X20CoCrWMo10-9//Co₃O₄: a Metal-Ceramic Composite with Unique Efficiency Values for Water-Splitting in Neutral Regime

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Determination of iron ions in the electrolyte after chronopotentiometry

When pH 7 electrolyte was used Iron ions could form with PO_4^{3-} ions as a precipitation of different species of iron phosphate, but no precipitation at all could be obtained in the electrolyte used for chronopotentiometry. No mass loss of the working electrode could be detected whilst long-term chronopotentiometry. In addition the concentration of Fe, Cr, Mn, W and Mo ions in the electrolyte used for chronopotentiometry was below the detection limit of the ICP OES system.

Determination of iron, chromium, molybdenum, manganese and cobalt in the electrolyte used for electro-activation upon Inductively coupled plasma optical emission spectrometry (ICP-OES)

In total five electro-activation procedures have been investigated to guarantee meaningful data. The results can be taken from Table S4. The CE was, subsequently after finishing the anodization, immersed into 2 M HCl for 12 hours. The solution samples were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP[™] 7400 Duo

equipped with MiraMist[®] Teflon nebulizer, Thermo Fisher Scientific Germany BV & Co KG) according DIN EN ISO 11885:2009-09. Concentrations of selected elements were determined at wavelengths of 228.6 nm (Co), 205.5 nm (Cr), 259.9 nm (Fe), 257.6 nm (Mn), and 202.0 nm (Mo). The NaOH-containing electrolyte solution was due to the high salinity (total dissolved solids (TDS > 300 g/L) first diluted by a factor of 100 with deionised water and then stabilized with hydrochloric acid (34 wt%) until pH 6 was reached. The HCl solution was analysed undiluted. The calibration standards were prepared according the matrices of the analyte solutions and contained 0.01, 0.1, 1.0 and (only for the HCl solution) [10.0 mg/L] of the selected elements.

Sample	Mass (g)	Mass difference (g)		
 Co-300 (1)	(8.30086) 8.30110	0.00024		
Co-300 (2)	(8.21362) 8.21319	-0.00043		
Co-300 (3)	(8.31900) 8.32001	0.00101		
Co-300 (4)	(8.28881) 8.28994	0.00113		
Co-300 (5)	(8.34454) 8.34412	-0.00042		

Table S1. Column II: Mass of the steel samples before (in brackets) respectively after carrying out long term chronoptentiometry (40000 s at 10 mA/cm²) in pH 7 corrected 0.1 phosphate buffer solution. Column III: Mass difference occurred during the long-term measurement.

Sample	Current	Amount of 0.1 M	Dissolved oxygen Runtin		Dissolved	Faradaic	
	density	K ₂ HPO ₄ /KH ₂ PO ₄	at the beginning		oxygen after	efficiency after	
			(t=0 s)		runtime	runtime	
Co-300	10 mA/cm ²	2.31	0.07 mg/l	2000 s	1.16 mg/l	75.58%	
Co-300	5 mA/cm ²	2.31	0.06 mg/l	2000 s	0.66 mg/l	83.2%	

Table S2. Determination of the Faradaic efficiency in pH 7 corrected 0.1 M K_2HPO_4/KH_2PO_4 . The electrode area was 2 cm². The distance between WE and RE was adjusted to 1 mm, the distance between CE and RE was ~ 7 mm.



on the AFM images.



Figure S2. Results from BET measurements. Sample gas: N_2 (77K). Activation was performed by outgassing for 10 h at 100 °C (Sample Co;1*10⁻⁶ bar) and by 22 h at 100 °C (Sample Co-300;1.5*10⁻⁹ bar); Equilibrium time: 10 min. (a) Adsorption/desorption plot of sample Co. Total amount used for the BET measurement: 4.407 g (b) Adsorption/desorption plot of sample Co-300. Total amount used for the BET measurement: 4.57 g.



Figure S3. Tafel plots of samples Co, Co-300 and Ir/Ru based on 200 second chronopotentiometry scans at current densities 0.65, 1.33, 2, 2.66, 4, 5.33, 6.66, 8, 10 and 13.3 mA/cm² in pH 7 corrected 0.1 M KH_2PO_4/K_2HPO_4 solution. IR compensation was performed on the basis of the electrolyte resistance (3.4 Ω). The resistance was corrected for 0.5 mm distance between WE and RE from literature values reported for 10 mm RE-WE distance (68 Ω)

Sample Activation Process	Mass (g)	Mass difference (g)		
1	8.30086 (8.30688)	-0.00602		
2	8.21362 (8.21950)	-0.00588		
3	8.31900 (8.32511)	-0.00611		
4	8.28881 (8.29506)	-0.00625		
5	8.34454 (8.35053)	-0.00599		

Table S3. Column II: Mass of the steel samples before (in brackets) respectively after carrying out the electro activation procedure. Column III: Mass difference during electro-activation.

I	II	III	IV	V	VI	VII
Mass loss [mg]	V (NaOH) [ml]	lon concentration (Electrolyte) [mg/l]	Amount of ions in Electrolyte [mg]	Precipitation on CE [mg]	∑detected ions [mg]	∑detected material [mg]
6.05	200	<0.01 (Fe)	<0.01 (Fe)	3.159 (Fe)	3.159 (Fe)	4.273
		<0.01 (Co)	<0.01 (Co)	0.025 (Co)	0.025 (Co)	
		<0.01 (Mn)	<0.01 (Mn)	0.01 (Mn)	0.01 (Mn)	
		3.50 (Cr)	0.70 (Cr)	0.01 (Cr)	0.71 (Cr)	
		1.85 (Mo)	0.278 (Mo)	0.091 (Mo)	0.369 (Mo)	

Table S4. ICP OES analysis of the electrolyte used for electro-activation (7.2 M NaOH) as well as analysis of the precipitation formed on the counter electrode. The values in column I-VII are **averaged values** representing the results from 5 activation procedures. Column I represents the mass loss of the steel sample while carrying out the electro activation procedure. Column II presents the volume of the 7.2 M NaOH electrolyte determined after the electro activation procedure. Column III: Ion concentration measured in the 7.2 M NaOH after electro activation procedure. Column IV: Amount of Fe, Co, Mn, Cr and Mo in the 7.2 M NaOH calculated on the basis of the ICP OES results (column III). Column V: Composition of the material deposited on the CE. Column VI: Total amount of detected Fe, Co, Mn, Cr, Mo. Column VII: Total amount of detected material.

	Cationic distribution (at. %)								
Samples	Fe	Со	Cr	Mn	Mo	W	0	K	Р
Со	63.5	17.1%	5.9%	6.7%	1.1%	2.7%	3.0%	0%	0%
	%								
Co-300	4.3%	71.6%	0%	4.4%	0%	0.82%	14.2%	4.3%	0.41%

Table S5. Cationic distribution of Fe, Co, Cr, Mn, Mo, W, O, K, P of samples Co and Co-300 derived from the XPS measurements presented in Figure 4.



compounds ⁵¹⁻⁵³ are indicated by vertical lines as visual aid. (a) O 1s core level spectra. Fitting results for sample Co at peak position 530.199 eV. (b) O 1s core level specta. Fitting results for sample Co-300 at peak positions 529.703 eV and 531.148 eV. (c) Mn 2p core level spectra. Fitting results for sample Co at peak positions 642.424 eV and 654.411 eV. (d) Cr 2p core level spectra. Fitting results for sample Co at peak positions 586.301 eV and 576.644 eV. (e) Mo 3d core level spectra. Fitting results for sample Co at peak positions 227.979 eV and 231.151 eV. (f) Mn 2p core level spectra. Fitting results for sample Co-300 at peak positions 637.399 eV and 653.253 eV. (g) K 2p core level spectra. Fitting results for sample Co-300 at peak positions 292.699 eV and 295.434 eV. (h) W 4f core level spectra. Fitting results for sample Co at peak positions 200 at peak positions 292.699 eV and 231.4029 eV.



Figure S5. High resolution XPS spectra of sample Depos-30. Binding energies of reference compounds ⁵¹ are indicated by vertical lines as visual aid Co 2p core level spectra. Fitting results for sample Depos-30 at peak positions 779.98 eV, 781.101 eV, 786.922 eV, 794.982 eV, 796.201 eV and 802.78 eV

Sample Co-300







Figure S5. EDS spectra (b-c) taken along the cross section (a) of sample Co-300. The concentration of Mn, Mo and W was below the detection limit.







Figure S6. EDS spectra (d-f) taken along the cross section (a) of sample Co-300. The concentration of Mn, Mo and W was below the detection limit.

Sample Depos-30













Figure S7. EDS spectra of sample Depos-30 (b-f) taken along the cross section (a). The concentration of Mn, Mo and W was below the detection limit.



Figure S8. Tafel plots of samples Co, Co-300 and Ir/Ru based on 200 second chronopotentiometry scans at current densities 0.65, 1.33, 2, 2.66, 4, 5.33, 6.66, 8, 10, 13.3, 16.6 and 20 mA/cm² in 0.1 M KOH solution. IR compensation was performed on the basis of the electrolyte resistance (2.5 Ω). The resistance was corrected for 0.5 mm distance between WE and RE from literature values reported for 10 mm RE-WE distance (50 Ω) ⁴⁷.