ChemElectroChem

Supporting Information

Geopolymer Based Electrodes as New Class of Material for Electrochemical CO$_2$ Reduction

Jürgen Schuster, Neven Ukrainczyk,* Eddie Koenders, and Markus Stöckl*

Results and Discussion

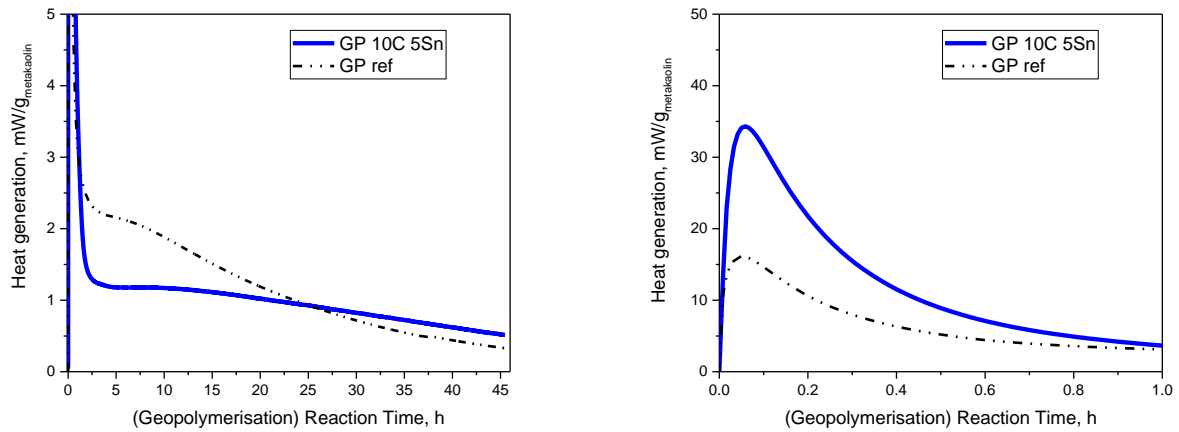**Supporting Information 1:** Isothermal reaction calorimeter measurements

Figure S1. *Left Image:* Reaction kinetics of polymerisation hardening process obtained by isothermal calorimetry of geopolymer (GP) mortar with the addition of graphite and Sn (GP 10C 5Sn), compared to unmodified GP (GP ref). *Right image:* zoom in for an initial dissolution period of 1 h.

Supporting Information 2: Numerical values of formate concentrations and current efficiencies from experiments conducted at different current densities.

Table S2: Formate concentrations (c) and current efficiencies (CE) of the single experiments conducted at different current densities and the average values ($c_{avg,4h}$ and $CE_{avg,4h}$) after 4 h with corresponding standard deviations (σ).

i / mA cm^{-2}	electrode	c / mmol L^{-1}			$c_{avg, 4h}$ / mmol L^{-1}	σ_c / mmol L^{-1}	CE / %			$CE_{avg,4h}$ / %	σ_{CE} / %
		1h	2h	4h			1h	2h	4h		
	1	0,03	0,04	0,09			0,73	0,51	0,56		
5	2	0,03	0,04	0,06	0,07	0,01	0,68	0,52	0,40	0,46	0,08
	3	0,04	0,06	0,07			1,01	0,72	0,43		
	1	0,20	0,70	2,25			2,57	4,47	7,12		
10	2	0,17	0,60	1,98	2,02	0,21	2,17	3,85	6,27	6,40	0,66
	3	0,08	0,47	1,84			1,04	3,03	5,81		
	1	0,72	1,63	3,53			6,19	6,92	7,44		
15	2	1,09	2,34	5,03	4,37	0,77	9,31	9,96	10,61	9,21	1,62
	3	0,91	2,06	4,54			7,79	8,74	9,57		
	1	1,64	3,37	7,85			10,54	10,74	12,41		
20	2	1,50	3,19	7,61	8,09	0,63	9,67	10,19	12,04	12,79	1,00
	3	1,55	3,55	8,81			9,95	11,34	13,93		
	1	2,06	4,28	8,44			8,81	9,11	8,90		
30	2	1,97	3,96	7,60	8,19	0,52	8,43	8,41	8,01	8,63	0,55
	3	2,04	4,19	8,53			8,73	8,92	9,00		
	1	1,80	3,74	7,47			5,79	5,97	5,91		
40	2	2,17	4,27	8,16	8,02	0,49	6,99	6,80	6,45	6,34	0,39
	3	2,04	4,17	8,43			6,57	6,64	6,67		

Supporting Information 3: Course of cell voltage (U_c) and formate concentration in the 10-hour experiments.
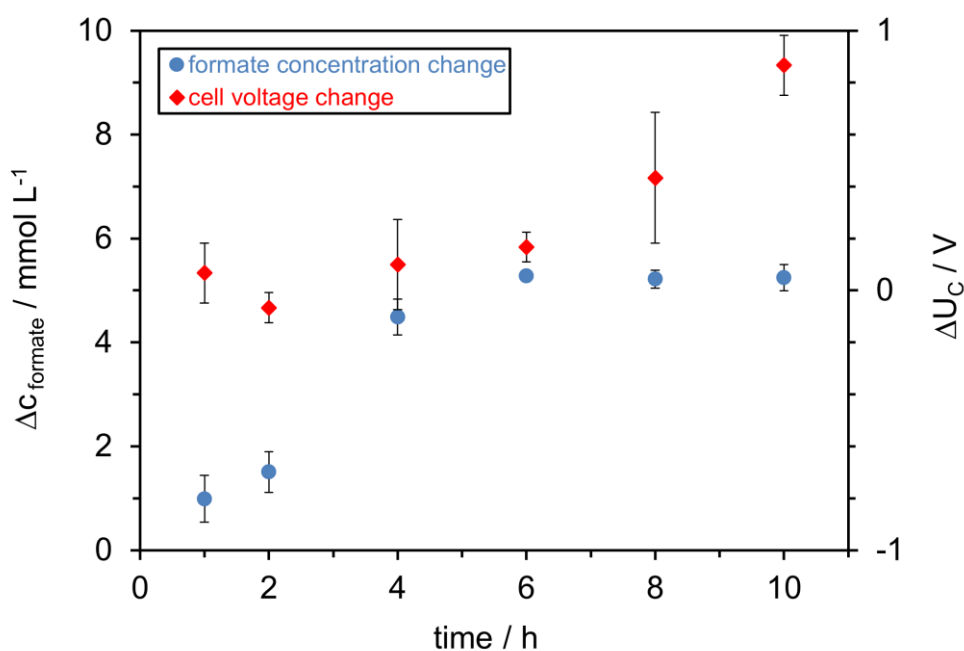

Figure S3: Average values of the formate concentration changes and cell voltage changes during 10 h of electrolysis at 20 mA cm^{-2}. Standard deviations of 3 individual runs are shown in error bars.

Table S3: Cell voltages (U_C) and formate concentrations (c) of the single electrolysis experiments with 20 mA cm^{-2} conducted over a period of 10 hours and the average values of the cell voltage changes ($\Delta U_{C,avg}$) and formate concentration changes (Δc_{avg}) with corresponding standard deviations (σ).

time / h	electrode	U_C / V	ΔU_C / V	$\Delta U_{C,avg}$ / V	σ_{Uc} / V	c / mmol L^{-1}	Δc / mmol L^{-1}	Δc_{avg} / mmol L^{-1}	$\sigma_{\Delta c}$ / mmol L^{-1}
0	1	9	-	-	-	-	-	-	-
	2	9,70							
	3	9,70							
1	1	9,2	0,2	0,07	0,1	1,444	1,44	0,99	0,45
	2	9,70	0			0,971	0,97		
	3	9,70	0			0,546	0,55		
2	1	9,2	0	-0,07	0,1	3,394	1,95	1,51	0,39
	2	9,6	-0,1			2,191	1,22		
	3	9,6	-0,1			1,893	1,35		
4	1	9,2	0	0,10	0,2	8,276	4,88	4,49	0,35
	2	9,9	0,3			6,422	4,23		
	3	9,6	0			6,25	4,36		
6	1	9,4	0,2	0,17	0,1	13,615	5,34	5,28	0,05
	2	10	0,1			11,663	5,24		
	3	9,8	0,2			11,499	5,25		
8	1	10,1	0,7	0,43	0,3	18,687	5,07	5,22	0,17
	2	10,2	0,2			16,835	5,17		
	3	10,2	0,4			16,906	5,41		
10	1	11,1	1	0,87	0,1	23,707	5,02	5,25	0,25
	2	11	0,8			22,035	5,20		
	3	11	0,8			22,427	5,52		

Supporting Information 4: Appearance of an electrode after the 10-hour experiment.
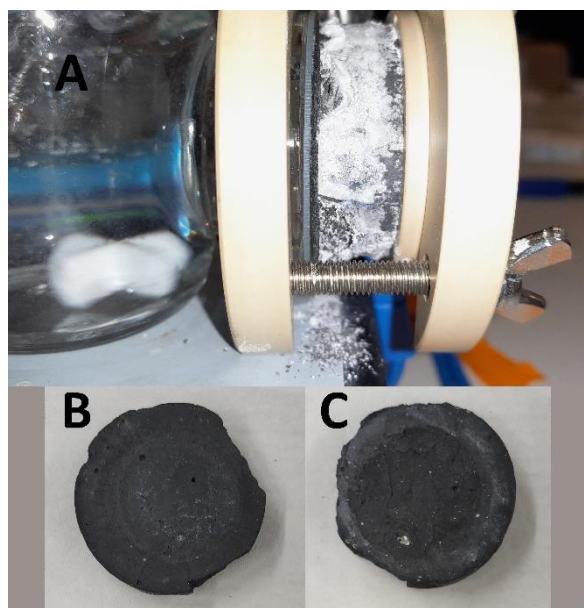

Figure S4: Side view of an electrode after 10 h electrolysis at 20 mA cm^{-2} (A), view of the electrode side facing the electrolyte (B) and the outside of the electrode (C) after removal and rinsing of the electrode.

Supporting Information 5: Formate and oxalate concentration measured in electrolysis experiments at different current densities.

Table S5: Mean values and standard deviations (σ) of the formate and oxalate concentrations and the corresponding mean values of the current efficiencies (*CE*) determined at electrolysis experiments with different current densities after 4 hours

current density / mA cm^{-2}	$c_{avg, formate}$ / mmol L^{-1}	σ / mmol L^{-1}	$CE_{formate}$ / %	$c_{avg, oxalate}$ / µmol L^{-1}	σ / µmol L^{-1}	$CE_{oxalate}$ / %
5	0.07	0.01	0.46	5.5	3.2	0.035
10	2.02	0.21	6.40	4.2	3.5	0.013
15	4.37	0.77	9.21	1.2	0.1	0.003
20	8.09	0.63	12.79	6.4	0.2	0.01
30	8.19	0.52	8.63	3.6	0.1	0.004
40	8.02	0.49	6.34	2.8	0.8	0.002

Supporting Information 6: Formate and oxalate concentration measured in 10-hour electrolysis experiments at 20 mAcm^{-2}.

Table S6: Mean values and standard deviations (σ) of the formate and oxalate concentrations determined in an electrolysis experiment with a duration of 10 hours at 20 mA cm^{-2}

duration / h	$c_{avg, formate}$ / mmol L^{-1}	σ / mmol L^{-1}	$CE_{formate}$ / %	σ / %	$c_{avg, oxalate}$ / µmol L^{-1}	σ / µmol L^{-1}	$CE_{oxalate}$ / %	σ / %
1	0.99	0.45	6.35	2,89	4.2	1.2	0.027	0,008
2	2.49	0.8	7.95	2,53	4.8	1.4	0.015	0,005
4	6.98	1.12	11.04	1,78	5.8	1.6	0.009	0,003
6	12.26	1.18	12.81	1,23	7.3	2.1	0.008	0,002
8	17.48	1.05	13.58	0,82	8.3	2.5	0.006	0,002
10	22.72	0.87	14.01	0,54	9.4	3.4	0.006	0,002

Supporting Information 7: SEM/EDX element mapping of an unused GP 10C 5Sn-electrode surface and a GP 10C 5Sn-electrode that was used in all experiments over a total period of approx. 34 hours.
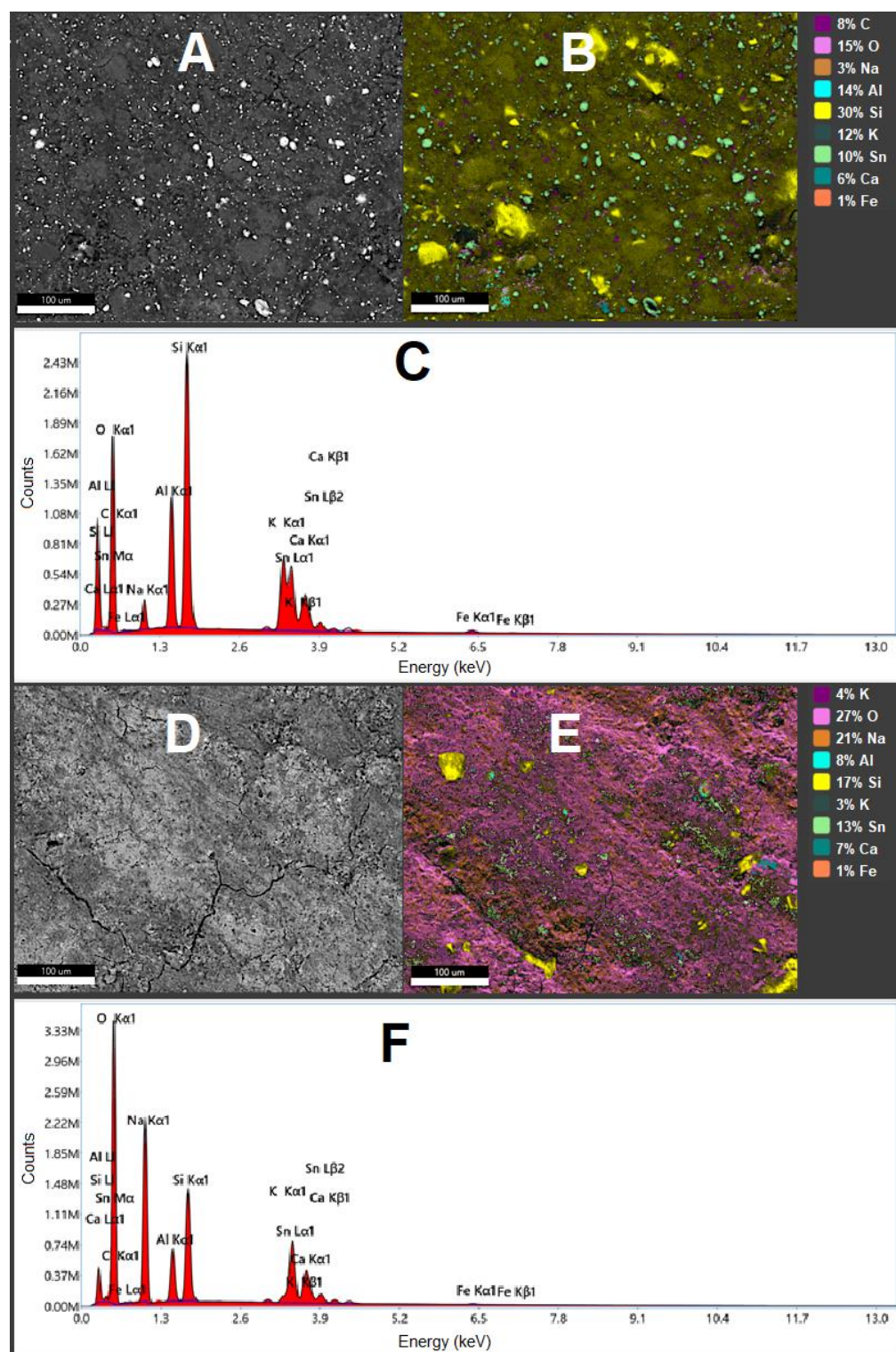

Figure S7: SEM/EDX images of GP 10C 5Sn-electrode surfaces. SEM-BSE image of an unused electrode (A), SEM/EDX element mapping of an unused electrode (B), EDX spectra of an unused electrode (C), SEM-BSE image of an electrode that was used in all experiments (D), SEM/EDX element mapping of an electrode that was used in all experiments (E), EDX spectra of an electrode that was used in all experiments (F). The element contents are given in weight percent.
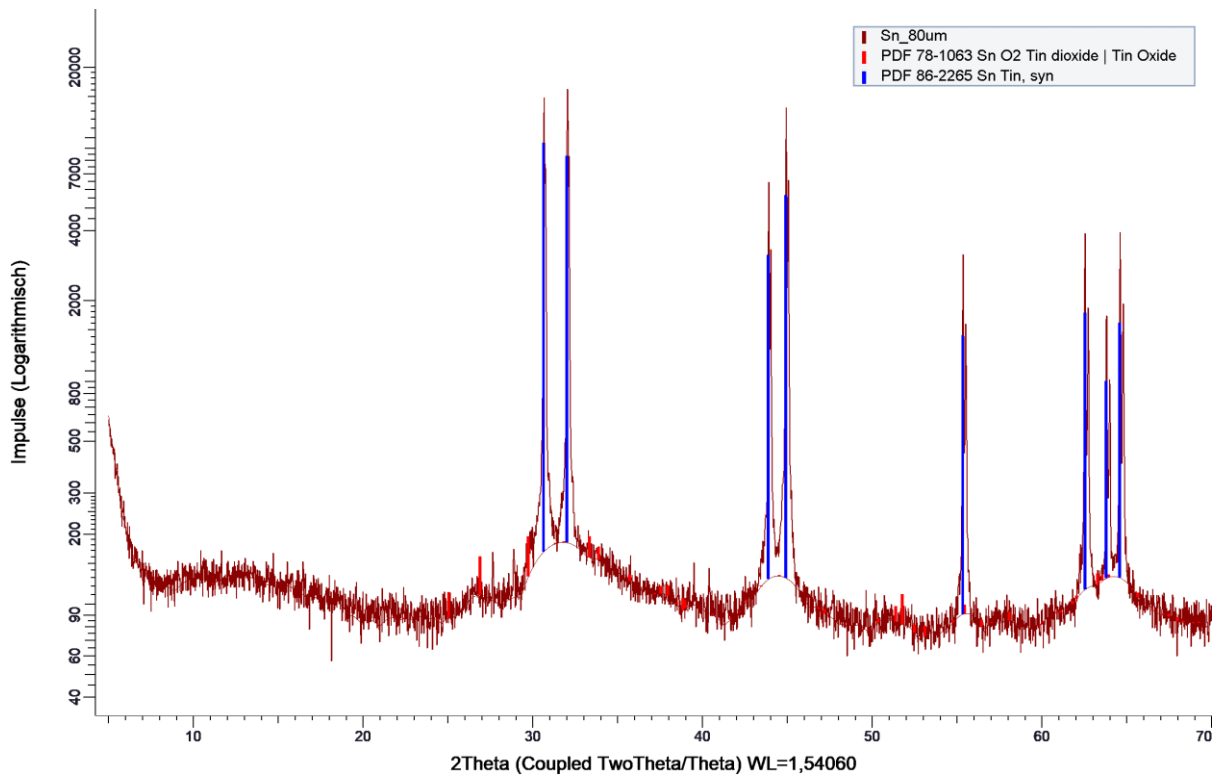
Supporting Information S8: XRD analysis

Figure S8.1: Powder X-ray diffraction of Sn raw material(dark red) compared with reference peak positions for Sn (blue) and SnO_2 (red).
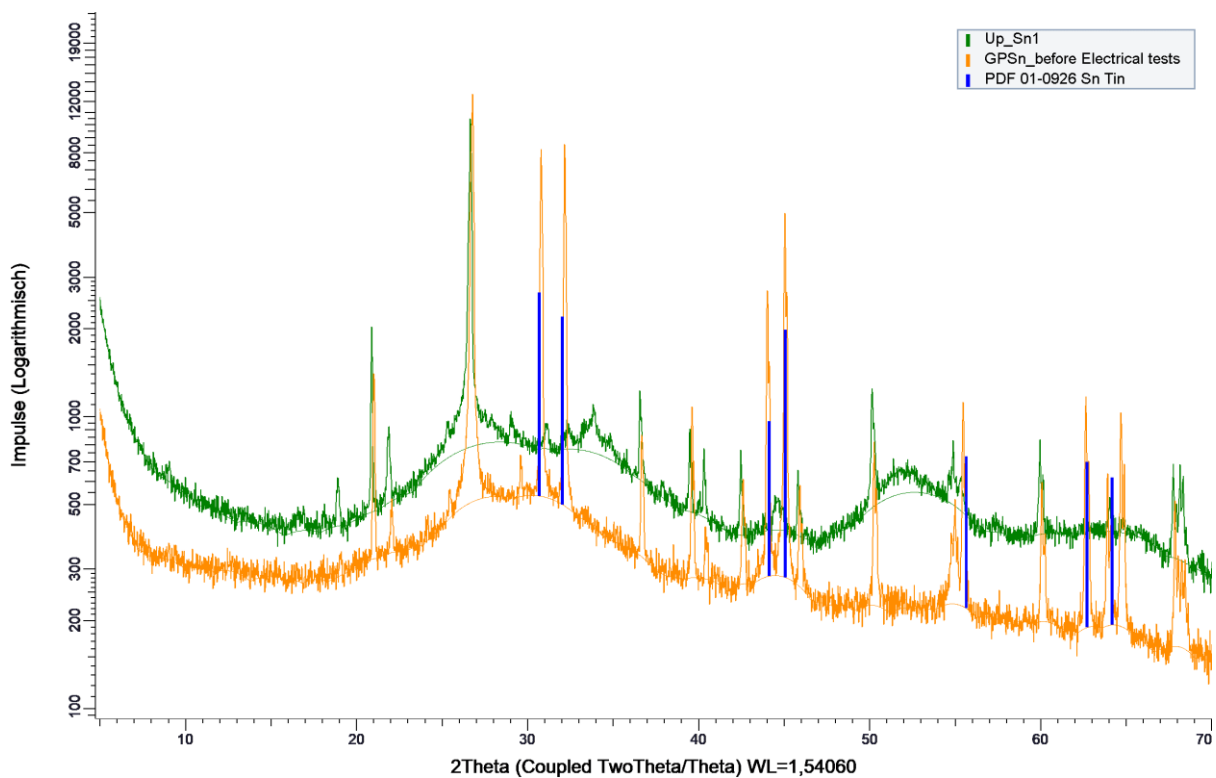

Figure S8.2: Powder X-ray diffraction of (GP 10C 5Sn) sample before (orange line) and after electrochemical tests (green) indicating almost complete depletion of metal Sn (reference intensities in blue) and increase in amorphous content (broad peaks centered at 30, 52 and 65 degrees of 2Theta).
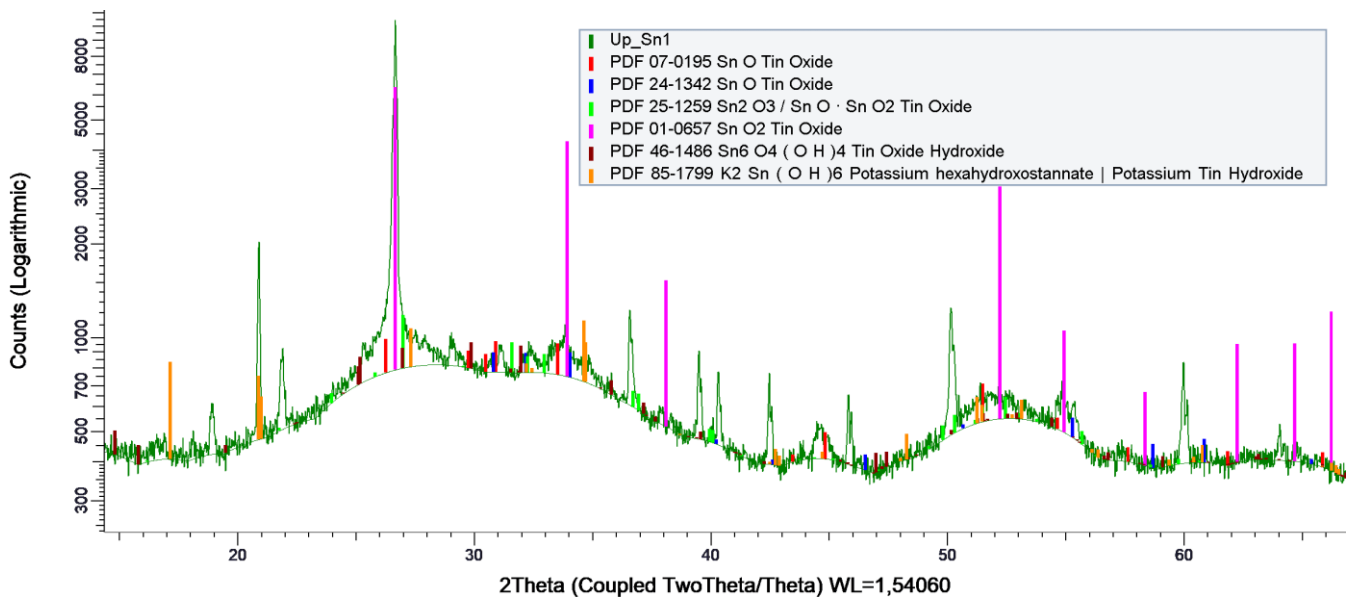
Figure S8.3: Powder X-ray diffraction of (GP 10C 5Sn) sample after electrochemical tests indicating presence of Tin Oxides (SnO, SnO_2) and Hydroxide ($Sn_6O_4(OH)_4$ and $K_2Sn(OH)_6$) phases.

Supporting Information 9: ICP-OES analysis of the working electrode electrolytes from experiments carried out at different current densities for 4 hours.
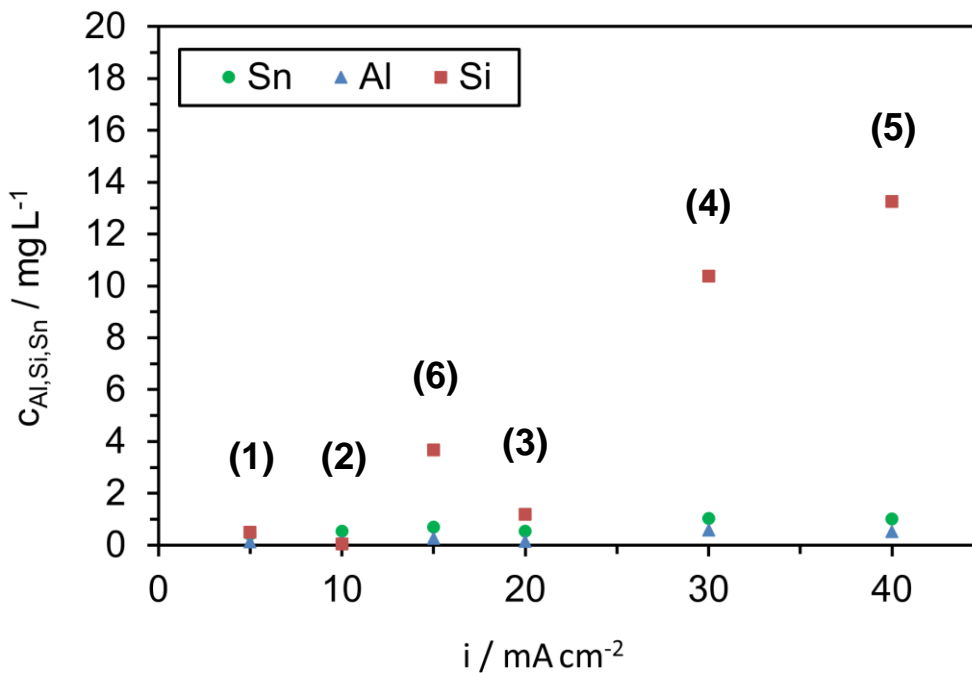

Figure S9: ICP-OES analysis of tin, aluminum and silicon concentrations of the working electrode electrolytes from experiments carried out at different current densities for 4 hours. The order in which the experiments were carried out is indicated in the brackets. The mean values of the determined concentrations are given.

Table S9: Order of experiments conducted at different current densities for 4 hours and the mean values of tin, aluminium and silicon concentrations determined from ICP-OES analyses.

order of experiment	i / mA cm^{-2}	c_{Sn} / mg L^{-1}	c_{Al} / mg L^{-1}	c_{Si} / mg L^{-1}
1	5	0,42	0,13	0,51
2	10	0,54	0,12	0,04
3	20	0,54	0,15	1,19
4	30	1,03	0,58	10,38
5	40	1,02	0,51	13,26
6	15	0,69	0,26	3,68

Experimental Section

Supporting Information S10: Laboratory Electrochemical H-Cell assembly

The H-shaped reactor consists of two modified 100 mL laboratory bottles connected by flanges. Between the flanges, which are fixed with a clamping ring, there is a circular proton exchange membrane on a sealing ring. A second flange is attached to the working electrode chamber (WE chamber), via which the working electrode is fixed from the outside with a clamping system. Between the working electrode and the flange is a 1 mm thick circular silicone seal with a 0.13mm thick graphite foil (RCT-DKA-SBGR) for electrical contacting (Figure S1 shows a ready-cut graphite foil). The inner diameter of the flange is 2.5 cm, resulting in a geometrically accessible area of $4.9\ cm^2$. The counter electrode chamber (CE chamber) contains a dimensionally stable anode (DSA, immersed geometric area approx. $20\ cm^2$) which can be immersed via the neck of the bottle through a screw cap with septum. To ensure constant potential control, a reference electrode can be inserted into the WE chamber through a screw cap with fixing rings. Figure S2 shows a fully assembled H-cell.

Figure S10: Mounted H-cell without reference electrode (left), ready-cut graphite foil for electrical contacting of the working electrode (right), the graphite foil is placed between the silicone seal and the working electrode.

Supporting Information S11: Method for formate and oxalate analysis with HPLC

Formate concentrations of the samples taken during the experiments were analysed by HPLC (Shimadzu) employing the following parameters: Column: Rezex-ROA, 300×7.8 mm (Phenomenex, California, USA) Method: 5 mm H_2SO_4, 0.6 mLmin^{-1}, 30°C, 25 min, wavelength detector (λ=209 nm). As standard for calibration sodium formate solutions were used in the range of 0–220 mmol/L and dipotassium oxalate solutions in the range of 0,0125 – 1,6mmol/L.

Supporting Information S12: Elemental analysis with ICP-OES

Evaluation of the electrode stability by analysing the electrolytes after each experiment (electrolysis at different current densities for 4 hours) was carried out using ICP-OES. The aluminium, silicon and tin and potassium concentrations were measured.

Elemental analysis for potassium, aluminium, silicon, and tin was performed by ICP-OES using an Agilent 5800 ICP-OES instrument equipped with an Agilent Easy-fit 1.8 mm torch (one-piece) in combination with a double-pass spray chamber and a concentric sea spray glass nebuliser. The samples were fed with an Agilent SPS 4 autosampler. For the measurements, all solutions used were acidified with nitric acid to a content of 3wt.%. For elemental analysis of aluminium, silicon, and tin a blank solution and up to 8 calibration standards ranging from 0.025 to 10 mg L^{-1} were used for calibration. For elemental analysis of potassium, a blank solution and 5 calibration standards ranging from 0.5 to 50 mg L^{-1} were used for calibration. The samples were diluted 10-fold. The following settings in Table S1 were used for the measurements.

Table S12: Conditions for ICP-OES measurements

Conditions autosampler	
Replicate Count	3
Pump Speed (rpm)	12
Sample Uptake Time (s)	25
Sample Uptake Fast Pump	True
Rinse Time (s)	30
Rinse Time Fast Pump	True
Condition plasma and spectrometer	
Read Time (s)	5
RF Power (KW)	1.2
Stabilization Time (s)	15
Viewing Mode	Radial
Viewing Height (mm)	8
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	12
Aux Flow (L/min)	1
Calibration/Measurement	
Wavelength Al (nm)	396.152
Wavelength Si (nm)	251.611
Wavelength Sn (nm)	283.998
Wavelength K (nm)	766.491
Background Correction	Fitted