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Supporting Information

Electrooxidation of a Cobalt based Steel in LiOH: A Non-Noble Metal based Electro-Catalyst suitable for Durable Water-Splitting in Acidic Milieu

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Sample preparation

Preparation of the sample series Co-Cy and Co-300.1

Samples Co (preparation see experimental part of the main text) were used as starting material

Samples Co-300.1.

Pre-treatment: Prior to each surface modification the surface of the metal was cleaned intensively with ethanol and polished with grit 400 SiC sanding paper. Afterwards the surface was rinsed intensively with deionized water and dried under air for 50 min at room temperature. For the electro-oxidation a two-electrode set-up was used consisting of the steel sample as WE, and a platinum wire electrode (4x5 cm) used as CE. The WE (anode) was immersed exactly 2.1 cm deep (around 4.5 cm^2 geometric area), and the CE (cathode) was completely immersed into the electrolyte.

The anodization was performed in 200 mL of 4.8 M NaOH filled in a 300 mL glass beaker under stirring (450 r/min.) using a magnetic stirrer and a stirring bar (21 mm in length, 6 mm in diameter). The electrolyte was prepared as follows: In a 1500 mL glass beaker, 269 g (4.8 mol) of NaOH (VWR, Darmstadt, Germany) were dissolved under stirring and under cooling in 800 g deionized water. Deionized water was added till the final volume reached 1000 mL. The distance between WE and CE was adjusted to 6 mm. A power source (Electra Automatic, Vierssen, Germany) EA-PSI 8360-15T which allows to deliver a constant high current for longer operating time was used for the electrochemical oxidation. The procedure was carried out in current controlled mode. The current was set to 9 A according to ~1875 mA/cm^2 current density. The voltage varied during the electro-activation. At the beginning of the experiment it amounted to around 6.5 V but was reduced over a period of 300 min to around 4.3 V. These data proved to be reliably reproducible for all 4 replicates. If, however, for some reasons the decrease of the voltage is more abrupt, *i.e.* the voltage drops down to 4.3 V earlier, the activation procedure should be stopped when this value is reached. The electro activation procedure should be stopped after 300 min at the latest. The temperature of the electrolyte increased within the first 30 min and reached a value of 323 K. Approximately 2.5 mL of fresh 4.8 M NaOH were added hourly to the electrolysis vessel in order to compensate the loss occurred due to evaporation. After 300 min of electro-activation the CE and the WE were taken out of electrolyte and rinsed intensively with tap water for 15 min and then with deionized water for a further 10 min. Prior to the electrochemical characterization the samples were dried under air at ambient temperature and the weight was determined upon a precise balance (Sartorius 1712, 0.01 mg accuracy). The sample preparation was repeated four times, *i.e.* in total 5 samples of Co-300.1 have been prepared this way (Table 1, column I).

Determination of Faradaic efficiency for OER (Figure 4c) was carried out in close accordance with the procedure described in Schäfer *et al.*, *Energy Environ. Sci*., **2015**, DOI:10.1039/C5EE01601K.

This measurement has been performed with sample Co-Cy after 25000 s of chronopotentiometry (10 mA/cm^2 current density; pH 1) had been applied this specimen.

Faradaic efficiency of OER was calculated by determining the dependence of the oxygen concentration in the electrolyte during the time of chronopotentiometry at constant current. Experimental details see figure caption of Figure 4c. The working compartment was completely sealed with glass stoppers before starting the chronopotentiometry measurement. The results can be taken from Figure 4c.

Impedance spectroscopy

Impedance spectroscopy of the samples was conducted under stirring in 0.05 M H_2SO_4 within frequency range 0.1-50469 Hz with an Autolab PGStat 20 potentiostat, controlled by *FRA* Windows software (Frequency Response Analysis for Windows version *4.9.007*). To ensure accurate results more five measurements were made for each sample at defined potential. The reported results in this paper are average ones of the five derived from each sample. The preparation of the electrolyte as well as the electrode geometry can be taken from below (Electrochemical Measurements).

XPS Spectroscopy

XPS measurements were performed using a PHI 5600ci multitechnique spectrometer equipped with a monochromatic Al Kα source with 0.3 eV full width at half-maximum. The overall resolution of the spectrometer is 1.5% of the pass energy of the analyzer, 0.45 eV in the present case. The measurements were recorded with the sample at room temperature. No argon etching was applied to the samples.

X-Ray Diffraction

XRD patterns of the oxidized samples were obtained by q/2q scans measured in reflection mode by using a PANalytical X’Pert Pro MRD diffractometer equipped with an Eulerian cradle, which was operated with CuKa radiation at 40 kV and 40 mA.

Electron microscopy

The plane-view SEM images of the samples were taken using a Zeiss Auriga scanning electron microscope. Cross sectional analysis (vertical plane imaging) of samples was realized by a dual beam FIB (focused ion beam)-SEM technique. The SEM images of the cross sections were taken using a Zeiss Auriga scanning electron microscope equipped with a Cobra FIB-column and a Ga ion source using the Feature Milling software module for modeling. The accelerating voltage was adjusted to 20 kV and the SEM images were acquired using a secondary electron- or back scatter detector. Further details can be taken from Figure 7.

Gas sorption

Gas sorption experiments (adsorption/desorption) were carried out using a Quantachrome Autosorb AS-1C. Physisorption was determined at 77 K and 100 K for N_2 (Linde Gas, purity > 99.999%) with dynamic p_0-determination via a p_0-cell at p = 760 mmHg and an Oxford Instruments cryostat model Optistat MK1 equipped with an Oxford Instruments controller model ITC 503. Analyses and interpretation of data were carried out utilizing the Quantachrome AS1Win software package, version 2.11. Prior to the determinations, the samples were activated at 100 °C and pressures of $1\cdot10^{-3}$ mbar for 24h and at $1.5\cdot10^{-6}$ mbar for 24h. All samples were treated in the outgas station until outgassing rates were below 3 microns/minute pressure increase and subsequently contacted with He (Linde Gas, purity > 99.999%) before the analyses were carried out. An equilibration time of 10 min per analysis point was used and ten points were recorded each for adsorption and desorption. In total five specimens of each sample have been investigated to guarantee meaningful data

Determination of iron, chromium, molybdenum, manganese, cobalt, nickel, tungsten, titanium, silicon and potassium in the electrolyte used for 50000 s of chronopotentiometry performed at 10 mA/cm^2 with samples Co, Co-300.1 and Co-Cy via ICP-OES (Table S1).

In total three specimens of each sample have been investigated to guarantee meaningful data. The results can be taken from Table S1. 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 228.616 nm (Co), 267.716 nm (Cr), 202.030 nm

(Mo), 257.610 nm (Mn), 216.556 nm (Ni), 209.860 nm (W), 209.860 nm (Ti) and 212.412 nm (Si) by using the axial view mode, and at wavelengths of 239.562 nm (Fe), 670.784 nm (Li) and 766.490 nm (K) by using the radial view mode. The calibration standards were prepared according the matrix of the analyte solution and contained 0.001, 0.01, 1.0 and 10 mg/l of the selected elements.

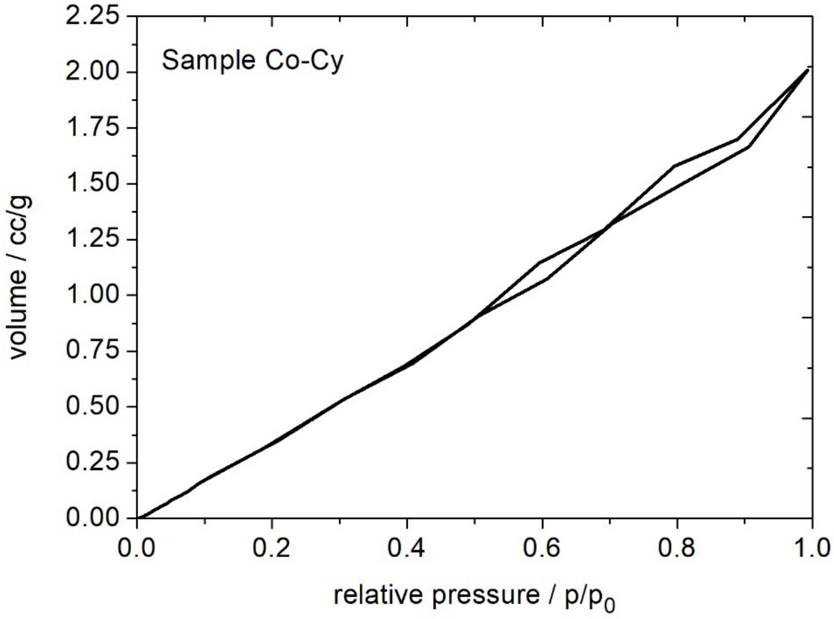

Figure S1. Results from BET measurements. Adsorption/desorption plot of sample Co-Cy Sample gas: N2 (77K). Activation was performed by outgassing for 24 h at 100 °C ($1*10^{-6}$ bar) and by 24 h at 100 °C ($1.5*10^{-9}$ bar); Equilibrium time: 10 min.

Table S1. Outcome of the ICP-OES analysis. Column II presents the mass loss of the steel samples while carrying out chronopotentiometry for 50000 s at 10 mA cm^{-2} in 0.05 M H_2SO_4. Column III presents the volume of the 0.05 M H_2SO_4. Column IV: Ion concentration measured in the electrolyte. Column V: Total amount of detected Co, Cr, Fe, Mo, Mn, Ni, W, Si, K.

I	II	III	IV			V
Sample	**Total Mass loss [mg]**	**V (Electrolyte) [ml]**	**Ion concentration (Electrolyte) [mg/l]**			**∑detected ions in the electrolyte [mg]**
Co	19.78	141.98	18.16 (Co) 16.07 (Cr) 115.31 (Fe)	2.31 (Mo) 0.77 (Mn) 0.21 (Ni)	5.36 (W) 0.04 (Si)	22.465
Co-Cy	7.82	148.7	6.82 (Co) 6.23 (Cr) 43.13 (Fe)	0.924 (Mo) 0.231 (Mn) 0.095 (Ni)	2.24 (W) 0 (Si)	8.191
Co-300.1	18.99	134.88	13.79 (Co) 12.57 (Cr) 86.89 (Fe)	2.50 (Mo) 0.625 (Mn) 0.217 (Ni)	6.86 (W) 0.048 (Si) 0.192 (K)	16.68

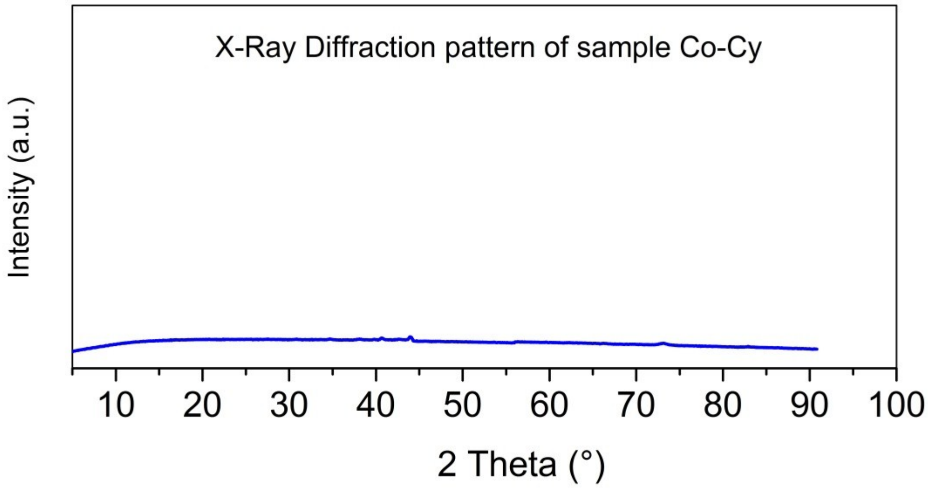

Figure S2. X-Ray Diffraction pattern acquired by a theta/2theta scan in reflection of sample Co-Cy.

Table S2. Cationic distribution of Fe, Co, Cr, Mn, Mo, W, O, K, P of samples Co and Co-Cy derived from the XPS measurements presented in Figure 5a.

	Cationic distribution (at. %)								
Samples	Fe	Co	Cr	Mn	Mo	W	O	K	P
Co	63.5 %	17.1%	5.9%	6.7%	1.1%	2.7%	3.0%	0%	0%
Co-Cy	89%	0%	9.78%	0%	1.22%	0%	0%	0%	0%

Table S3. Weight loss during electro oxidation resulting in samples Co-Cy. 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.

Sample	**Mass (g)**	**Mass difference (g)**
Co-Cy (1)	5.71199 (5.71206)	-0.00007
Co-Cy (2)	6.49821 (6.49811)	+0.00010
Co-Cy (3)	5.87196 (5.87186)	+0.00010