Supporting Information: P-type Cobaltite Oxide Spinel Enables Efficient Electrocatalytic Oxygen Evolution Reaction

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• Figure S24: Gas-chromatogram (He) of the anode headspace before/after 1h electrolysis.
Additional tables and equations

Table 1 FWHM analysis of p-doped Zn-Co spinels.

| substrate                  | peak spinel (222) / 2θ | FWHM / 2θ | τ° / nm |
|----------------------------|------------------------|-----------|---------|
| sapphire                   | 38.0 deg               | 0.25 deg  | 31.8    |
| rutile                     | 38.092 deg             | 0.25 deg  | 32      |
| Ti-mesh (native TiO₂)      | 38.092 deg             | 0.28 deg  | 28.6    |
| Al:ZnO (wurtzite)          | 38.3 deg               | 0.39 deg  | 21      |

*Scherrer analysis.

Table 2 Electrochemical impedance spectra of electrolysis cell.

| WE                  | CE   | R ele. / Ω cm⁻² | R me. / Ω cm⁻² | C / μF cm⁻² |
|---------------------|------|-----------------|----------------|-------------|
| Pt                  | Pt   | 1.8             | 16             | 27          |
| Zn₁.₂Co₁.₈O₃.₅/Ti-mesh* | Ni   | 2.0             | 16             | 21.3        |

* Including Ti-corrosion effects. ** WE = working electrode, CE = counter electrode, ele. = electrolyte, me. = membrane.

Table 3 Statistical data.

| Anode                   | η av. / V | η av. / V | η min. / V | standard deviation / mV |
|-------------------------|-----------|-----------|------------|-------------------------|
| Zn₁.₂Co₁.₈O₃.₅/Ti-mesh  | 0.35      | 0.363     | 0.345      | ±6                      |
| Zn₁.₂Co₁.₈O₃.₅/Al:ZnO   | 0.41      | 0.425     | 0.39       | ±7                      |

* at 10 mA cm⁻²

Appendix: Scherrer analysis

The domain size (τ) is calculated using the Scherrer formula:

\[ \tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \]  

(1)

with the excitation length \( \lambda = 0.15406 \text{ nm} \) (Cu K_{α1}), the shape factor \( K = 0.89 \) (spherical), the Bragg angle \( \theta \) (deg) of the peak and the (radial) peak full width (at half maximum, FWHM, deg, Figure S7).
Fig. S1 Samples used for OER characterization: blank Ti-mesh, Ti-mesh covered with Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ and patterned substrate on sapphire (0001) with Al:ZnO as conducting layer buried under Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ and Au, respectively.

Fig. S2 SEM images of the Ti-mesh: We show the geometric factor of 0.75 (projected versus geometric area).
Fig. S3 Al:ZnO as conductive substrate for OER: high-quality Al:ZnO is co-deposited prior the Zn-Co-O spinel on sapphire (0001). To protect the Al:ZnO from dissolution in alkaline media, the conducting oxide is covered in the center with spinel $\text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5}$ (active area) and, concomitantly, on the edges with Au (schematic in (a)). In (b), the actual electrolysis cell used for characterization is depicted.
Fig. S4 Conductivity of Al:ZnO on sapphire (0001): Prior the catalytic Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$, 200 nm Al:ZnO are deposited (doping at approx. 2% Al) resulting in a conductivity of 1100 S cm$^{-1}$ and a sheet resistance of 45.4 Ω per square.
Fig. S5 Ti-mesh calibration: X-ray diffraction patterns of Ti-mesh with and without Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$. 
Fig. S6 Detailed diffraction patterns of $\text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5}$: (222), (333) and (444) pattern on sapphire and Al:ZnO.
Fig. S7 Comparison of the FWHM/Scherrer analysis: Diffraction peaks of the (222) Zn-Co-O spinel pattern (semi-log scale) on following substrates: TiO$_2$ (rutile, tetragonal) and Al$_2$O$_3$ (sapphire 0001, hexagonal) as the reference substrates; Ti-mesh with native TiO$_2$ and Al:ZnO (on sapphire 0001, hexagonal) used as electrocatalytic anodes. On the bottom, the spinel we include the structure of the Zn-Co-O system and the corresponding full widths according to the diffraction pattern. From that we calculated the average domain size $\tau$ according to equation 1 summarized in Table 1.
Fig. S8 Structure of the Ti-mesh by bright field STEM: (a) the overview displays the homogeneous thick $\text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5}$ on top of the TiO$_2$ covered Ti-mesh. (b) Most of the columnar grains reach from the TiO$_2$ to the surface with diameters in the region from 10-40 nm.
Fig. S9 TEM lattice image of the Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ layer: The lattice fringes of the marked grain and its neighboring grains are well visible in the right-hand high-resolution phase contrast image proving the good crystal quality of the active Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ layer. The average domain size $\tau$ corresponds to the XRD Scherrer analysis (Figure S7 and Table S1).
Fig. S10 X-ray reflection measurement on Hall-specimen: Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ grown on sapphire (0001) for the van-der-Pauw Hall specimen yielding 165 ± 3 nm.
Fig. S11 Electrochemical characterization of Ti/Au (10 nm) / Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$. (a) Cyclic voltammetry and (b) chronopotentiometry for 50 h to test the stability at 10 mA cm$^{-2}$. 

@ $\eta = 0.405$ V
Fig. S12 Ti-corrosion: Cyclic voltammogram reveals an increase of the anodic current after cycling at anodic potentials.
**Fig. S13** Detailed Tafel analysis: Extraction of Tafel slopes in the linear regime of the semilogarithmic Tafel-plots.
Fig. S14 Electrochemical impedance spectroscopy: The electrochemical cell constants ($R_{\text{electrolyte}}$, $R_{\text{membrane}}$, capacitance) are presented in Table 2.

Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$

Pt ref.
**Fig. S15** Linear sweep voltammogram exceeding 500 mA cm$^{-2}$.

**Fig. S16** Current density versus scan rate to determine the electrochemical surface area (ECSA) in organic electrolyte (acetonitrile, 0.1 M TBA-PF$_6$). The measurement was performed at the equilibrium potential of the O$_2$ evolution at +1 V vs. Ag/AgCl (quasi) reference electrode.
Fig. S17 Schematic of the electrochemical H-cell for conducting the electrocatalytic splitting of water.
Fig. S18 Statistical evaluation: Different experiments on electrocatalytic anodes: $\text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5}$ on Ti-mesh and Al:ZnO, respectively.
Fig. S19 XPS survey before/after electrolysis of \( \text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5} \) on titanium: surface composition (Zn:Co at \( \approx 0.65 \)) remains similar after electrolysis of \( \text{O}_2 \) for 50 h.
Step 3.1: Hall measurement (at 300K)

Run-time operator

Sample

| ID       | CoZnOx Spinell |
|----------|----------------|
| Type     | van der Pauw   |
| Thickness| 165            |

Other dimensions

| L_p [mm] |
|----------|
|          |

Hall factor: 1
Max voltage [V]: 100
Max current [mA]: 20
Gate bias voltage [V]: 0

Comment:

Final results

|        | Mean value | Limit  |
|--------|------------|--------|
| \( \mu \) | Hall mobility [cm²/V-s] | 4.7167E-2 |
|        | Carrier type | P |
| \( n \) | Carrier concentration [1/cm³] | 1.4382E21 |
| \( n_{\text{sheet}} \) | Sheet carrier concentration [1/cm²] | 3.0489E16 |
| \( R \) | Hall coefficient [cm²/C] | 4.3399E-3 |
| \( R_{\text{sheet}} \) | Sheet Hall coefficient [cm²/C] | 2.0471E2 |
| \( \rho \) | Resistivity [Ω-cm] | 9.2011E-2 |
| \( \rho_{\text{sheet}} \) | Sheet resistivity [Ω-cm] | 4.3401E3 |
| \( V_H \) | Hall voltage [V] | 1.2800E-6 |
|        | Phase [deg.] | -7.7 |
|        | Worst case Ohmic check correlation (1-3) | 9.9893E-1 |

Measurement comment

**Fig. S20 Summary of Hall measurement:** A LakeShore 8400 Hall measurement system was used to measure the van der Pauw-type specimen of \( \text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5} \) grown on sapphire (0001) (here shown at 300K).

**Fig. S21 Ohmic Check:** Contacting \( \text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5} \) in the van der Pauw geometry shows ohmic linear behavior.
Resistivity measurement

| Setup |  |
|---|---|
| Resistance measurement method: | High resistance |
| Excitation current | Manual |
| Current [mA]: | 1 |
| Current reversal: | Yes |

| General |  |
|---|---|
| Sample geometry: | Geometry averaged |
| Average count: | 10 |
| Wait mode: | Auto |
| Measure current lead voltages: | No |

| Environment |  |
|---|---|
| Start | Finish | Average | Status |
| Date | Monday, November 17, 2021 | Monday, November 17, 2021 | 300.2 | 300.2 | Time out |
| Time | 11:26:36 PM | 11:28:36 PM | 0.0000 | 0.0000 |
| Temperature [K] | 300.2 | 300.2 | 1.0931E-13 | 1.0931E-13 |
| Field [T] | 0.0000 | 0.0000 |
| Gate bias voltage [V] | 0.0000E0 | 0.0000E0 |
| Gate bias current [A] | 4.3397E-13 | 4.3397E-13 |

| Final average | Geometry A | Geometry B |
|---|---|---|
| Resistivity [Ω·cm] | 9.2146E-2 | 9.1875E-2 |
| Sheet resistivity [Ω·cm] | 4.3465E3 | 4.3337E3 |
| F value | 0.99 | 0.99 |

| Intermediate results | Geometry A | Geometry B |
|---|---|---|
| Resistance [Ω] | 8.0865E2 | 1.1277E3 | 8.0570E2 | 1.1251E3 |
| Standard deviation of resistance [Ω] | 1.1460E-2 | 1.6047E-2 | 9.8568E-3 | 1.9360E-2 |
| Voltage [V] | 8.0859E-1 | 1.1276E0 | 8.0565E-1 | 1.1250E0 |
| Standard deviation of voltage [V] | 5.2217E-6 | 6.5738E-6 | 4.2001E-6 | 1.3625E-5 |
| Current [A] | 9.9992E-4 | 9.9991E-4 | 9.9993E-4 | 9.9994E-4 |
| Standard deviation of current [A] | 1.2614E-8 | 1.2979E-8 | 1.1067E-8 | 1.2222E-8 |

| Average measurements (I+) | Geometry A | Geometry B |
|---|---|---|
| Voltage [V] | 8.0934E-1 | 1.1291E0 | 8.0427E-1 | 1.1264E0 |
| Standard deviation of voltage [V] | 7.5468E-6 | 8.4175E-6 | 6.9433E-6 | 1.1666E-5 |
| Current [A] | 1.0000E-3 | 1.0000E-3 | 1.0000E-3 | 1.0000E-3 |
| Standard deviation of current [A] | 2.1591E-8 | 1.3743E-8 | 1.7665E-8 | 1.7115E-8 |
| Current lead voltage [DC V] | N/A | N/A | N/A | N/A |

| Average measurements (I-) | Geometry A | Geometry B |
|---|---|---|
| Voltage [V] | -8.0783E-1 | -1.1261E0 | -8.0703E-1 | -1.1237E0 |
| Standard deviation of voltage [V] | 7.2187E-6 | 1.0100E-5 | 4.7278E-6 | 2.4627E-5 |
| Current [A] | -9.9983E-4 | -9.9982E-4 | -9.9984E-4 | -9.9985E-4 |
| Standard deviation of current [A] | 1.3048E-8 | 2.2022E-8 | 1.3335E-8 | 1.7453E-8 |
| Current lead voltage [DC V] | N/A | N/A | N/A | N/A |

Fig. S22 Resistivity at 300K: 8-fold probing in the van der Pauw geometry to obtain the isotropic resistivity of the 165 nm thick Zn$_{1.2}$Co$_{1.8}$O$_{3.5}$ on sapphire.
Fig. S23 AC-Hall measurement at 300K: the AC-Hall method developed by LakeShore (8400 HMS Series) allows to induce an AC-magnetic sinusoidal sweep of the magnetic field (amplitude maximum at 0.91 T, average at 0.625 T, frequency 100 mHz), while the electric parameters (DC-current, voltage) are measured in DC-mode. Using this, the sensitivity is increased below $0.7 \cdot 10^{-6}$ V (high-sensitivity Hall voltage probing). Details of the measurements at 300K of the 165 nm thick $\text{Zn}_{1.2}\text{Co}_{1.8}\text{O}_{3.5}$ on sapphire are presented.
Fig. S24 Gas-chromatogram (He) of the anode headspace: Before and after composition of the headspace showing the rise of anodically produced $O_2$ gas.

**ratios:**
before: $N_2:O_2 = 6:1$
after: $N_2:O_2 = 2:1$