Supporting Information

Particle Size-Controlled Synthesis of High-Performance MnCo-based Materials for Alkaline OER at Fluctuating Potentials

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1. Experimental Procedures

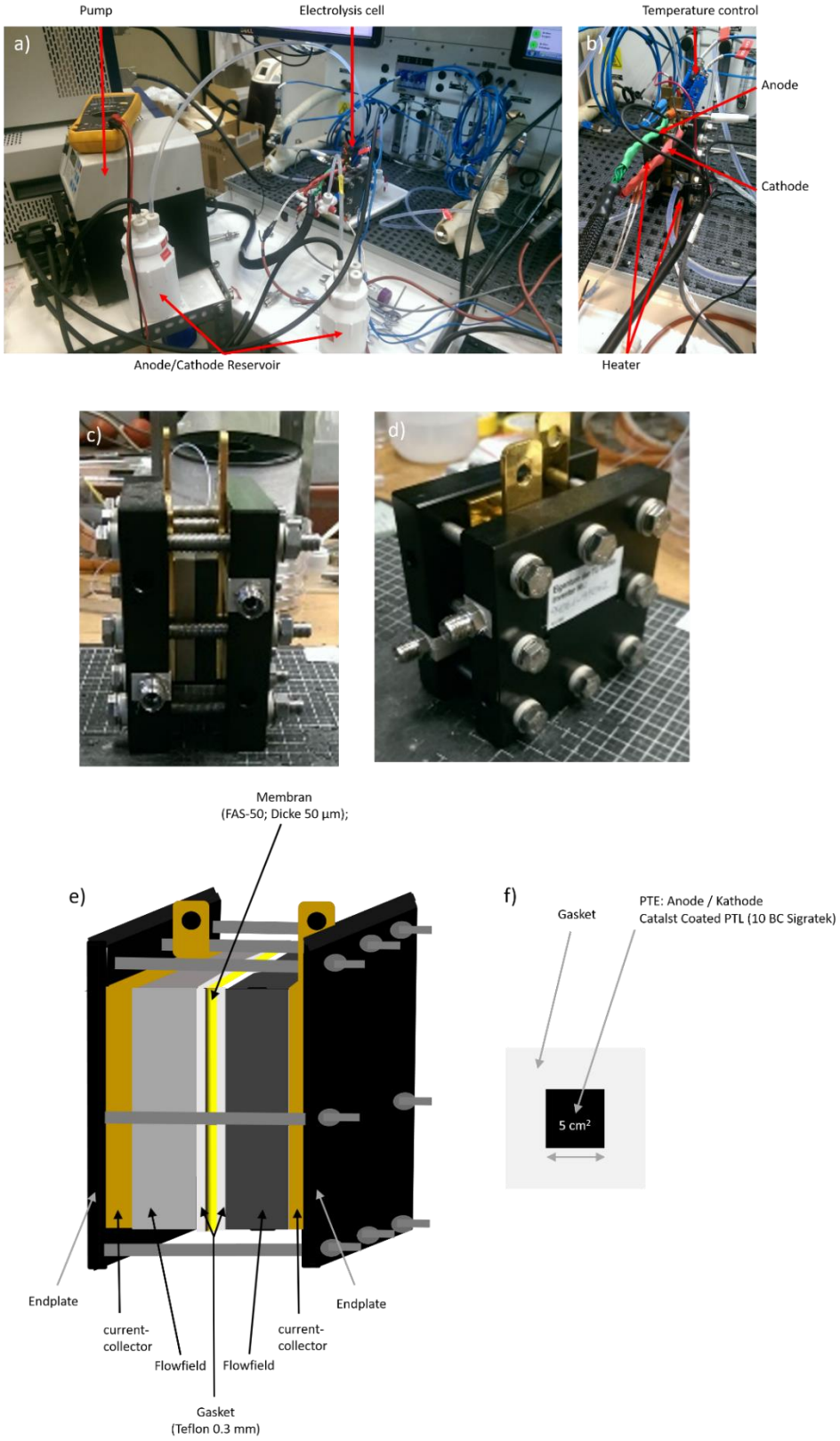

Figure S1: a, b) Depiction of the electrolyser setup, including electrolyte reservoirs and pump. c, d) Detailed view of the used electrolysis cell. e, f) cell components and PTL preparation.

Table S1: Protocol applied for the full cell measurements.

WE testing
CV: 50 cycles, 1.1 V – 1.7 V. 50 mV s^{-1}
CA: 1.83 V, 1 h
Loop:
MP: 1.3 V – 2.2 V, 100 mV potential steps, 180 sec each, average over the last 20 sec.
PEIS: 1.6 V
Loop: Technique 3, two times

2. Characterization of the Electrode Materials

2.1 SEM images of MnCo-pH3, MnCo-pH5.5 und MnCo-pH7

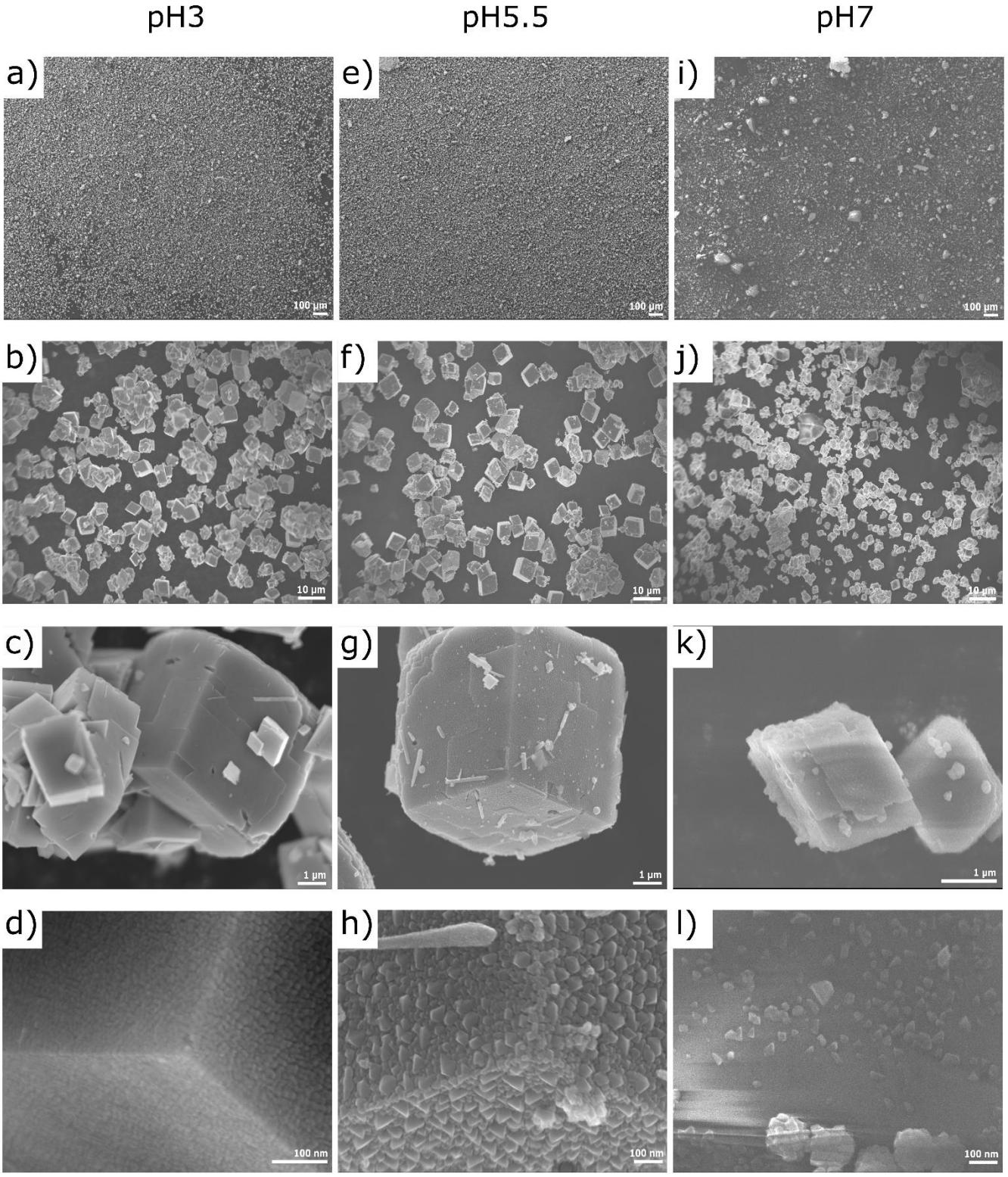

Figure S2: SEM images of MnCo-pH3, MnCo-pH5,5 und MnCo-pH7. (a, e, i) overview images, 50x magnification, (b, f, j) particle size distribution at 10 kV, 1000x magnification 10 µm, (c, g, k) 10 kV, 10,000x magnification 1 µm, (d, h, l) 10 kV, 200000x magnification 0.1 µm.

2.2 N_2-Physisorption

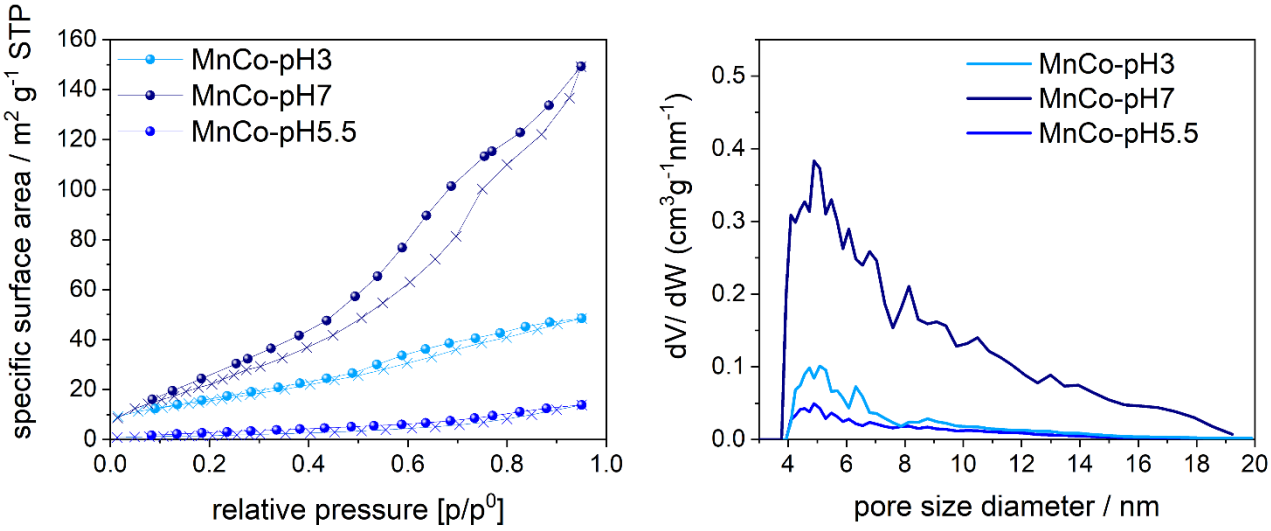

Figure S3: a) N_2-physisorption isotherms and b) corresponding pore size distributions of the synthesised MnCo-materials at different pH values.

2.3 Powder XRD and Rietveld refinement

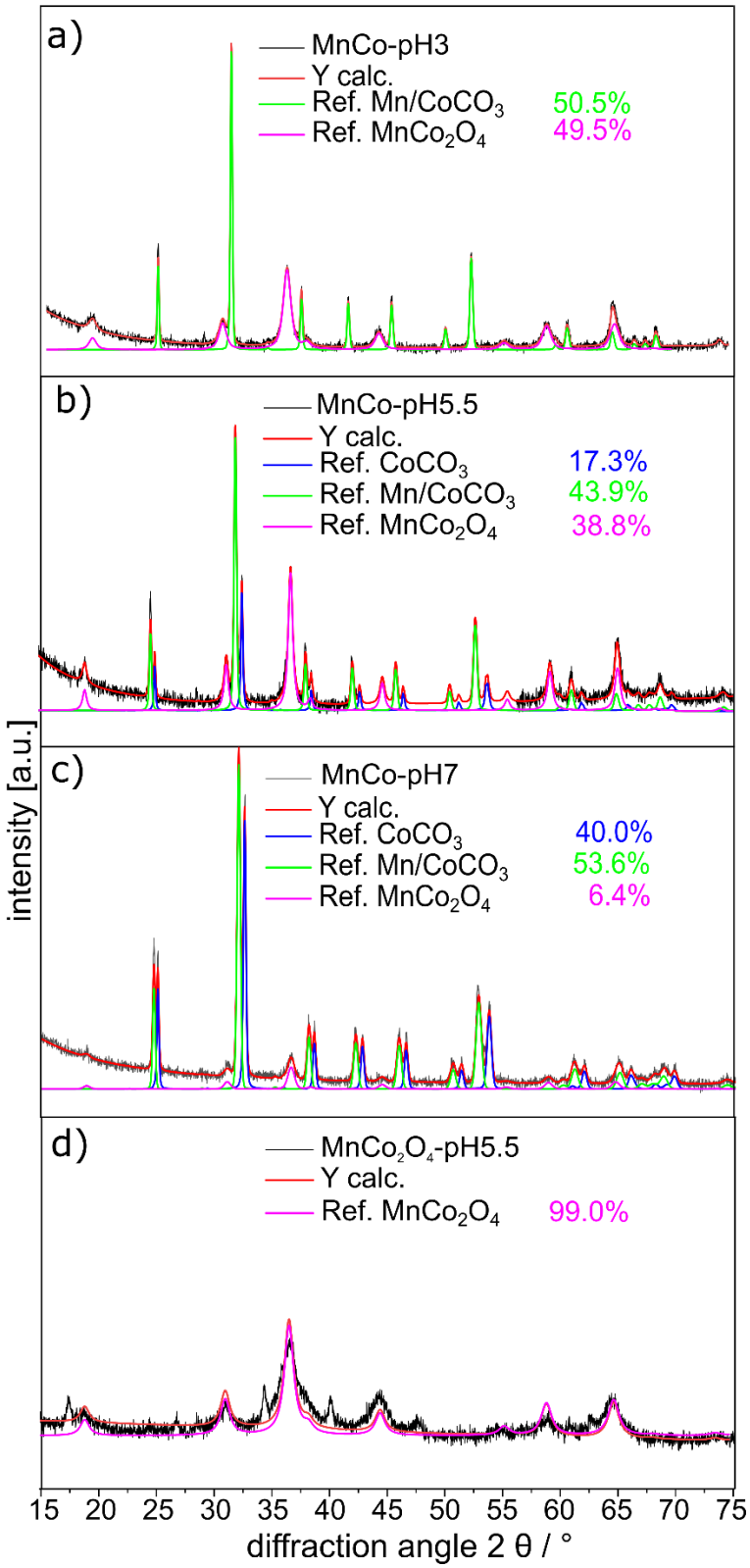

Figure S4: Powder XRD patterns and corresponding Rietveld refinements of the synthesised MnCo-materials at different pH values and the reference sample consisting of 100 % $MnCo_2O_4$ spinel phase.

2.4 XPS

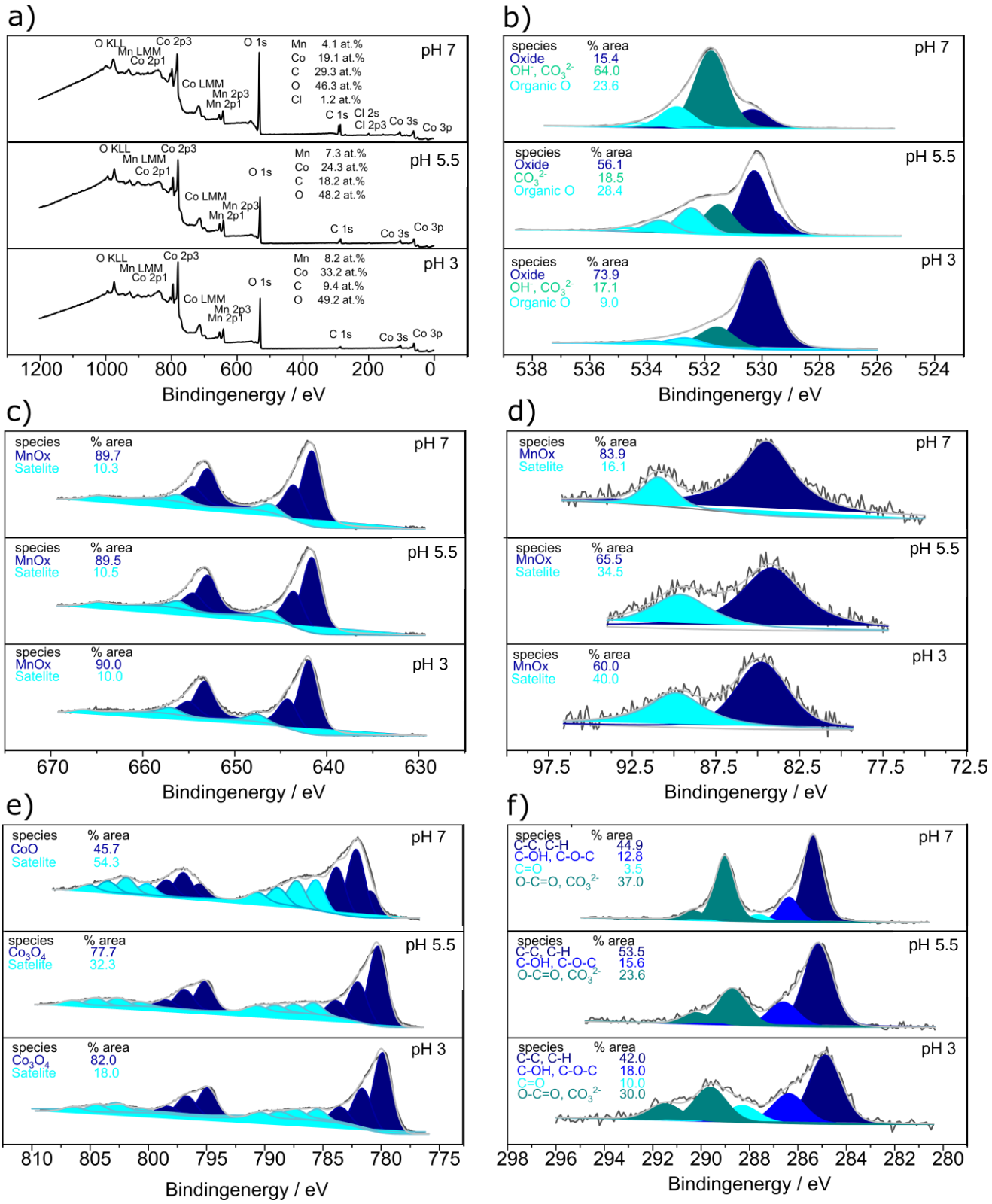

Figure S5: a) XPS survey spectra and b-f) element spectra for the MnCo-materials synthesised at pH 3, 5.5 and 7 (b) O 1s, c) Mn 2p, d) Mn 3s, e) Co 2p and f) C1s). The XPS spectra were referenced to C 1s with a binding energy of 285.0 eV.

3. Electrochemical characterization of the Electrode Materials

3.1 Comparison of MnCo-pH7 to IrO_2 and RuO_2 in linear sweep voltammetry

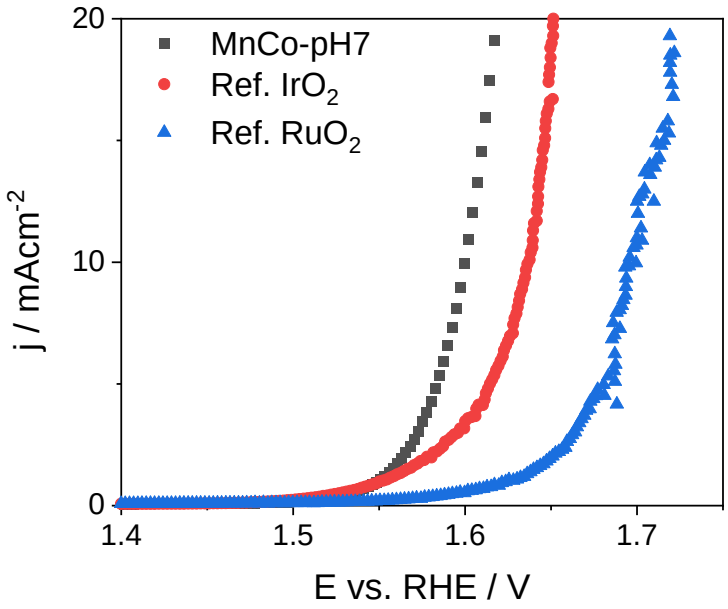

Figure S6: Activity plot: current density *vs.* potential (*vs.* RHE) for MnCo-pH7 compared to IrO_2 and RuO_2.

3.2 Double layer capacitance c_{DL} in 1.0 M KOH

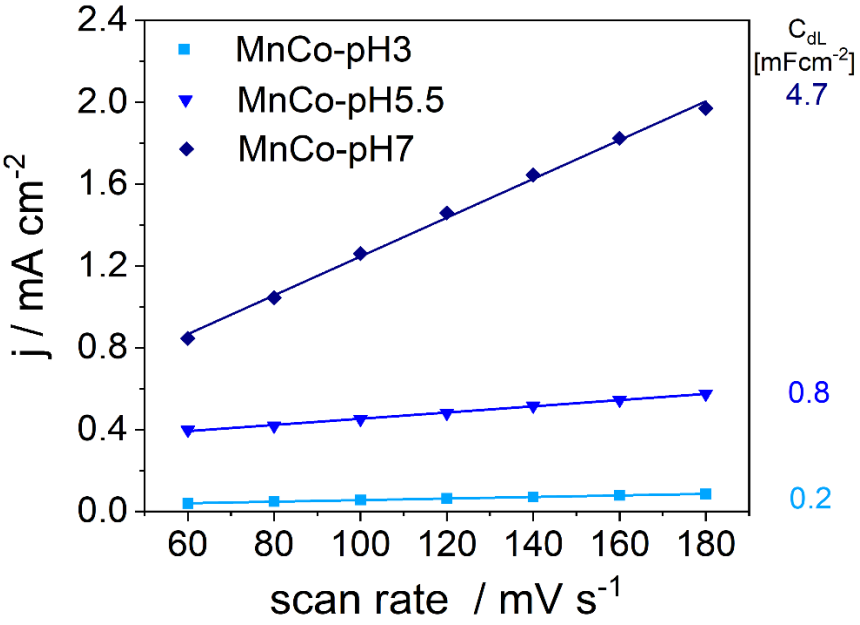

Figure S7: Double layer capacitance c_{DL} measurements for the determination of the electrochemical surface area *ECSA*.

3.3. Calculation of the electrochemical surface area *ECSA*

$$ECSA = r_F \cdot S_g \quad \text{(S1)}$$

$$r_F = \frac{c_{DL}}{c_S} \quad \text{(S2)}$$

$ECSA$ electrochemical surface area [cm^2]

r_F roughness factor [-]

S_g geometric surface area of the working electrode [cm^2]
in our case: 0.1396 cm^2

c_{DL} double layer capacitance [mF·cm^{-2}]

c_s specific capacitance [mF·cm^{-2}]
0.04 F·cm^{-2} were used as typically observed for aqueous NaOH solutions

3.4 Calculation of the Turnover Frequency *TOF* for Cubic MnCo-Materials

The TOF calculation usually serves as an activity descriptor for an electrocatalyst. In general, the *TOF* is defined as the number of moles of reactant consumed $n(substrate)_0 - n(substrate)_t$ divided by mole of catalyst $n(cat)$ per time of reaction *t* (see eq. S3).

$$TOF = \frac{n(substrate)_0 - n(substrate)_t}{n(cat) \cdot t} \quad \text{(S3)}$$

$$TOF(OER) = \frac{n(O_2)}{n(active\ metal\ centers)} \quad \text{(S4)}$$

As given in eq. S4, in the case of the OER, the amount of formed oxygen $n(O_2)$ as well as the fraction of active metal centres at the surface have to be determined. $n(O_2)$ can be calculated as follows: The obtained current density *j* of the LSV polarization measurement is multiplied using the Avogadro constant (N_A = 6.023·10^{23} molecules O_2) and divided by the number of transferred electrons per O_2 molecule times the Faraday constant (F = 96485.3 C; 1 C = 1000 mAs) (eq. S5).

$$n(O_2) = \frac{j \cdot N_A}{4 \cdot F} \quad \text{(S5)}$$

$$n(O_2) = 10\ \frac{mA}{cm^2}\ x\ \frac{1\ A}{1000\ mA}\ x\ \frac{1\frac{C}{S}}{1A}\ x\ \frac{1\ mol\ \ e^-}{96453.8\ C}\ x\ \frac{1\ mol\ O_2}{4\ mol\ \ e^-}\ x\ \frac{6.023 * 10^{23}\ molecul\ O_2}{1\ mol\ O_2}$$

$$= 10\ \frac{mA}{cm^2}\ x\ \frac{6.023*10^{23}}{4\ mol * 1000\ mA * 96453.8\ C}\ =\ \mathbf{1.56 * 10^{16}\ molecules\ O_2}$$

The herein presented approach relies on a geometric model for the calculation of the *TOF* at a certain overpotential η. The approach assumes that all surface atoms of the catalytically active phase are active centres. The calculated roughness factors R_f were used for the calculation of the TOF. The loading of the catalyst on the working electrode amounts to 0.000394 g·cm^{-2}. The effective electrode area for the measurements amounts to 0.1396 cm^2.

For MnCo-5.5, a composition of 17.4 % $CoCO_3$, 43.7 % $(Mn/Co)CO_3$ and 38.9 % $MnCo_2O_4$ was determined *via* Rietveld analysis. Accordingly, an average molar mass of 163.89 g·mol^{-1} results. The fraction of total Co atoms amounts to 39.0 % of the material. Hence, the total number of Co atoms is 7.88·10^{16} atoms per electrode area:

$$0.39 \cdot \frac{0.000055\ \frac{g}{0.1396\ cm^2}}{163.69\ \frac{g}{mol}} \cdot 6.023 \cdot 10^{23} \frac{1}{mol} = 7.88 \cdot 10^{16}\ \frac{Co\ atoms}{0.1396\ cm^2}$$

The average edge length was determined to be 3.2 µm for MnCo-5.5. A density of 3.6 g·cm^{-3} for the synthesised MnCo materials was obtained using a pycnometer. Considering the density of the material and the average edge length of the cubes, a mass of 1.18·10^{-10} g per cube can be calculated. This corresponds to a number of 4.33·10^{11} atoms per cube.

Using a density of 3.6 g·cm^{-3}, a volume density of 1.32·10^{22} atoms·cm^{-3} can be calculated. From this volume density, a density of 5.59·10^{14} atoms·cm^{-2} results. Accordingly, a surface-to-volume ratio of 7.93·10^{-4} can be determined:

$$\frac{6 \cdot 5.59 \cdot 10^{14}\ \frac{atoms}{cm^2} \cdot (3.2 \cdot 10^{-4}\ cm)^2}{1.32 \cdot 10^{22}\ \frac{atoms}{cm^3} \cdot (3.2 \cdot 10^{-4}\ cm)^3} = 7.93 \cdot 10^{-4}$$

By taking XPS results into account (24.3 at.-% Co), a number of 8.35·10^7 surface Co atoms per cube can be calculated.

An average edge length of 3.2 µm implies a number of 4.66·10^5 cubes per electrode area. The total number of surface Co atoms per electrode area thus amounts to 3.89·10^{13}. This number can now be compared to the total number of Co atoms per electrode area. Roughly every 5190th Co atom can be treated as exposed at the surface of the cubes and is thus considered for the calculation of the corresponding *TOF* values :

$$\textit{TOF @ 1.6 V vs. RHE (MnCo-5.5)} = \frac{\frac{5.4\ mA\ cm^{-2}}{10\ mA\ cm^{-2}} \cdot 1.56 \cdot 10^{16}\ molecules\ O_2}{3.89*10^{13}\ surface\ Co\ atoms \cdot 32} = \mathbf{6.8\ s^{-1}}$$

3.5 Tafel and Nyquist plots for Cubic MnCo-Materials

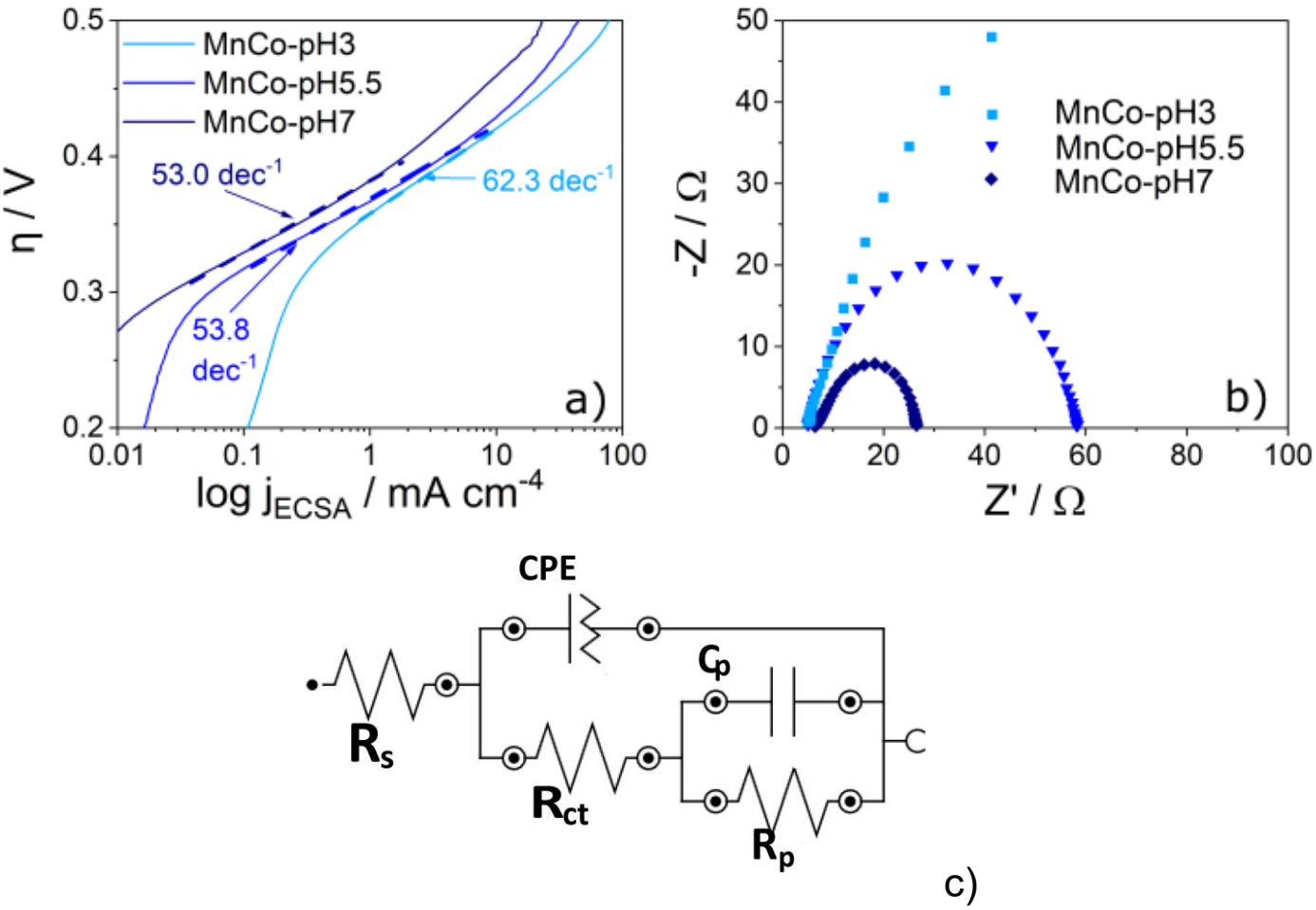

Figure S8: a) Tafel plots (η vs. log(j)) (conditions: scan rate 10 mV/s, 1600 rpm, 1 M KOH), b) Nyquist plots in a frequency range between 0.05 Hz to 100 kHz obtained from electrochemical impedance measurements (conditions: scan rate 10 mV/s, 1600 rpm, 1 M KOH at 0.6 V *vs. RHE*) and c) equivalent circuit diagram (dual constant equivalent circuit, where: R_S = solution resistance, *CPE* = constant phase element related to layer capacitance, R_{CT} = charge transfer resistance, C_p / R_p = capacitance and resistance related to oxygen adsorption).

3.6 Polarisation curves of the full-cell measurement of MnCo-materials

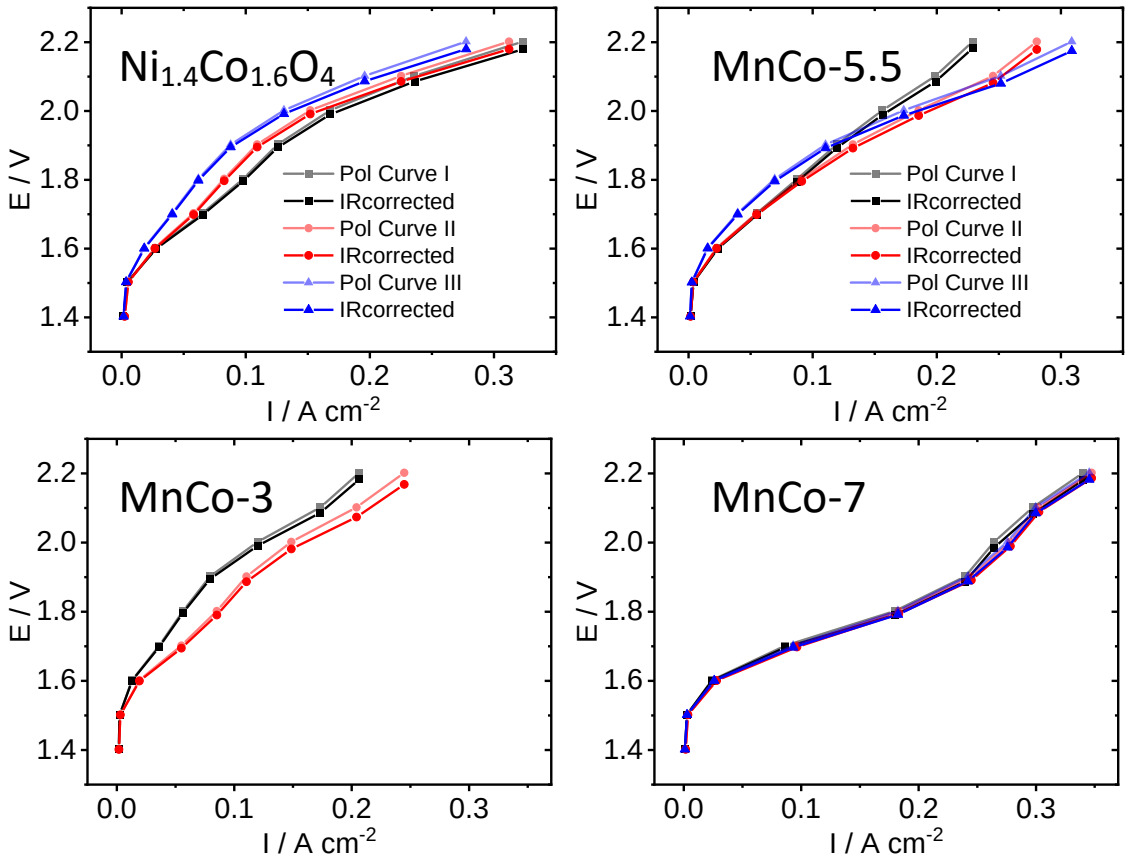

Figure S9: Polarisation curves for synthesised electrocatalysts.

4. Characterisation of the spent MnCo-pH7 catalyst

4.1. XPS Analysis

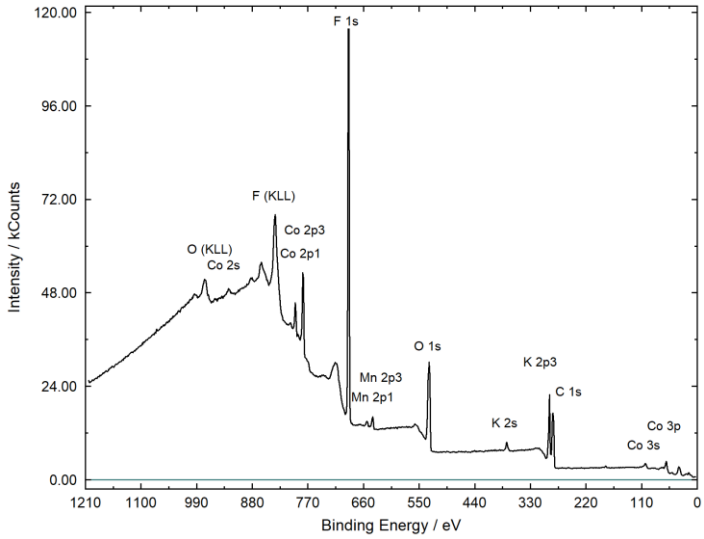

Figure S10: XPS survey spectrum of MnCo-pH7 after OER testing in an electrolyser setup using 1.0 M KOH as electrolyte at 333 K. The XPS spectra were referenced to C 1s with a binding energy of 285.0 eV.

Table S2: Summary of the elements present at the electrode surface after electrochemical test in an electrolyser setup applying 1.0 M KOH as electrolyte.

Peak name	E_B [eV]	Quantity [at.%]
Co 2p	780	3.98
Mn 2p	642	0.71
F 1s	690	40.51
O 1s	530	22
C 1s	285	27.03
K 2p	292	5.77

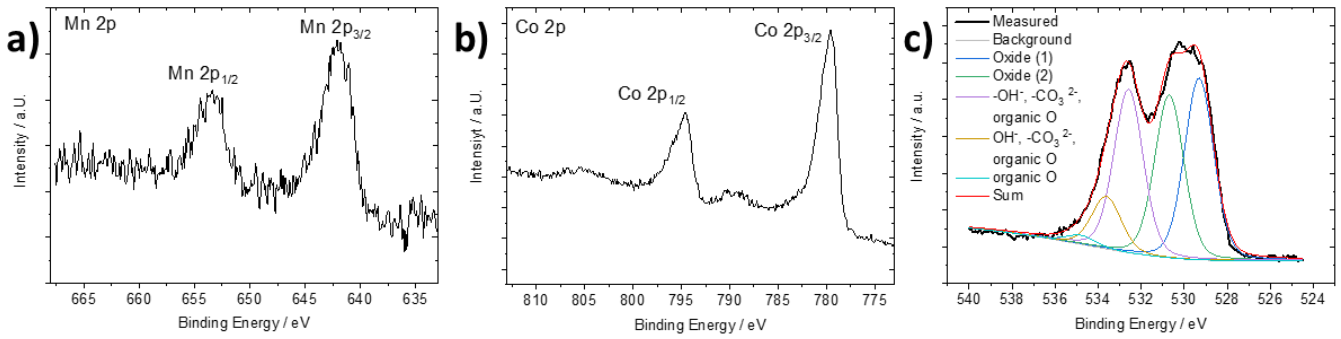

Figure S11: XPS element spectra of a) Mn 2p, b) Co 2p and c) O 1s. The XPS spectra were referenced to C 1s with a binding energy of 285.0 eV.