Supporting Information

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

Cornelia Broicher ‡, Malte Klingenhof ‡ ‡, Marvin Frisch ‡ ‡, Sören Dresp ‡ ‡, Nikolas Mao Kubo †, Jens Artz †, Jörg Radnik ‡ ‡ ‡, Stefan Palkovits †, Anna Katharina Beine ‡ ‡ ‡ ‡, Peter Strasser ‡ ‡ ‡ ‡ and Regina Palkovits ‡ ‡ ‡ ‡ ‡ ‡

‡ The authors contributed equally.
† Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany.
‡ ‡ Department of Chemistry, Chemical and Materials Engineering Division, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany.
‡ ‡ ‡ Bundesanstalt für Materialforschung und -prüfung, BAM, Unter den Eichen 44-46, 12203 Berlin, Germany.
‡ ‡ ‡ ‡ Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany.

Corresponding Authors
palkovits@itmc.rwth-aachen.de
pstrasser@tu-berlin.de
katharina.beine@cec.mpg.de

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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$_2$O$_4$ spinel phase.
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

![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

![Double layer capacitance $c_{DL}$ measurements for the determination of the electrochemical surface area ECSA.](image)
3.3. Calculation of the electrochemical surface area $ECSA$

$$ECSA = r_F \cdot S_g$$  \hspace{1cm} (S1)

$$r_F = \frac{c_{DL}}{c_s}$$  \hspace{1cm} (S2)

$ECSA$  \hspace{0.5cm} \text{electrochemical surface area [cm$^2$]}

$r_F$  \hspace{0.5cm} \text{roughness factor [-]}

$S_g$  \hspace{0.5cm} \text{geometric surface area of the working electrode [cm$^2$]}

in our case: 0.1396 cm$^2$

$c_{DL}$  \hspace{0.5cm} \text{double layer capacitance [mF·cm$^{-2}$]}

$c_s$  \hspace{0.5cm} \text{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).

$$TOF = \frac{n(substrate)_0 - n(substrate)_t}{n(cat) \cdot t}$$ \hspace{1cm} (S3)

$$TOF(OER) = \frac{n(O_2)}{n(\text{active metal centers})}$$ \hspace{1cm} (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 ($N_A = 6.023\cdot10^{23}$ 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).

$$n(O_2) = \frac{j \cdot N_A}{4 \cdot F}$$ \hspace{1cm} (S5)

$$n(O_2) = 10 \frac{mA}{cm^2} \cdot \frac{1 A}{1000 mA} \cdot \frac{1 C}{1 A} \cdot \frac{1 mol \ e^-}{96453.8 C} \cdot \frac{1 mol O_2}{4 mol \ e^-} \cdot \frac{6.023 \cdot 10^{23} \ text{molecule O}_2}{1 mol O_2}$$
\[
= 10 \text{ mA cm}^{-2} \left( \frac{6.023 \times 10^{23}}{4 \text{ mol} \cdot 1000 \text{ mA} \cdot 96453.8 \text{ C}} \right) = 1.56 \times 10^{16} \text{ molecules } O_2
\]

The herein presented approach relies on a geometric model for the calculation of the TOF at a certain overpotential \( \eta \). 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\(_2\)O\(_4\) 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 \times 10^{16} atoms per electrode area:

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

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 \times 10^{-10} g per cube can be calculated. This corresponds to a number of 4.33 \times 10^{11} atoms per cube.

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

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

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

An average edge length of 3.2 µm implies a number of 4.66 \times 10^5 cubes per electrode area. The total number of surface Co atoms per electrode area thus amounts to 3.89 \times 10^{13}. This number can now be compared to the total number of Co atoms per electrode area. Roughly every 5190\(^{th}\) 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:

\[
\text{TOF @ 1.6 V vs. RHE (MnCo-5.5)} = \frac{5.4 \text{ mA cm}^{-2}}{10 \text{ mA cm}^{-2}} \cdot \frac{1.56 \times 10^{16} \text{ molecules } O_2}{3.89 \times 10^{13} \text{ surface Co atoms} \cdot 32} = 6.8 \text{ s}^{-1}
\]
3.5 Tafel and Nyquist plots for Cubic MnCo-Materials

Figure S8: a) Tafel plots ($\eta$ 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, 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

![Graphs showing polarisation curves for different MnCo materials](image)

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.