NANO MICRO small

Supporting Information

for *Small,* DOI: 10.1002/smll.202205412

Sol-Gel-Derived Ordered Mesoporous High Entropy Spinel Ferrites and Assessment of Their Photoelectrochemical and Electrocatalytic Water Splitting Performance

Marcus Einert, Arslan Waheed, Stefan Lauterbach, Maximilian Mellin, Marcus Rohnke, Lysander Q. Wagner, Julia Gallenberger, Chuanmu Tian, Bernd M. Smarsly, Wolfram Jaegermann, Franziska Hess, Helmut Schlaad, and Jan P. Hofmann**

Supporting Information

Sol-gel-derived Ordered Mesoporous High Entropy Spinel Ferrites and Assessment of their Photoelectrochemical and Electrocatalytic Water Splitting Performance

Marcus Einert[1], Arslan Waheed[1], Stefan Lauterbach[2], Maximilian Mellin[1], Marcus Rohnke[3], Lysander Q. Wagner[3,4], Julia Gallenberger[1], Chuanmu Tian[1], Bernd M. Smarsly[3,4], Wolfram Jaegermann[1], Franziska Hess,[5] Helmut Schlaad[6], and Jan P. Hofmann[1*]*

1 Surface Science Laboratory, Department of Materials and Earth Sciences, Technical University of Darmstadt, Otto-Berndt-Strasse 3, 64287 Darmstadt, Germany

2 Institute for Applied Geosciences, Geomaterial Science, Technical University of Darmstadt, Schnittspahnstrasse 9, 64287 Darmstadt, Germany

3 Center for Materials Research, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

4 Institute for Physical Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

5 Institute of Chemistry, Technical University Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany

6 University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany.

E-mail: meinert@surface.tu-darmstadt.de; hofmann@surface.tu-darmstadt.de

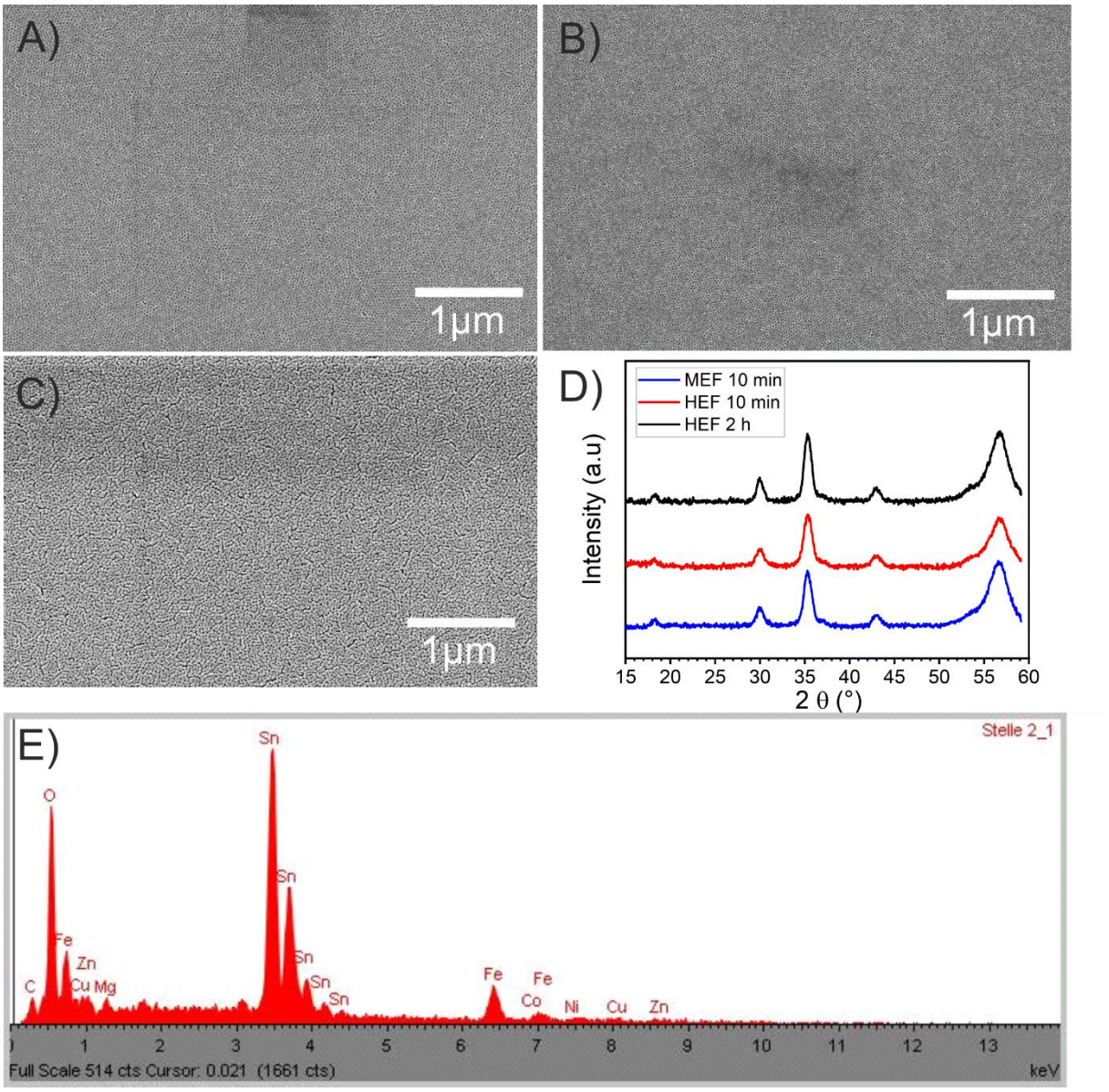

Figure S1. Top-view SEM investigations of A) MEF thins films calcined at 600 °C for 10 min and HEF thins films annealed at 600 °C for B) 10 min and C) 2 h. D) GIWAXS diffractogram of $Co_{0.25}Ni_{0.25}Cu_{0.25}Zn_{0.25}Fe_2O_4$ (black, MEF) calcined for 10 min at 600 °C and $Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}Mg_{0.2}Fe_2O_4$ calcined at 600 °C for 10 min (red) and 2 h (blue). E) EDS based elemental mapping conducted on 600 °C annealed HEF thin films deposited on FTO-glass.

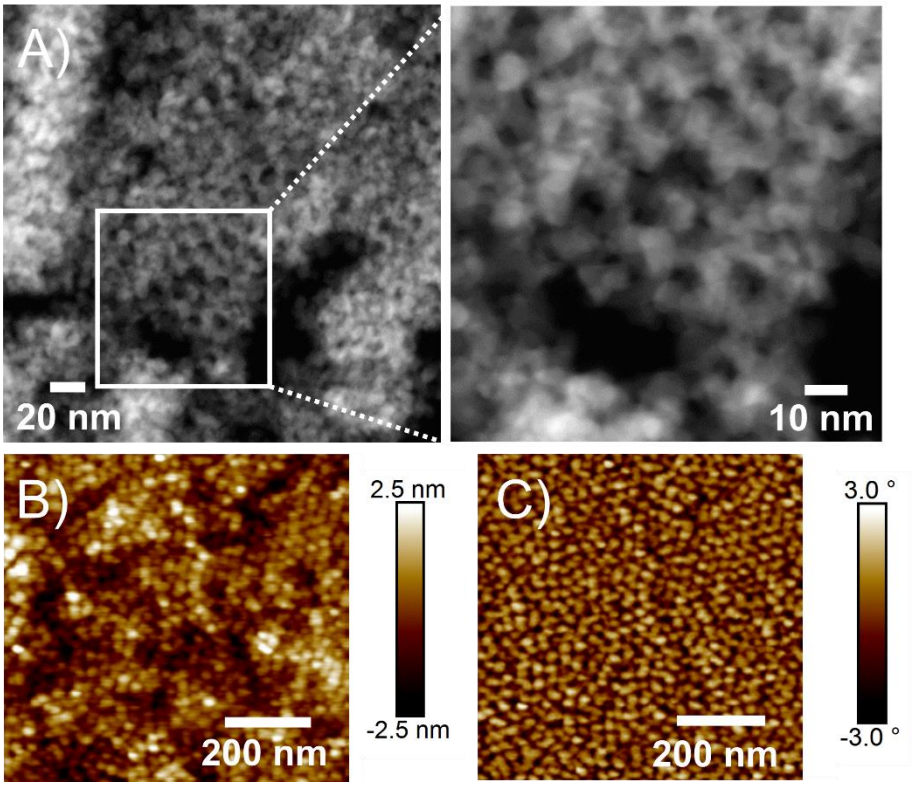

Figure S2. A) Dark field STEM pictures of the mesoporous HEF thin films annealed for 10 min at 600 °C. AFM analysis of the same sample surface detected in the B) topographic and C) phase-mode with a color code visualizing the height difference and the phase shift of the cantilever, respectively.

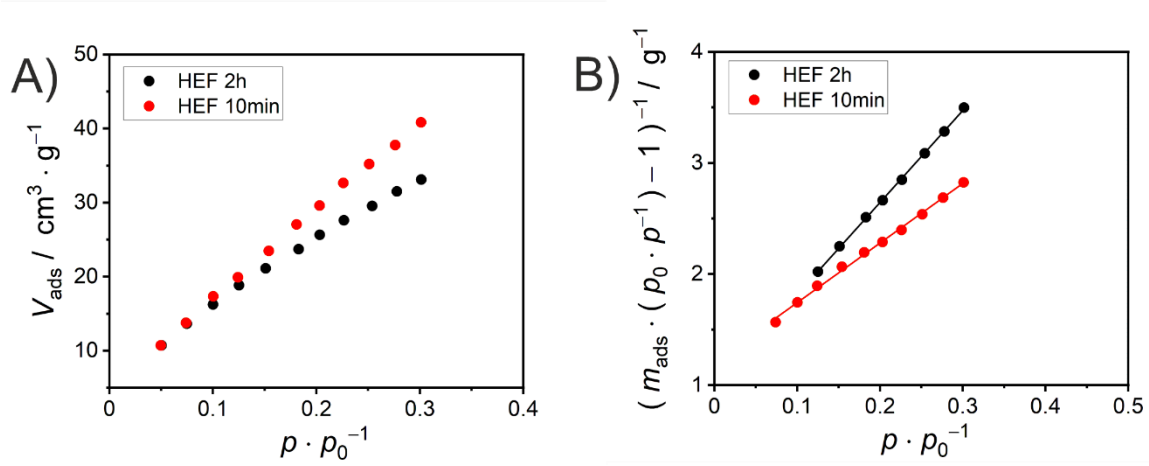

Figure S3. A) Isotherms and B) BET-plots of the at 600 °C for 10 min (red) and 2h (black) mesoporous HEF thin films elucidated by Kr physisorption.

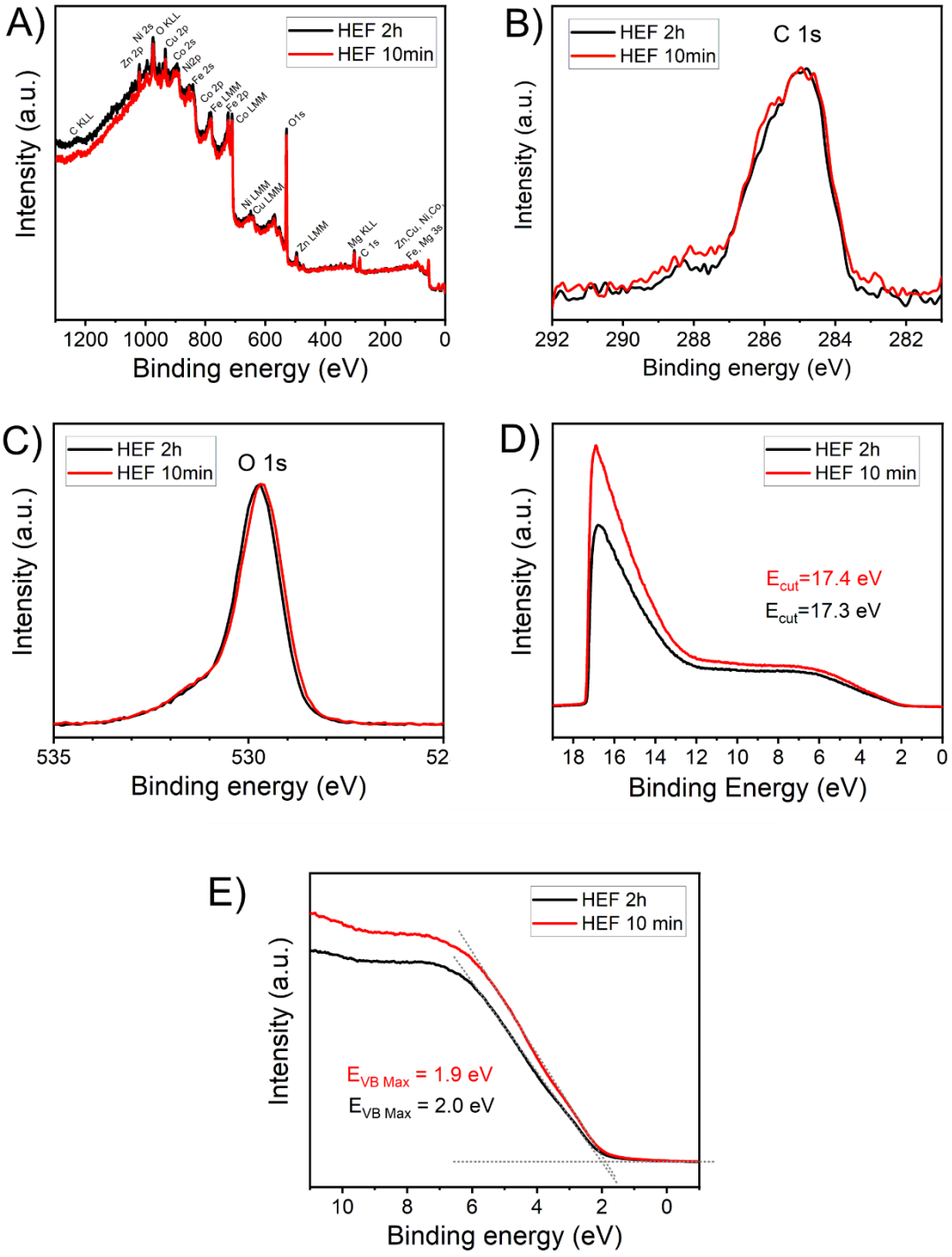

Figure S4. A) XPS survey spectra and fine-scan spectra of the B) C 1s and C) the O 1s emission lines of the at 600 °C for 10 min (red) and 2h (black) calcined HEF thin films. D) Valence band spectra for binding energies between 0 and 18 eV analyzed by UPS. E) Evaluation of the valence band maximum by graphical linear fitting of the data for binding energies between 2 eV and 6 eV.

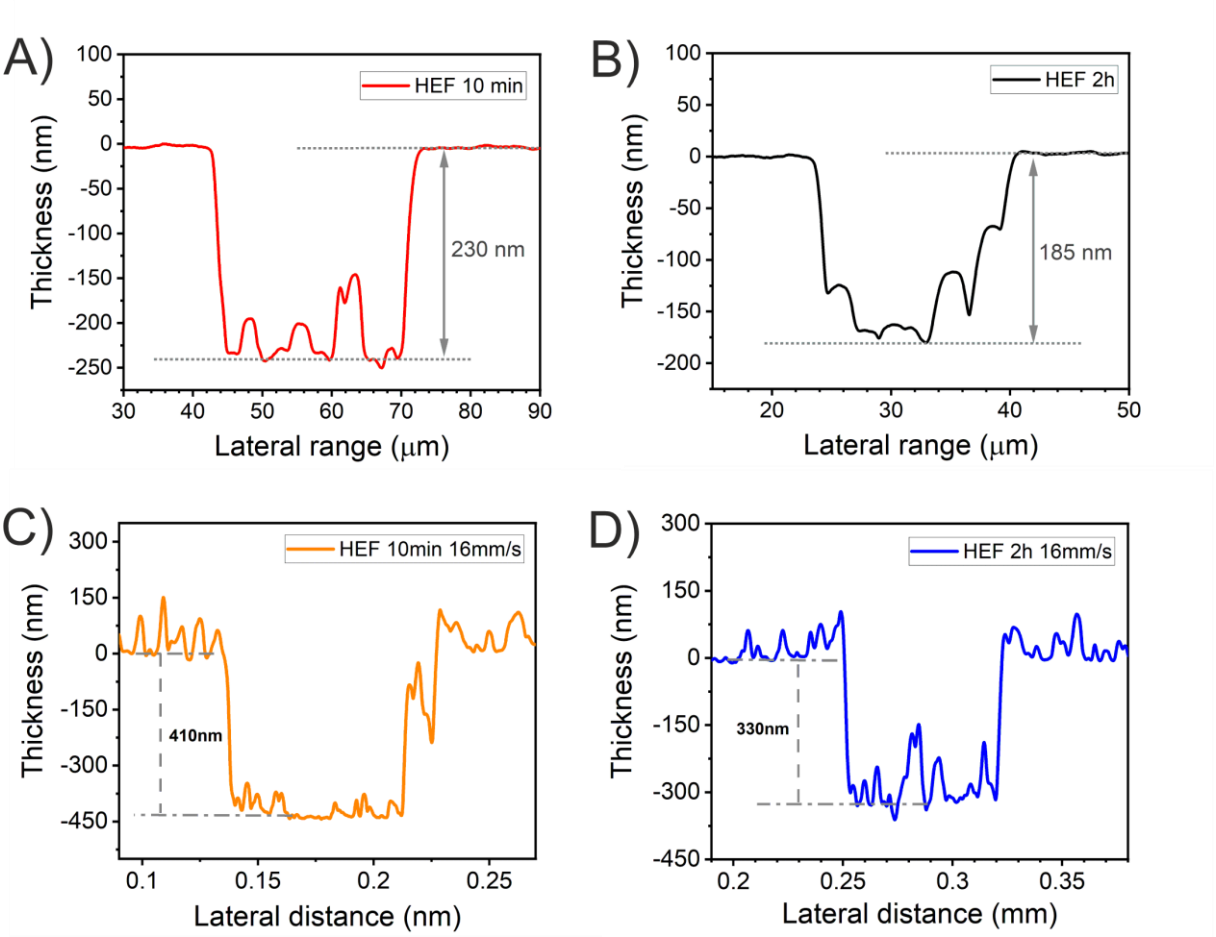

Figure S5. Determination of the film thickness by profilometry dip-coated with 8 mm/s for A) HEF-10min and B) HEF-2h and with 16mm/s for C) HEF-10min and D) HEF-2h all calcined at 600 °C.

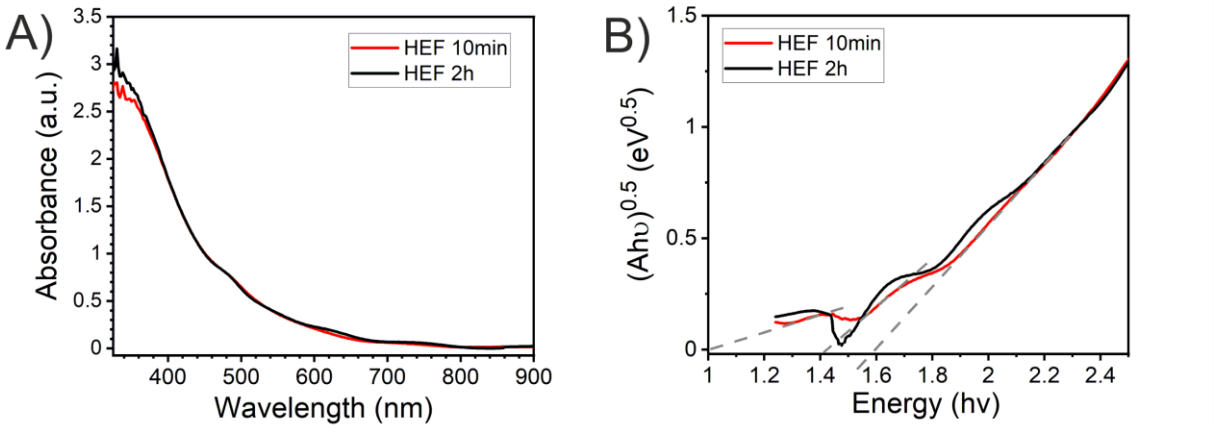

Figure S6. A) Absorbance spectra for the 10 min (red) and 2 h (black) at 600 °C calcined HEF thin films and B) the corresponding Tauc plots for an indirect optical transition.

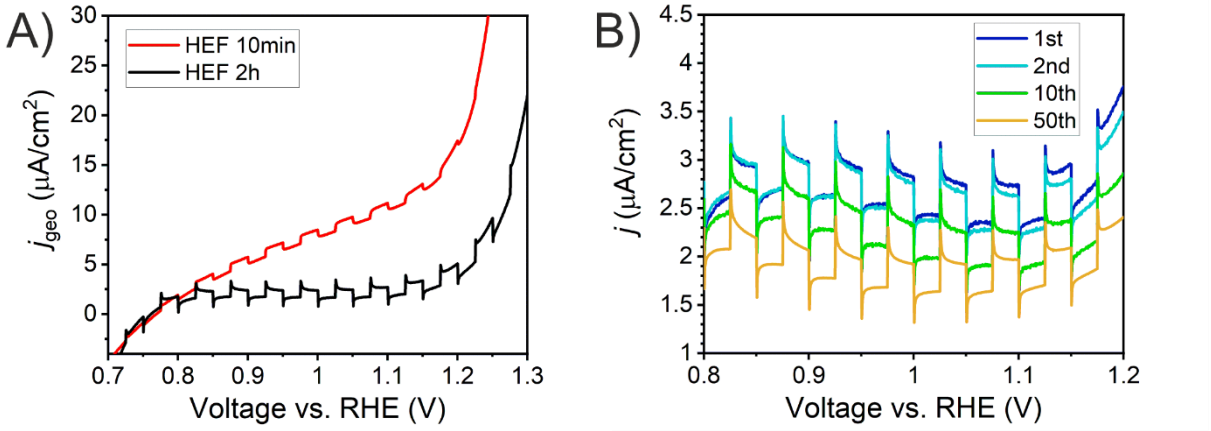

Figure S7. A) Photocurrent densities determined by intermittent-light voltammetry of 10 min and 2h at 600 °C calcined HEF samples. B) Photostability tests recording consecutive intermittent light voltammetry measurements for multiple times: 1 (blue), 2 (turquoise), 10 (green), and 50 times (orange).

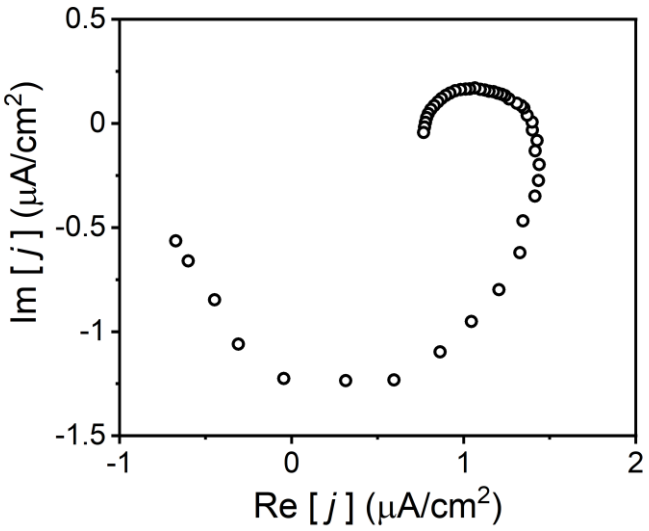

Figure S8. Intensity modulated photocurrent spectroscopy (IMPS) based Nyquist plots for the 2 h calcined HEF thin film showing characteristic semi circles measured at 1.4 V vs RHE in 0.1 m NaOH and 1 m Na_2O_3. The photoresponse of the 10 min calcined HEF sample was too low to obtain reliable data.

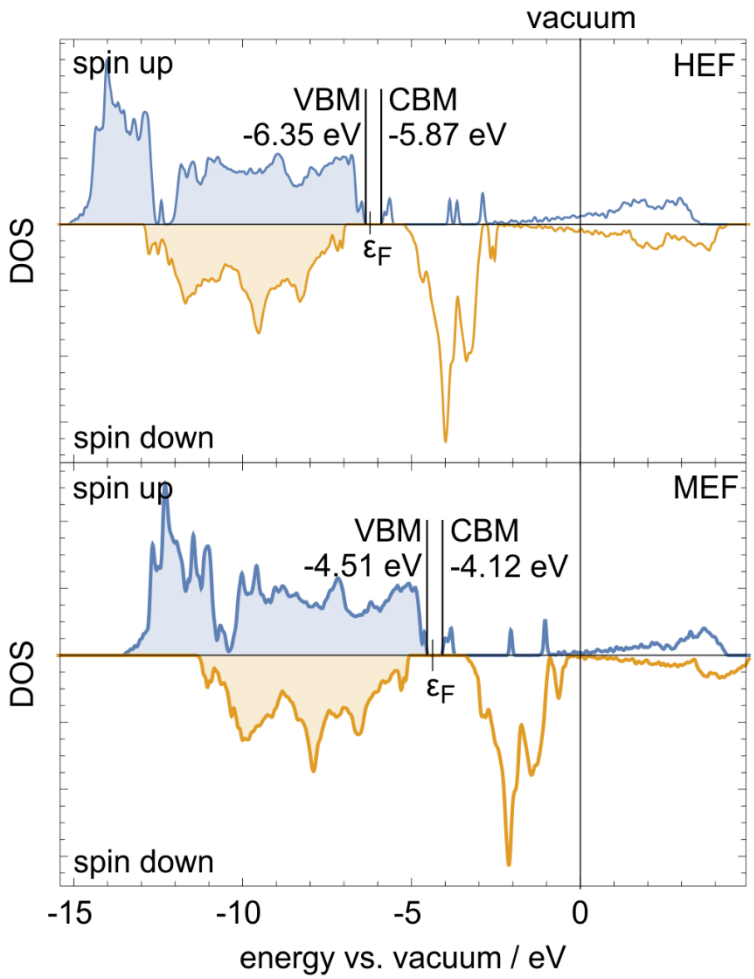

Figure S9: Computed density of states (DOS) versus the vacuum level for the high entropy assisted ferrite $Mg_4Co_3Ni_3Cu_4Zn_4Fe_{36}O_{72}$ (HEF, top image) and the medium entropy assisted ferrite $Co_4Ni_4Cu_5Zn_5Fe_{36}O_{72}$ (MEF, bottom image).

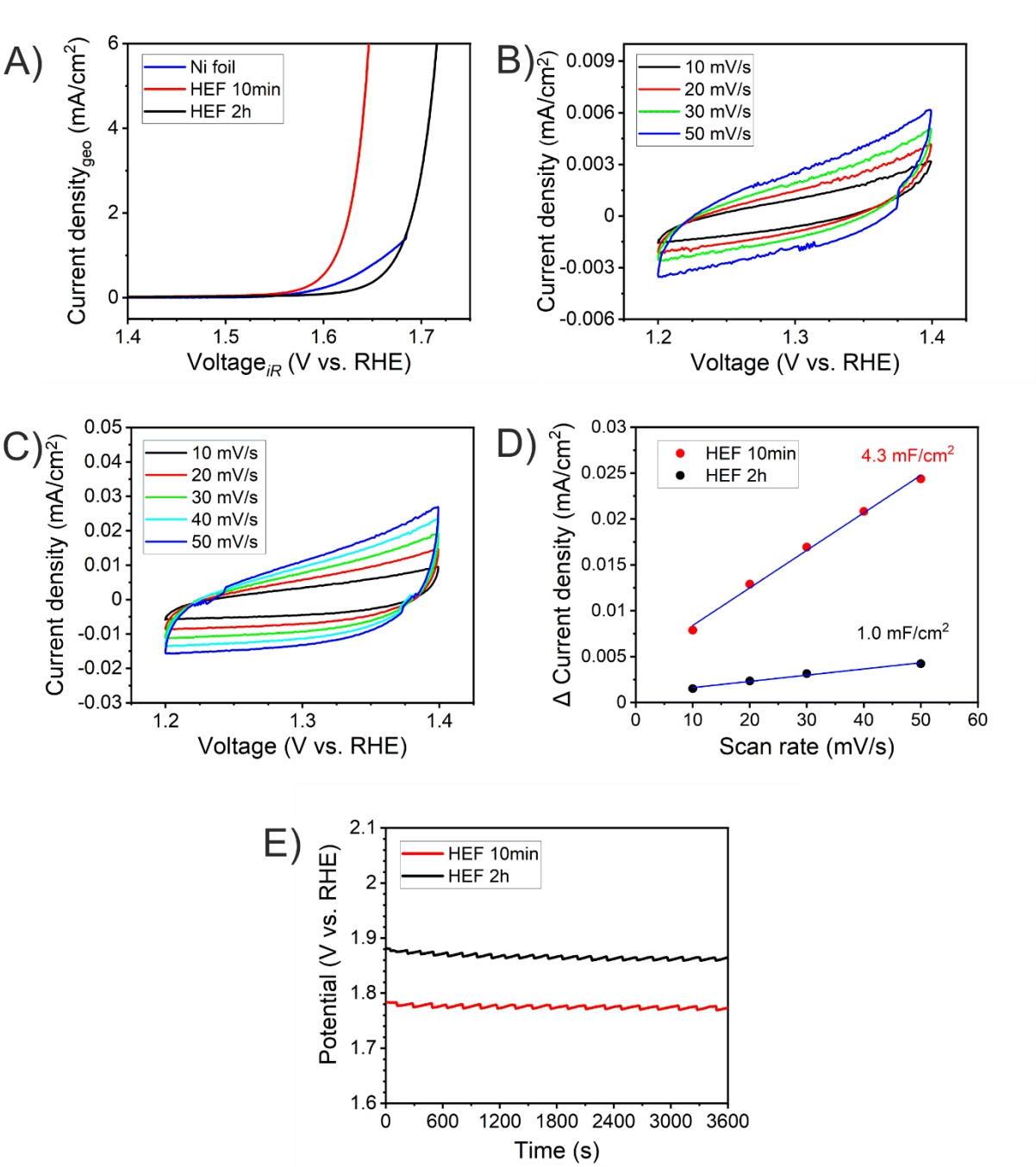

Figure S10. A) LSV curves of Ni foil (blue), HEF calcined for 10 min (red), and for 2 h (black) at 600 °C (with a scan rate of 10 mV/s). CV sweeps for B) 2 h and C) 10 min calcined HEF thin films recorded for distinct scan rates from 10 mV/s to 50 mV/s. D) Differential current densities and the corresponding specific double-layer capacities, C_{DL}, determined by linear fitting of the data points. E) Chronopotentiometric stability investigations of 10 min (red) and 2 h (black) HEF electrodes performed for 3600 s. All electrochemical experiments were conducted in 1 M KOH and in a 3-electrode set-up.

Table S1: Tabular comparison of the atomic concentrations of the corresponding elements for HEF and MEF samples detected by EDS analyzed on 17 distinct spots. Average values and standard deviations are presented.

	HEF						MEF				
EDS #	**Mg**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
	(at.-%)						**(at.-%)**				
1	1.55	9.16	1.08	0.60	0.91	1.66	5.2	1.10	0.50	0.70	0.10
2	0.91	7.97	1.36	0.42	1.36	1.24	5.4	0.80	0.70	0.90	1.30
3	0.92	8.21	0.88	0.70	0.57	1.23	4.00	0.00	1.00	0.10	0.00
4	1.08	8.4	1.18	1.42	0.64	0.90	4.20	0.90	0.50	1.50	1.00
5	1.36	7.63	0.75	0.87	1.15	1.11	3.90	0.90	0.30	0.10	0.00
6	1.64	9.11	1.35	1.21	1.09	1.29	4.40	0.90	1.00	0.20	0.00
7	0.95	8.17	0.55	0.60	0.99	0.46	5.40	0.90	0.30	1.00	1.50
8	0.97	8.65	1.35	1.18	1.94	0.83	4.70	0.10	1.20	0.80	1.50
9	1.21	9.52	1.07	0.72	0.12	0.88	4.60	0.40	0.70	0.60	0.30
10	1.98	6.99	1.07	1.01	1.08	1.18	5.50	0.80	0.80	0.90	1.10
11	0.77	8.54	0.97	1.10	0.62	0.83	4.40	0.70	0.90	1.20	0.00
12	1.64	10.5	1.00	1.10	0.80	1.30	5.30	1.20	0.40	0.50	0.40
13	1.5	8.0	0.50	0.90	0.90	1.00	5.90	0.90	1.10	0.60	1.30
14	1.5	8.90	1.10	1.00	1.00	1.90	3.80	0.30	0.80	0.40	0.10
15	1.1	8.0	1.30	1.60	1.30	2.70	4.90	0.90	1.40	1.00	1.00
16	1.5	8.60	1.0	0.60	1.50	0.30	6.20	0.70	0.90	0.90	0.80
17	1.1	8.70	1.0	1.20	1.90	0.30	4.80	0.50	0.20	0.70	1.60
Average	**1.26**	**8.53**	**1.03**	**0.96**	**1.05**	**1.10**	**4.86**	**0.71**	**0.74**	**0.71**	**0.71**
Standard Deviation	**0.34**	**0.79**	**0.25**	**0.32**	**0.46**	**0.59**	**0.70**	**0.33**	**0.34**	**0.38**	**0.61**

Calculation of configurational entropy

The calculation of the configurational entropy on a single crystallographic site can be derived by statistical thermodynamics according the following equation: [1,2]

$$\Delta S_{config} = -R \sum_{i=1}^{n} x_i \, ln x_i \qquad \text{(Equation S1)}$$

with R being the ideal gas constant and x_i stands for the molar fraction of the ith component for a total number of n elements.

The configurational entropy, S_{config}, for the HEF (with Mg = 0.24 mol, Co = 0.20 mol, Ni = 0.19 mol, Cu = 0.20 mol, and Zn = 0.21 mol) and the MEF samples (with Co = 0.25 mol, Ni = 0.24 mol, Cu = 0.25 mol, and Zn = 0.25 mol) was calculated as followed:

ΔS_{config} (HEF) = –R ((0.24 ln 0.24) + (0.20 ln 0.20) + (0.19 ln 0.19) + (0.20 ln 0.20) + (0.21 ln 0.21))

= –R (–0.343 – 0.322 – 0.316 – 0.322 – 0.328)

= **1.63 R**

ΔS_{config} (MEF) = –R ((0.25 ln 0.25) + (0.24 ln 0.24) + (0.25 ln 0.25) + (0.25 ln 0.25)

= –R (–0.347 – 0.343 – 0.347 – 0.347)

= **1.38 R**

References

[1] B. S. Murty, J.-W. Yeh, R. Srikanth, P. P. Bhattacharjee, High-Entropy Alloys, *Elsevier*, 2019.

[2] Gao, Michael C., et al. High-entropy alloys. *Cham: Springer International Publishing*, 2016.