Discovery of High-Entropy Oxide Electrocatalysts
– From Thin-Film Materials Libraries to Particles

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For each characterization method on each material library (ML), the 342 measurement areas (MAs) arranged in a regular grid were measured to obtain comparable points for high-throughput analysis.

Energy-dispersive X-ray spectroscopy

Maps of the chemical composition of the various elements of the MLs, with the exception of oxygen, were obtained by high-throughput energy dispersive X-ray spectroscopy (EDX). Oxygen was not determined by EDX due to the interfering oxygen signal of the Si/SiO\textsubscript{2} wafer substrate.
Figure S1. Chemical composition gradients of the three permutations at 773 K (a) ML 2-1, b) 2-2, and c) 2-3).
Figure S2. Chemical composition gradients of permutation 1 at a) 573 and b) 773 K (ML 1 and 3).

X-ray diffraction

X-ray diffraction (XRD) angle maps were obtained by plotting the diffraction angle of the most intense plane (311) for all MAs of each ML. All color-coded activity maps use the same color scale range. At each temperature, the entire composition space exhibits a single-phase spinel structure, as well as the synthesized powder catalyst.
**Figure S3.** Phase analysis of the MLs regarding different deposition temperatures. a), c), and e) show exemplary XRD patterns of the three temperature depositions of permutation 1 (ML 1, 2-2, and 3). Reference lines are from Wang et al.\(^1\) b), d), and f) show the corresponding (311) diffraction angle maps.
Figure S4. XRD pattern of synthetized particles. Reference lines for the spinel oxide (black) are from Wang et al.\textsuperscript{1} and for CaCO\textsubscript{3} (green, residues of filter paper) from Wei et al.\textsuperscript{2}

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out to determine the oxygen content of the MLs. For the calculation of the total oxygen content in the material, it is necessary to subtract the carbon-bonded oxygen from the total oxygen. For this purpose, the amount of carbon-oxygen species was determined from the C 1s spectrum.

Table S1. Peak positions from the XPS analysis.

| Element | Orbital | ML 2-1 MA 259 | ML 2-2 MA 155 | ML 2-3 MA 018 |
|---------|---------|---------------|---------------|---------------|
| Cr\textsuperscript{3} | 2p1/2 | 586.1 | 586.1 | 586.2 |
|          | 2p3/2 | 576.4 | 576.5 | 576.5 |
| Mn\textsuperscript{4} | 2p1/2 | 653.5 | 653.3 | 653.4 |
|          | 2p3/2 | 641.9 | 642.0 | 641.9 |
| Fe\textsuperscript{5} | 2p1/2 | 724.3 | 724.2 | 724.0 |
|          | 2p3/2 sat. | 731.7 | 731.6 | 731.5 |
|          | 2p3/2 | 711.3 | 711.3 | 711.6 |
|          | 2p3/2 sat. | 718.5 | 718.6 | 718.5 |
| Co\textsuperscript{6} | 2p1/2 | 796.2 | 795.9 | 796.0 |
|          | 2p1/2 sat. | 802.6 | 802.7 | 802.8 |
|          | 2p3/2 | 780.5 | 780.4 | 780.6 |
|          | 2p3/2 sat. | 786.4 | 786.3 | 786.5 |
| Ni\textsuperscript{7} | 2p1/2 | 872.2 | 872.6 | 872.5 |
|          | 2p1/2 sat. | 879.4 | 879.9 | 879.8 |
|          | 2p3/2 | 854.6 | 854.8 | 854.7 |
|          | 2p3/2 sat. | 861.2 | 861.4 | 861.4 |
| O\textsuperscript{3,8} | Lattice | 529.9 | 529.9 | 529.9 |
|          | Hydroxide | 531.4 | 531.4 | 531.4 |
|          | Organic | 532.7 | 532.7 | 532.7 |
| C\textsuperscript{9} | C-C, C-H | 284.8 | 284.8 | 284.8 |
|          | C-OH, C-O-C | 286.3 | 286.3 | 286.3 |
|          | C=O | 287.8 | 287.8 | 287.8 |
|          | O-C=O | 288.5 | 288.5 | 288.5 |
**Figure S5.** XPS spectra of ML 2-1 MA 259. a)-e) show the 2p spectra of the different metals, f) shows the 1s spectrum of oxygen.

**Figure S6.** XPS spectra of ML 2-3 MA 018. a)-e) show the 2p spectra of the different metals, f) shows the 1s spectrum of oxygen.
Resistance

The resistance was determined by 4-point probe measurements of the MLs (variant A). The low electrical conductivity of the oxide thin films lead to high resistance and MAs beyond the measurement range (> 211 MΩ). All color-coded activity maps use the same color scale range. Due to the high resistance, the OER activity measurements were performed on 50 nm thin films with an underlying electrode layer (variant B), each being a replication of the corresponding 500 nm thin film (A), with identical chemical composition gradients.

Scanning electron microscopy analysis

The surface morphology investigated via scanning electron microscopy (SEM) did not show significant changes within a ML. The most rough ML 3 exhibits the lowest electrocatalytic activity results, despite the resulting higher surface area. No significant changes were observed in the morphology between the permutated MLs either.

Figure S7. C 1s XPS spectrum of a) ML-2-1 MA 259, b) ML-2-2 MA 155, and c) ML-2-3 MA 018 with peak fitting.⁹

Figure S8. Resistance maps of the three permutations at 773 K (a) ML-2-1, b) 2-2, and c) 2-3) and permutation 1 at d) 573 and e) 773 K (ML 1 and 3) with cathode positions in the edges.
Figure S9. SEM analysis of several ML areas from the depositions at different temperatures. The images were taken with 30k magnification. The white bar at the lower right edge of each image represents 100 nm. a) ML scheme with the positions of the sputter targets Fe, Cr, MnNi, and Co during the deposition process and the positions of the SEM images, marked by numbers. The MLs were prepared at b) 573 K (ML 1), c) 773 K (ML 2-2), and d) 973 K (ML 3).
Figure S10. SEM analysis of several ML areas from the different permutation depositions. The images were taken with 30k magnification. The white bar at the lower right edge of each image represents 100 nm. The MLs were prepared at 773 K and with a) permutation 1 (ML 2-1), a) permutation 2 (ML 2-2), and c) permutation 3 (ML 2-3). Each sub-image shows also a ML scheme with the positions of the sputter targets Fe, Cr, MnNi, and Co during the deposition process and the positions of the SEM images, marked by numbers.
High-throughput electrochemical measurements

Electrochemical activity maps were obtained by plotting the current density values at a chosen potential for all MAs of each ML. All activity maps use the value of the current density at 1.7 V vs RHE. This potential is on the one hand high enough to observe significant oxygen evolution reaction (OER) currents, and on the other hand sufficiently low to avoid possible limitation of the currents by slow diffusion of the reactants. All color-coded activity maps use the same color scale range, which shows that in total the highest current was obtained for the sample prepared at 773 K with target permutation 2 (ML 2-2), and within this sample compositions containing significant amounts of Cr, Co and Ni (ca. 20-25 at.%) exhibit the highest OER activity.
Figure S11. Electrochemical activity of the MLs regarding different deposition temperatures. a), c), and e) show all linear sweep voltammetry curves obtained from scanning droplet cell measurements of the three temperature depositions with permutation 1 (ML 1, 2-1, and 3). b), d), and f) show the corresponding current density maps at 1.7 V vs RHE.
Figure S12. Electrochemical activity of the MLs regarding different target permutations. a), c), and e) show all linear sweep voltammetry curves obtained from scanning droplet cell measurements of the three permutations at 773 K (ML 2-1, 2-2, and 2-3). b), d), and f) show the corresponding current density maps at 1.7 V vs RHE.
Figure S13. Comparison of the electrocatalytic OER activity of a) most similar compositions prepared at different temperatures and b) most active compositions from different samples.

Transmission electron microscopy analysis of the particles

The transmission electron microscopy (TEM) analysis of the particles shows an equal distribution of the different elements. The EDX line scan through the particle confirms this.

Figure S14. Cantor alloy oxide particles prepared by aerosol synthesis. EDX element distribution maps of synthesized particles and EDX line scan through the particle.
Aerosol-based particle synthesis

A homogeneous precursor solution containing metal nitrates with desired metal ratio is continuously stirred and transported with the use of syringe pump to the spray nozzle where it is mixed with compressed air. Next, precursor solution is sprayed onto the deflector plate to create an aerosol with droplets containing metal salts in set before ratios. With the use of a vacuum pump, aerosol droplets are transferred via the tube going through the tube furnace where the solvent evaporates. At the end of the tubing dry particles are collected on the filter paper, transferred subsequently to the ceramic boat placed in the oven (500°C) in the flow of oxygen to burn filter papers and oxidize the remaining particles.

Determination of the double-layer capacitance of electrode with Cr_{23}Mn_{19}Fe_{18}Co_{25}Ni_{15}-O_x particles

Double-layer capacitance of the electrode with the powder derived from the hit composition was determined by recording cyclic voltammograms at various scan rates (100, 250, 500, 750, 1000, 2500 mV/s) within the potential range where no redox processes take place (0.84 V to 1.35 V vs. RHE), extracting from them the values of cathodic and anodic current and subsequently obtaining double layer capacitance from the slope of current vs. scan rate plot. For each scan rate 20 cyclic voltammograms were recorded and the current values were extracted from the last one.
Figure S16. a) Current as a function of scan rate. Dashed lines represent linear regression fits. The resulting double-layer capacitance ($C_{DL}$) values are shown with corresponding $R^2$ values.

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