Supplementary material

A transition metal oxofluoride offering advantages in electrocatalysis and potential use in applications

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Compound	Molar mass	Weighed	Amount	Amount	Amount	Volume
_	(g/mol)	amount	metal	PVDF (mg)	CB (mg)	NMP
		(mg)	(µmol)			(ml)
x=1 (no. 1)	873.79	250.02	858.40	50.02	33.15	0.8
x=1 (no. 2)	873.79	249.77	857.54	50.00	33.10	0.8
x=0.75	873.63	249.94	858.29	50.03	33.17	0.8
x=0.5	873.46	249.93	858.41	50.06	33.14	0.8
x=0.25	873.30	249.85	858.30	50.01	33.16	0.8
x=0	873.13	249.81	858.33	50.06	33.16	0.8
y=0.86	872.15	249.33	857.64	49.99	33.16	0.8
CoO/Co ₃ O ₄ *	74.93/240.79	64.38	832.94	67.57	45.39	0.9
no catalyst				75.00	50.00	1.0

Table S1Amount of chemicals used in the electrode manufacturing.

*The commercial CoO chemical (ABCR GmbH) was found to have a phase composition of $CoO/Co_3O_4 = 0.54 / 0.46$ obtained from PXRD data.

Sample	Interaction	N	d, Å	σ^2, A^2	S_{θ}^{2}	ΔE	F, %
Co ₃	Co – F	6	2.040	0.0050	0.86	-8.7	55
no potential	Co ··· Sb	4	3.331	0.0065			
	Co ··· Co	4	4.072	0.0018			
	Co ··· Co2	8	4.130	0.0049			
Co ₃	Co - F	4	2.037	0.0047	0.86	-5.5	61
$j = 1 \text{ mA cm}^{-1}$	Co - O	2	2.078	0.0047			
2	Co ··· Sb	4	3.335	0.0056			
	Co ··· Co	4	4.110	0.0057			
	Co ··· Co2	8	4.132	0.0096			
(Co _{0.5} Ni _{0.5}) ₃	Co - F	4	2.065	0.0024	0.78	-6.1	38
no potential	Co - O	2	1.983	0.0024			
	Co ··· Sb	4	3.322	0.0065			
	Co ··· Co	4	4.154	0.0061			
	Co ··· Co2	8	4.099	0.0206			
(Co _{0.5} Ni _{0.5}) ₃	Co-F	4	2.047	0.0061	0.97	-4.0	38
$j = 1 \text{ mA cm}^{-}$	Co - O	2	2.108	0.0061			
2	Co ··· Sb	4	3.337	0.0084			
	Co ··· Co	4	4.144	0.0055			
	Co ··· Co2	8	4.150	0.0015			

Table S2Mean bond distances, d, Å, number of distances, N, and Debye-Waller, $\sigma 2$,
factors in the EXAFS studies of Co K edge samples.

Sample	Interaction	N	d, Å	σ^2 , \AA^2	S_{θ}^{2}	ΔE	F, %
Co ₃	Ni – F	4	2.058	0.0031	0.89	-6.3	47
no potential	Ni – O	2	2.025	0.0031			
	Ni ··· Sb	4	3.297	0.0065			
	Ni ··· Ni	4	4.067	0.0030			
	Ni ··· Ni2	8	4.118	0.0077			
Co ₃	Ni – F	4	2.033	0.0028	0.75	-6.4	48
$j = 1 \text{mA cm}^{-2}$	Ni – O	2	2.008	0.0028			
	Ni ··· Sb	4	3.294	0.0060			
	Ni ··· Ni	4	4.098	0.0031			
	Ni ··· Ni2	8	4.134	0.0101			

Table S3Mean bond distances, d, \mathring{A} , number of distances, N, and Debye-Waller, σ^2 ,
factors in the EXAFS studies of Ni K edge samples



Figure S1a Quantification of O_2 (g) partial pressure at 1 atm on mass spectrometer. The standard curve fitted as a regression line was used for calculations.



Figure S1b Quantification of H_2 (g) partial pressure at 1 atm on mass spectrometer. The standard curve fitted as a regression line was used for calculations.



Figure S2a EXAFS function of Co K. Calculated model (red line) and experimental data (black line). The EXAFS data are offset by +10.



Figure S2b EXAFS function of Ni K. Calculated model (red line) and experimental data (black line). The EXAFS data are offset by +10.



S3a







S3c



S3d



S3e



S3f





Figure S4a Comparison of PXRD data (black) with the calculated diffractogram (blue) from single crystal XRD data for $Co_3Sb_4O_6F_6$.



Figure S4b Comparison of PXRD data (black) with the calculated diffractogram (blue) from single crystal XRD data for $(Co_{0.86}Mn_{0.14})_3Sb_4O_6F_6$.



Figure S5 PXRD data for the cobalt oxide powder used in the benchmarking electrode resulted in a molar fraction 0.54 CoO (red) and 0.46 Co₃O₄ (blue).



Figure S6 Typical plot obtained for ECSA analysis, here an example of $Co_3Sb_4O_6F_6$ in 1 M KOH.



Figure S7 Image of the single chamber open cell (left) with a standard three point set up using a working electrode centered and surrounded by the Pt mesh counter electrode, reference electrode in proximity of the working electrode and the magnet stirrer below. The working electrodes used in experiments (right). The electrodes were cut to similar sizes. The measurements were evaluated and presented as an average.



Figure S8 The *in situ* experimental set up at the I811 beamline at MaxLab synchrotron. The small white plastic cell of 1mm thickness containing the WE and CE and 0.23 ml of phosphate buffer electrolyte is seen in the centre of the picture with a two point set up of the potentiostat connectors.



Figure S9 SEM of a $Co_3Sb_4O_6F_6$ electrode before electrolysis in SE mode (left) and COMPO mode (right) in 250x, 20.000x and 80.000x magnification from top to bottom respectively.



Figure S10 SEM of a $Co_3Sb_4O_6F_6$ electrode after 0.5 h of electrolysis in SE mode (left) and COMPO mode (right) in 250x, 20.000x and 80.000x magnification from top to bottom respectively.



Figure S11 SEM of a CoO/Co₃O₄ electrode before electrolysis in SE mode (left) and COMPO mode (right) in 250x, 20.000x and 80.000x magnification from top to bottom respectively.



Figure S12 SEM of a CoO/Co₃O₄ electrode after 0.5 h of electrolysis in SE mode (left) and COMPO mode (right) in 250x, 20.000x and 80.000x magnification from top to bottom respectively.