Evaluation of electrospun spinel-type high-entropy $(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_3O_4$, $(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Zn_{0.2})_3O_4$ and $(Cr_{0.2}Mn_{0.2}Fe_{0.2}Ni_{0.2}Zn_{0.2})_3O_4$ oxide nanofibers as electrocatalysts for oxygen evolution in alkaline medium

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Supplementary Information



Figure S1. Schematic drawings of cations occupying (a) tetrahedral and (b) octahedral sites in the M²⁺M³⁺₂O₄ normal spinel lattice.

Syntheses

Materials

Chromium (III) acetate hydroxide, $Cr_3(OH)_2(CH_3CO_2)_7$ (purity: 98%; CAS No. 39430-51-8, Sigma Aldrich), manganese(II) acetate tetrahydrate, $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (purity: 99%; CAS No. 6156-78-1, Sigma Aldrich), iron (II) acetate, $Fe(CH_3CO_2)_2$ (purity 95%; CAS No. 3094-87-9 Sigma Aldrich), cobalt (II) acetate tetrahydrate, $Co(CH_3CO_2)_2 \cdot 4H_2O$ (purity: 99%; CAS No. 6147-53-1, Sigma Aldrich), nickel (II) acetate tetrahydrate, $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (purity: 98%; CAS No. 6018-89-9, Sigma Aldrich), zinc (II) acetate dehydrate, $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (purity: 98%; CAS No. 5970-45-6, Fischer Scientific) were utilised as TM sources for the synthesis of the catalysts. In the syntheses of HEO-NFs via ES, polyacrylonitrile, $(C_3H_3N)_n$ (average molecular weight: 150000 g mol⁻¹; purity: 99.9%; CAS No. 25014-41-9, Sigma Aldrich), and N,N-dimethylformamide, HCON(CH₃)₂ (anhydrous: 99.8%; CAS No. 68-12-2, Sigma Aldrich) acted as a polymer and a solvent, respectively. In addition, HEO-NPs were prepared via the SG method by using citric acid monohydrate, HOC(COOH)(CH₂COOH)₂·H₂O (purity: 98%; CAS No. 5949-29-1, Sigma Aldrich) as a complexing agent. All reagents were used without further purification.

Synthesis of the HEO-catalysts

The HEO-catalysts were prepared by following the procedures illustrated in detail in a previous work.¹ Briefly, to produce the NFs, a 7.14 % by weight polyacrylonitrile (PAN) in *N*,*N*-dimethylformamide (DMF) solution was first obtained. After stirring the PAN/DMF solution (350 rpm, 1h) at room temperature (RT), stoichiometric amounts of the selected acetates were added, one at a time, under continuous stirring. Homogeneous solutions containing equimolar combinations of (Cr,Mn,Fe,Co,Ni), (Cr,Mn,Fe,Co,Zn) and (Cr,Mn,Fe,Ni,Zn) were finally obtained with 38.46 wt% (relative to the polymer) total amount of metals. After slow mixing overnight at RT, the solution was loaded into a 20 mL syringe equipped with a 40 mm long, 0.8 mm gauge stainless steel needle. ES was operated via a CH-01 Electro-spinner 2.0 (Linari Engineering s.r.l.) at 25 ± 1 °C and 40% relative air humidity, under an applied DC voltage of 15–16 kV. The solution was fed at a rate of 18.8 μ L min⁻¹.

During the ES, most of DMF very rapidly evaporated. The PAN/TM-acetates NFs, acting as templates for the formation of onedimensional (1D) HEO structures upon calcination, were collected over a grounded aluminium foil, placed 15 cm from the needle tip. The non-woven membrane that they formed was allowed to dry at RT overnight. Then, it was detached from the collector and calcined in static air. During this process, the organic components of the as-spun NFs were completely removed and HEO-NFs were generated through combustion from the interconnected TM-network built up via sol-chemistry from the reaction among acetates. As typical of electrospun oxides,^{2–7} the strong PAN/TM-acetates interaction resulted in NFs with granular architecture, with the oxide grain size geometrically limited from that of the precursor NFs. Temperature was increased at a fast rate (10 °C min⁻¹) in order to obtain mainly hollow NFs,^{8,9} and then kept constant at 700 °C for 2 h and at 900 °C for 2 h.

(Cr,Mn,Fe,Co,Ni) HEO NPs were further produced via the SG method to investigate the role of the catalyst morphology. For this purpose, stoichiometric amounts of the selected acetates were dissolved in water, one at a time. After stirring (350 rpm, 1h), citric acid (11.56 wt% relative to water) was added. The resulting mixture, with 18.03 wt% (relative to the complexing agent) total amount of metals, was further stirred at 90 °C until the formation of a gel. After drying at 80 °C overnight, the product was calcined in static air through a four step heating process (350°C for 2 h, 500°C for 2 h, 800°C for 2 h, 900°C for 2 h).

Morphology



Figure S2. SEM micrograph of CN-NPs.



Figure S3. TEM images of (a) CN-NFs, (b) CZ-NFs and (c) NZ-NFs. Insets: SAED patterns.



Figure S4. HRTEM images and sketch of the typical cross section of (a) quasi-solid CN-NFs, (b) irregularly hollow CZ-NFs and (c) hollow NZ-NFs, as resulting from the projection analysis of the EDX elemental maps. The cross section scale is the same for all NFs. The drawings are inspired to [8].



Figure S5. (a,b,d,e) Representative AFM images with lateral size of (a,d) 3 μ m and (b,e) 1 μ m, and (c,f) profiles of height acquired along the dashed line in 1×1 μ m² AFM images (the size of the HEO grains marked by a dotted circle is also reported). The shown data refer to (a–c) CN-NFs and (d–f) CZ-NFs.

Surface properties

Table S1. Surface elemental composition of the HEO catalysts.

Sample	Cr / at.%	Mn / at.%	Fe / at.%	Co / at.%	Ni / at.%	Zn / at.%	O / at.%
CN-NPs	5.51	12.09	4.74	3.35	2.66		71.65
CN-NFs	5.71	7.14	2.79	3.10	2.45		78.82
CZ-NFs	6.09	8.06	3.23	3.23		6.57	72.83
NZ-NFs	8.45	7.99	1.52		2.37	5.07	74.61

Electrochemical properties



Figure S6. CV curves at different scan rates (5, 10, 20, 40, 60 mV s⁻¹) of (a) CZ-NFs, (b) NZ-NFs, (c) CN-NFs and (d) CN-NPs. (e) Current density differences (Δj) from CV curves plotted against the scan rate. C_{dl} is equivalent to linear slope.



Figure S7. LSV curves normalized to the ECSA.



Figure S8. Turnover frequency (TOF) for the investigated OER electrocatalysts.



Figure S9. Voltammograms of CN-NFs during CV after 1, 50, 100, 500, 1000, 1500, 2000, 2300, and 2306 cycles.

Table S2. Electrocatalytic performance of HEO-based OER electrocatalysts in 1M KOH at 10 mA cm⁻².

Electrocatalyst	Synthesis method	Overpotential / mV	Tafel slope / mV dec ⁻¹	Ref.
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_{3}O_{4}$	Reverse co-	220	100	10
	precipitation approach			
FeCoNiMn/Sn/CuBO _x	Liquid phase non-	258–266	64.5–73.9	11
	equilibrium reduction			
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Zn_{0.2})_{3}O_{4}$	Electrospinning	393	62.5	Present work
$Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$	Electrospinning	360	61.4	12
$(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})O$	Hydrothermal method	454	60	13
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Ni_{0.2}Zn_{0.2})_{3}O_{4}$	Electrospinning	376	59.6	Present work
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Ni_{0.2}Zn_{0.2})_{3}O_{4}$	Solvothermal method	295	53.7	14
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_{3}O_{4}$	Solid state reaction	332	54.5	15
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_{3}O_{4}$	Sol-gel	373	51.3	Present work
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_{3}O_{4}$	Solution combustion	275	50.3	16
$(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_{3}O_{4}$	Electrospinning	365	49.1	Present work
$(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})_{3}O_{3.2}$	Mechanical alloying	336	47.5	17
$(Mn_{0.2}Fe_{0.2}Ni_{0.2}Mg_{0.2}Zn_{0.2})_{3}O_{4}$	Nebulized-spray	293	46.5	18
(Cr _{0.2} Mn _{0.2} Fe _{0.2} Co _{0.2} Ni _{0.2}) ₃ O ₄	Dip-coating solution	350–390	35–40	19

Table S3. Comparison of the OER activities of CN-NPs, CN-NFs, CZ-NFs, and NZ-NFs.

Sample	Overpotential / mV @ 10 mA cm $^{-1}$	Tafel slope / mV dec ⁻¹	ECSA / cm ²	TOF / s ⁻¹
CN-NPs	373.15	51.3	48.5	0.025
CN-NFs	365.74	49.1	36.3	0.034
CZ-NFs	392.61	62.5	96.8	0.026
NZ-NFs	376.12	59.6	29.0	0.018

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