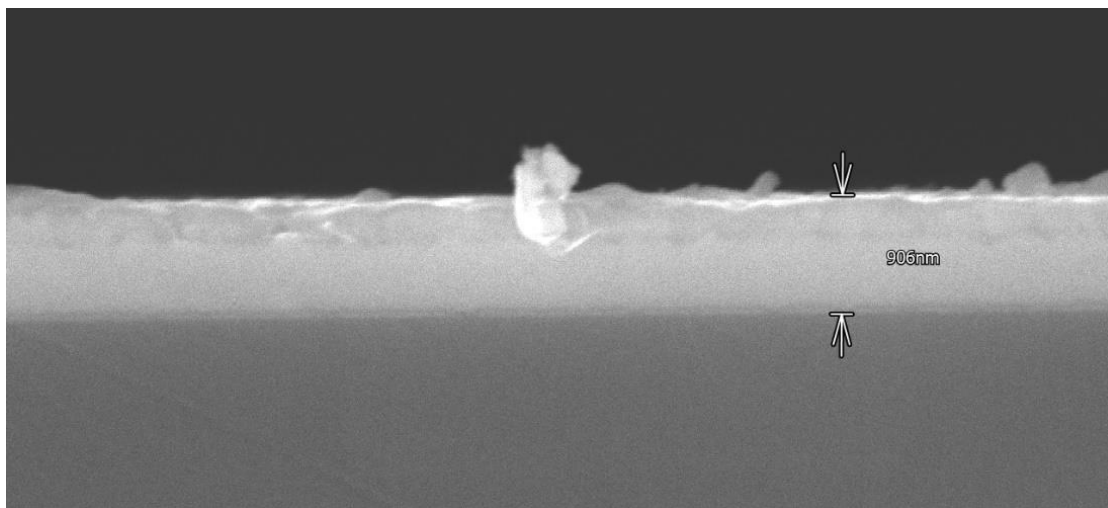
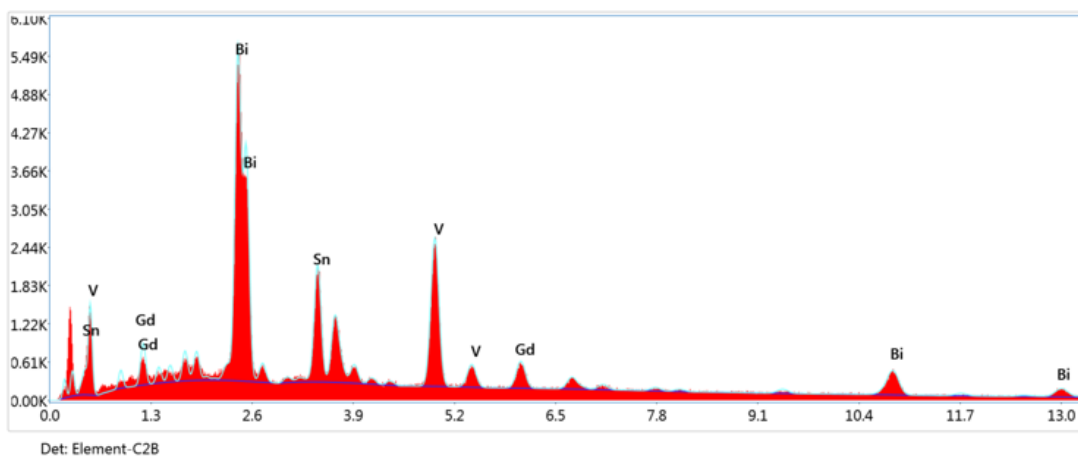


Figure S3: The cross-section of a BiVO₄ electrode in the SEM. The layer thickness is 906 nm, which corresponds well with the cross-section of the metallography.



Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	R	A	F
O K	10.16	43.13	121.62	12.61	0.7158	0.0688	1.0000
SiK	1.47	3.56	81.21	12.05	0.7521	0.3634	1.0124
V K	17.77	23.70	609.25	5.00	0.8066	0.7403	1.0429
MoL	1.28	0.91	39.59	21.22	0.7659	0.5541	1.0086
SnL	20.86	11.94	413.74	6.90	0.7885	0.6252	1.0099
GdL	9.44	4.08	120.46	12.94	0.8341	0.8285	1.0204
BiM	39.03	12.69	989.59	6.19	0.7678	0.5831	1.0163

kV:20

Mag: 1054

Takeoff: 30

Live Time(s): 50

Amp Time(μs): 3.84 Resolution:(eV)

Figure S4: EDX spectrum of an BiVO₄ electrode doped with molybdenum and gadolinium.

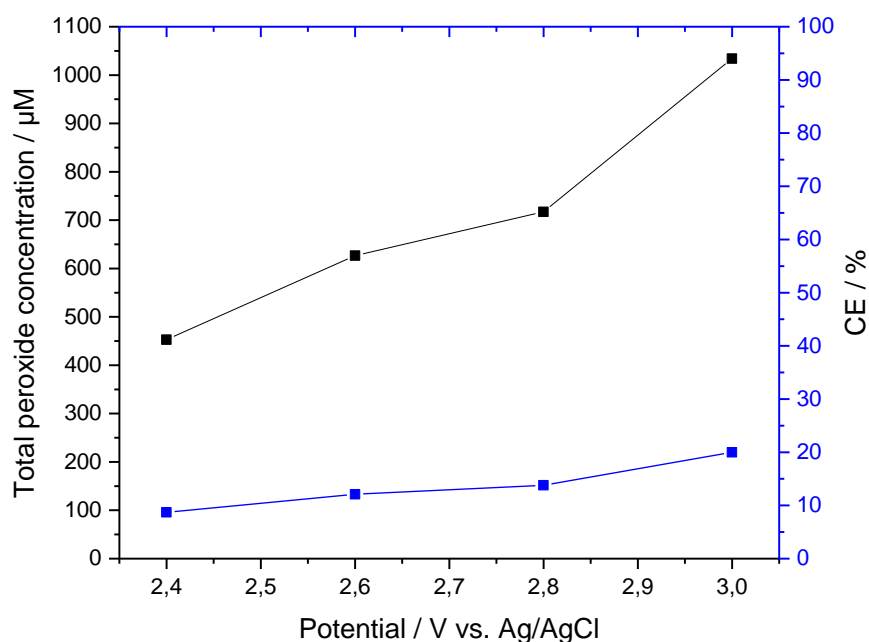


Figure S5: Chronocoulometry of an 3.2 cm^2 BiVO_4 working electrode (anode) and an 4.9 cm^2 gas diffusion electrode (cathode). The total peroxide concentration and the CE plotted against the respective applied potential vs. Ag/AgCl. Polarization was performed in 2 M KHCO_3 with stirring at a pH of 8.3. Total charge of 100 C passed during the experiments. The anode compartment contained 100 mL of electrolyte and was separated from the cathode compartment by a cation exchange membrane. In the gas compartment of the GDE, oxygen was passed through water for high humidity, which was then offered to the GDE at 15 mbar overpressure.

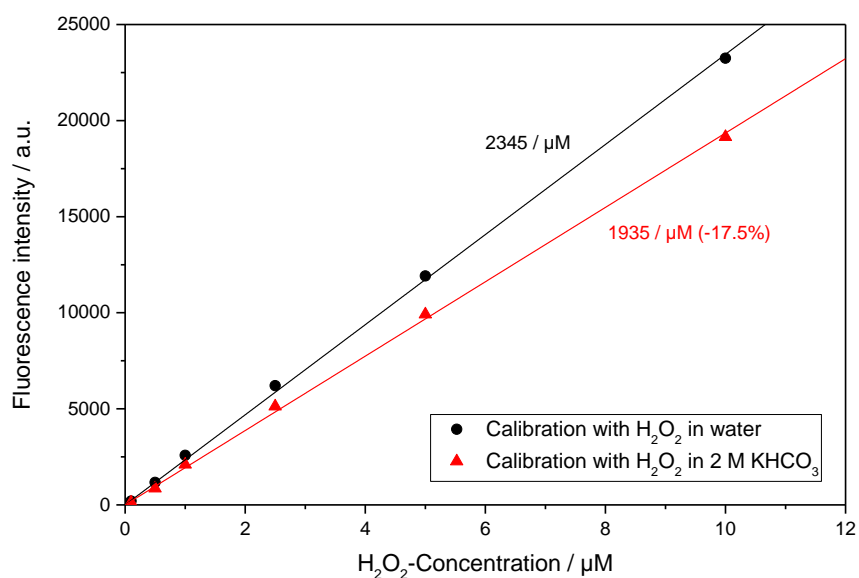


Figure S6: Calibration curves of the quantification assay based on horseradish peroxidase (HRP) using either a fixed concentration of H_2O_2 in water (black) or in 2 M KHCO_3 (red), the latter presumably containing a fraction of peroxomonocarbonate not detected by the assay.

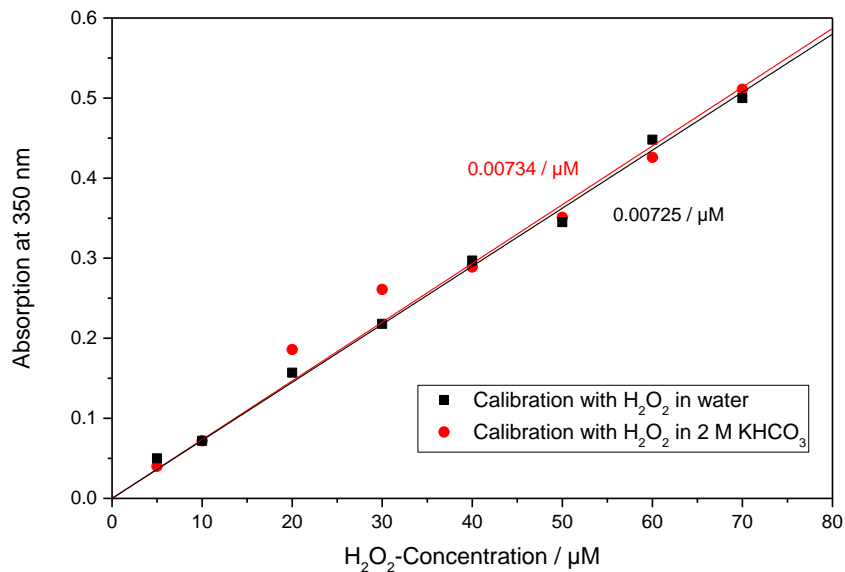


Figure S7: Calibration curves of the quantification assay based on colorimetric iodometry using either a fixed concentration of H₂O₂ in water (black) or in 2 M KHCO₃ (red), the latter presumably containing a fraction of peroxomonocarbonate.

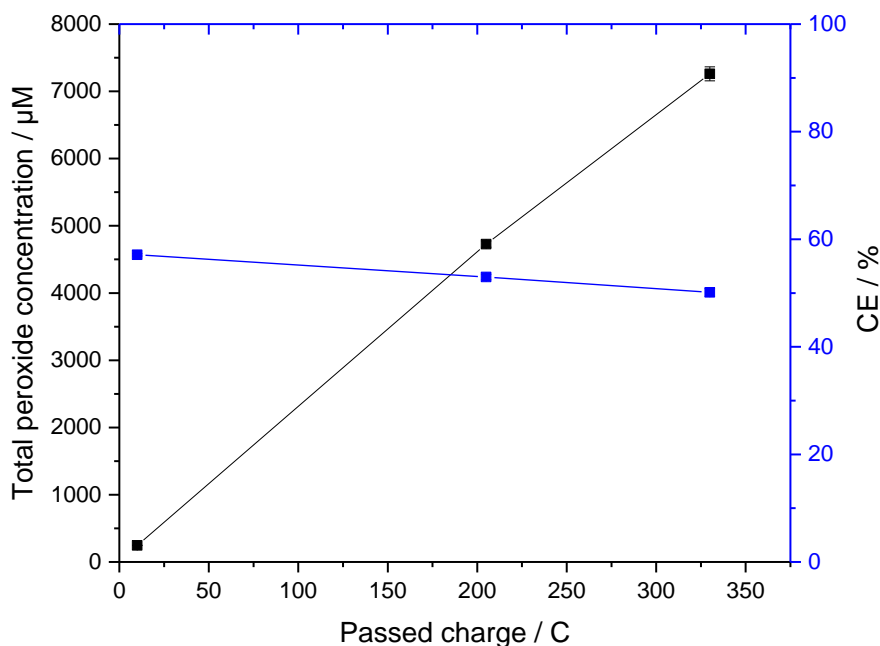


Figure S8: Total peroxide concentration and CE plotted against charge quantity. Chronocoulometry using InSbO_x/CuSb₂O_x/FTO as the working electrode. Polarization was performed at 2.385V vs Ag/AgCl in carbonate buffer under stirring with 0.5 M KHCO₃ and 3.5 M K₂CO₃ at a pH of 11.3. Total charge of 330 C passed during the experiment. The anode compartment contained 120 mL of electrolyte and were separated from the cathode compartment by a cation exchange membrane. A GDE was used as the cathode. In the gas compartment of the GDE, oxygen was passed through water for high humidity, which was then offered to the GDE at 15 mbar overpressure.

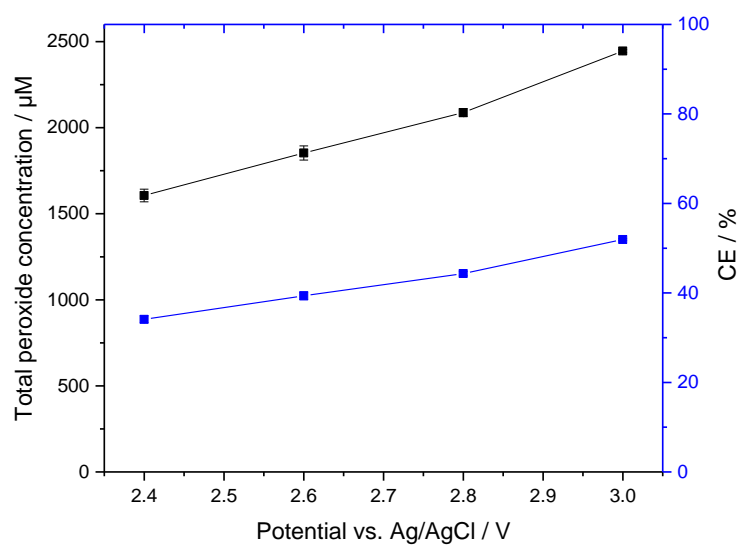


Figure S9: Chronocoulometry of an 4.4 cm^2 FTO working electrode (anode) and an 4.9 cm^2 gas diffusion electrode (cathode). The total peroxide concentration and the CE plotted against the respective applied potential vs. Ag/AgCl. Polarization was performed in 0.5 M KHCO_3 and $3.5 \text{ M K}_2\text{CO}_3$ at a pH of 11.3. Total charge of 100 C passed during the experiments. The anode compartment contained 110 mL of electrolyte and was separated from the cathode compartment by a cation exchange membrane. In the gas compartment of the GDE, oxygen was passed through water for high humidity, which was then offered to the GDE at 15 mbar overpressure.

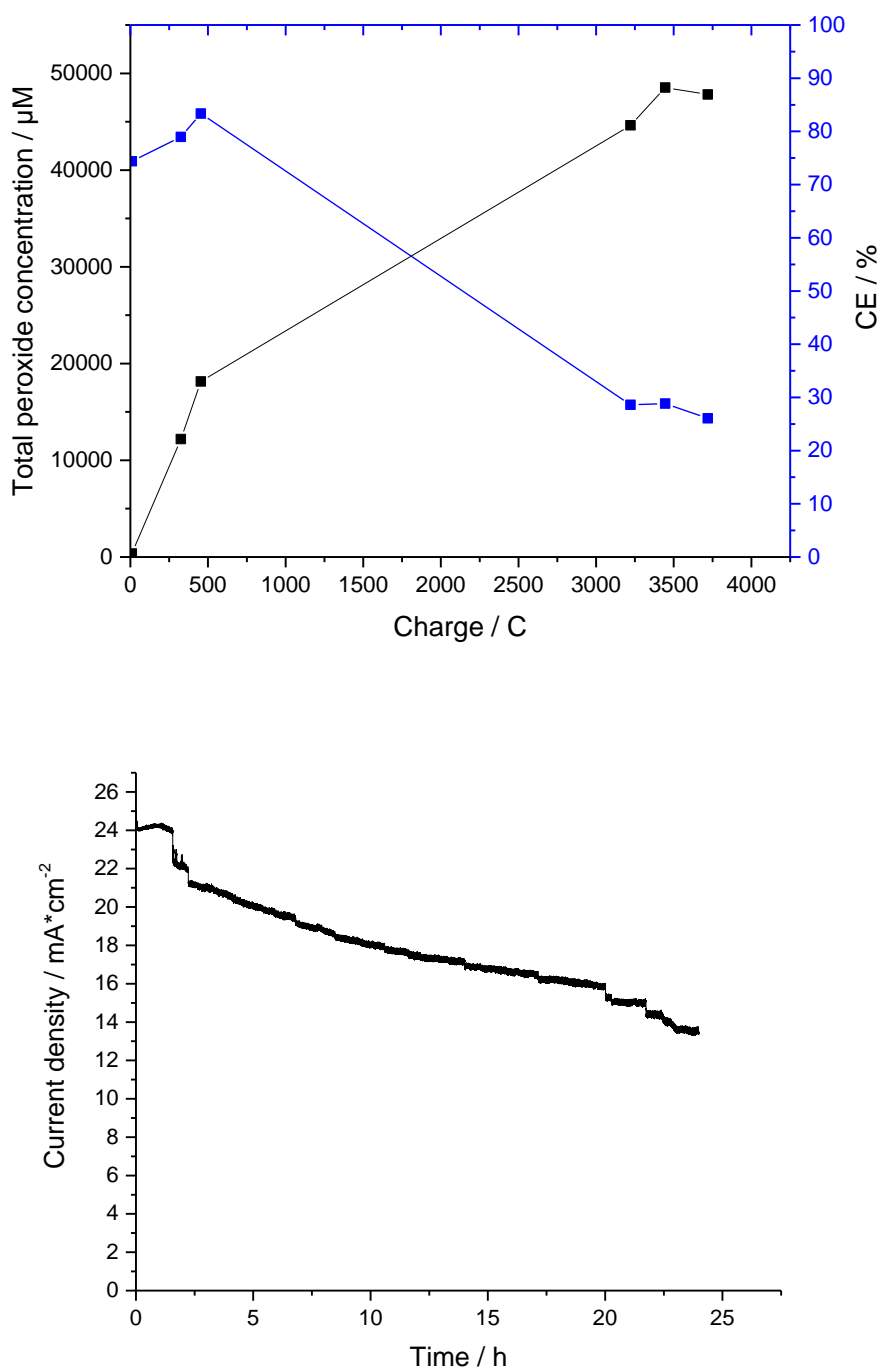


Figure S10: Total peroxide concentration and CE plotted against charge quantity. Chronocoulometry using InSbO_x/CuSb₂O_x/FTO as the working electrode. Polarization was performed for 24 h at 3V vs Ag/AgCl in carbonate buffer under stirring with 0.5 M KHCO₃ and 3.5 M K₂CO₃ at a pH of 11.3. The anode compartment contained 110 mL of electrolyte and were separated from the cathode compartment by a cation exchange membrane. A GDE was used as the cathode. In the gas compartment of the GDE, oxygen was passed through water for high humidity, which was then offered to the GDE at 15 mbar overpressure.

A



B

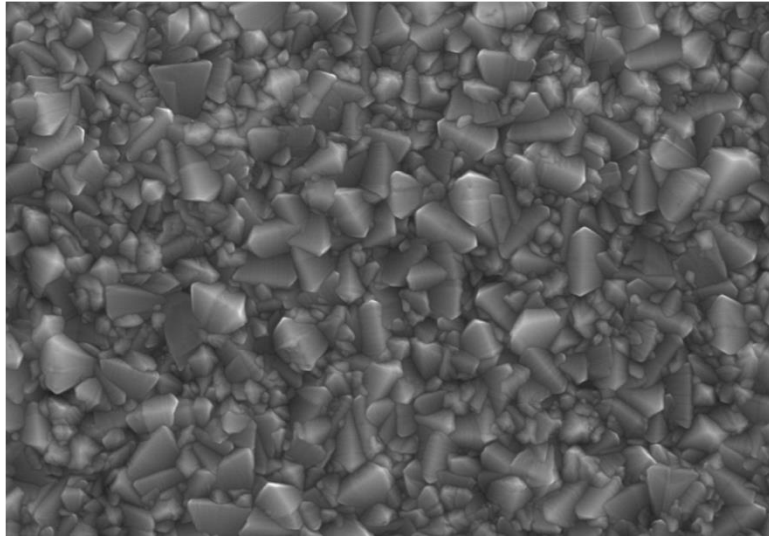


Figure S11: SEM images from above. A shows a mixed oxide electrode and B an FTO substrate.

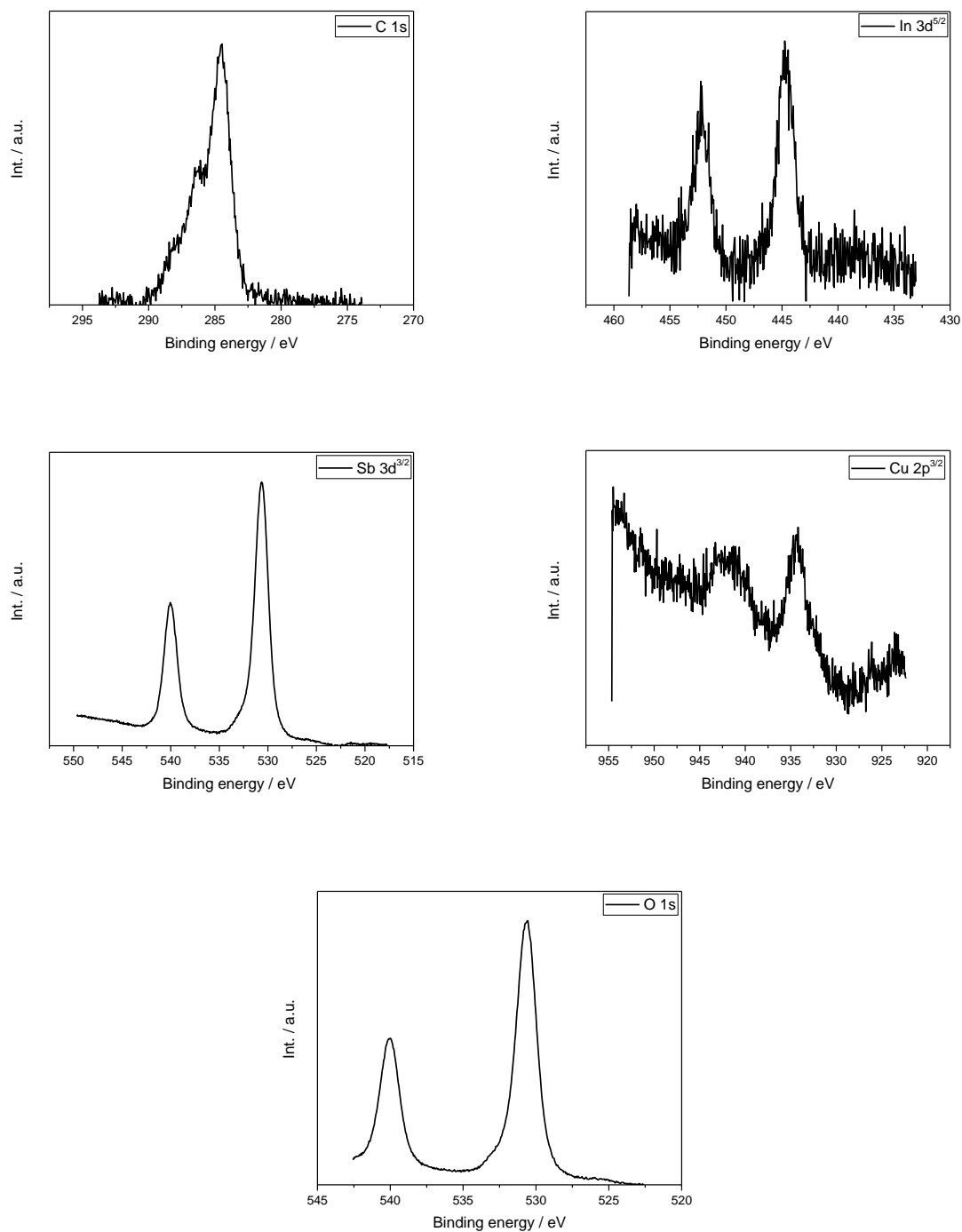


Figure S12: The XPS spectra of the InSbOx/CuSb2Ox/FTO electrodes. All spectra were corrected for the C1s peak of the environment at 284.5 eV. The radiation source was a Mg-K α (1253.6 eV). The power was 120 W with a pass energy of 10 eV. The respective areas with the binding energies of the corresponding elements are shown. Here an overlap of the O 1s with the Sb 3d^{5/2} can be seen. The Sb 3d^{3/2} is clearly visible. The elements indium and copper can also be seen. Due to the FTO as a carrier material, tin was also detected in addition to the elements of the mixed oxide.

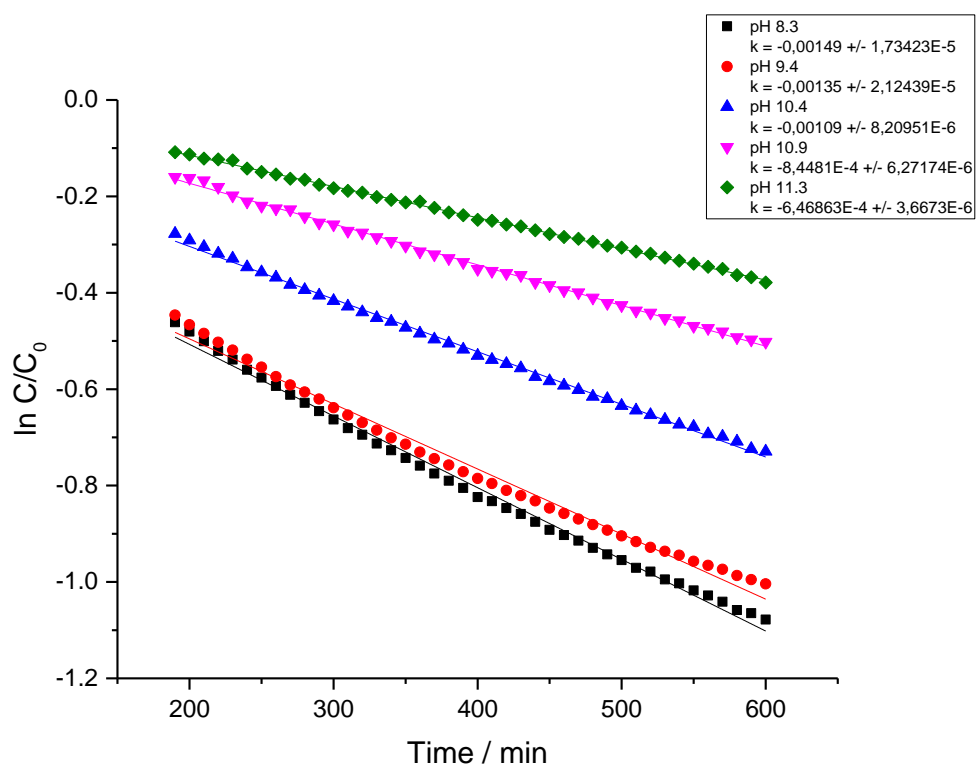
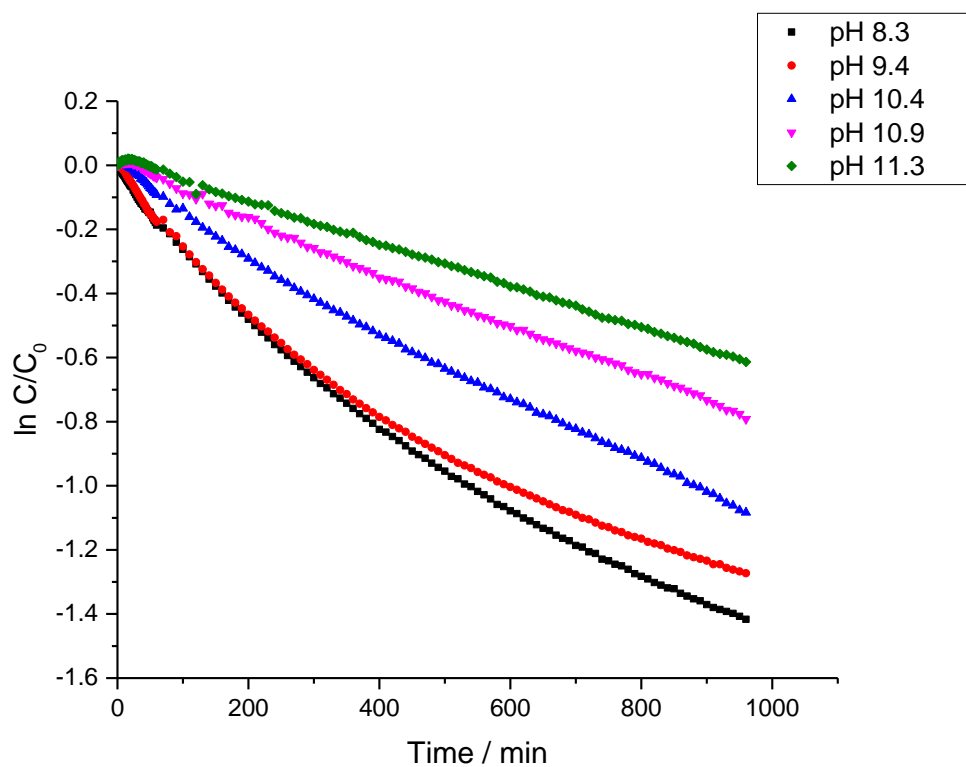


Figure S13: The decolorization of 20 μM methylene blue at 665 nm by 5 mM of hydrogen peroxide in (b) carbonate electrolytes of different pH shown as logarithmic plot for first-order type kinetics. The degradation rate was determined from 190 to 600 minutes (bottom graph) as this yielded best results free from artefacts sometimes appearing in the initial phase.