

Energy Advances

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ARTICLE

Anion Exchange Membrane Water Electrolysis over Superparamagnetic Ferrites

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Oxygen evolution reaction (OER) is usually the bottleneck in water electrolysis due to its sluggish kinetics, resulting in increased costs in the production of green hydrogen. Therefore, there is a need of more efficient, stable, and ideally, critical-raw-material-free catalysts. To this end, we have synthesized nanosized spinel ferrites CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and a high-entropy spinel ferrite $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ by simple coprecipitation reaction in an automated reactor on gram scale. The powder X-ray diffraction and transmission electron microscopy studies revealed crystallite sizes of 20–35 nm. Insight into the oxidation states and cation distribution in the mixed spinel systems was gained through X-ray photoelectron and Mössbauer spectroscopies. The activity of all spinel ferrites was tested for OER in half-cell laboratory measurements as well as full-cell anion exchange membrane electrolyzer (AEMEL), where $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ showed the lowest overpotential of 432 mV at the current density of 10 mA/cm². All the synthesized ferrites demonstrated good stability up to 20 h, with NiFe_2O_4 being the most active in high current density experiments up to 2 A/cm². In addition, studies on the magnetic properties at room temperature revealed largely superparamagnetic response of the prepared materials, indicating that quantum spin exchange interactions catalyze oxygen electrochemistry. Computational calculations shed light on the superior catalytic activities of NiFe_2O_4 and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, the two strongly correlated oxides that exhibit the highest magnetization and the smallest band gaps, corroborating the recent principles determining the activity of magnetic oxides for electron transfer reactions.

Keywords: Spinel structure, oxygen evolution reaction, high-entropy oxides, nanomaterials, magnetism, catalysis, hydrogen

Introduction

Hydrogen is an important energy vector with regard to meeting the targeted net-zero CO₂ emissions by 2050, allowing for the elimination of our dependence on fossil fuels.¹ When powered

by renewable electricity, water electrolysis is of profound and long-standing interest for green H₂ production.^{2,3} In the last decades, the industry has focused on two electrolysis systems that operate at low temperatures. The traditional alkaline water electrolysis (ALK), which typically operates in the temperature range of 60–80 °C with potassium hydroxide as the carrying electrolyte, with Ni-based electrodes, and a diaphragm (e.g., Zirfon).^{4,5} The usual maximum operating geometric current density is less than 0.4 A/cm², with an energy efficiency of about 60%.⁶ ALK is recognized as a mature technology, which is commercially available given its low cost. However, its major limitation is related to the poor dynamic operation capability, e.g., ability of the electrolysis system to rapidly adjust its operation to match the fluctuating power output of renewable energy sources.⁷ Proton exchange membrane water electrolysis (PEMEL) is the other key electrolysis technology in the near-term. PEMEL is advantageous in that it uses a semi-solid electrolyte in the form of proton exchange membranes (PEMs) with high proton conductivity (e.g., Nafion),⁸ pressurized set-

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



up, and good operation under dynamic load.^{4,9} Despite the inherent advantages, PEMEL is defined by high CAPEX, given the need of rare and expensive platinum-group-metal (PGM) electrodes,¹⁰ along with costly titanium gas-diffusion layers¹¹ and bipolar plates.¹²

The relatively recent anion exchange membrane electrolysis (AEMEL) offers a great opportunity to generate green H₂ in a cost-efficient and environmentally benign fashion. The use of anion exchange membranes (AEMs) may mitigate some of the limitations of ALK. Similarly to PEMEL, AEMEL is characterized by pressurized operation and high dynamic responsiveness, but it allows for the use of cheap, non-PGM catalysts and low-cost cell/stack materials.^{13,14} For instance, various hydroxide/oxyhydroxide/oxide nanoparticles (NPs) based on abundant non-PGM 3d transition metals, such as Mn, Fe, Co, Ni, Cu, Zn, and Mo, are commonly investigated and employed as catalysts for alkaline oxygen evolution reaction (OER) over AEMEL anodes. The fact that this type of non-PGM catalysts are more abundant and lower in cost than PGM-containing ones, as well as feature good chemical stability under alkaline conditions, shows the potential for the large-scale implementation of AEMEL.¹⁵⁻¹⁸ Despite great efforts in the recent years to develop non-PGM catalysts, a systematic analysis regarding their physicochemical properties in relation to *e.g.*, the effect of composition, particle size, surface area, and physical properties is of high relevance for the future implementation of the AEMEL technology at the industrial level.⁴

The efficiency of AEMEL relies highly on that of OER due to the slower reaction kinetics and associated high overpotentials as compared to hydrogen evolution reaction (HER), the other half-reaction of water electrolysis.¹⁹⁻²¹ Notably, the most active catalysts for OER have strongly correlated electrons,²² associated with itinerant spin conduction.^{23,24} For example, ferrites AFe₂O₄ with spinel structure are strongly correlated oxides with favorable spin-orbital orderings, and thus these have been postulated as promising catalysts for OER.²⁵ High activity and durability of the ferrites are commonly connected with their open-shell electronic configurations. Moreover, the structural and chemical stability of the ferrites under alkaline conditions coupled to their multiple cation valence (*i.e.*, A³⁺/A²⁺ and Fe³⁺/Fe²⁺) render them interesting catalysts for AEMEL anodes.^{14,26-30} While several ferrites with various compositions, structures, and nanostructures have been synthesized, characterized, and investigated in the laboratory in a half-cell alkaline OER experimental setting,³¹ their performance in industrially relevant full-cell AEMEL has not been evaluated in great detail to date.

Our laboratories have been exploring the chemical synthesis of ferrite NPs in the context of modulating their structural and magnetic properties, but not in relation with catalysis.^{32,33} Herein, we report the preparation of a series of ferrite AFe₂O₄ (A = Fe²⁺, Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺) NPs on gram scale and the study of their performance in alkaline OER, and importantly, in full-cell AEMEL. The spin-dependent theory in catalysis²² and computational calculations provided comprehensive insight into the structural, magnetic, and electronic properties of the

prepared ferrites, leading to structure-property relationships that will assist in the future design of active catalysts.

Experimental section

Materials

Iron(III) chloride hexahydrate (FeCl₃·6H₂O, >98%, Sigma-Aldrich), nickel(II) chloride hexahydrate (NiCl₂·6H₂O, >98%, Thermo Scientific), cobalt(II) chloride (CoCl₂·6H₂O, >98%, Thermo Scientific), zinc(II) chloride anhydrous (ZnCl₂, >98%, Thermo Scientific), manganese(II) chloride tetrahydrate (MnCl₂·4H₂O, 99%, Thermo Scientific), sodium hydroxide (NaOH, pellets, EMSURE[®], Supelco), potassium hydroxide (KOH, flakes, 90%, Sigma-Aldrich), 30% hydrogen peroxide solution (H₂O₂, Sigma-Aldrich), potassium permanganate (KMnO₄, ≥99.0%, Sigma-Aldrich), isopropanol (≥99.5%, Sigma-Aldrich), carbon black Vulcan XC 72 (Fuel Cell Store) and ethanol (≥99.5%, Honeywell) were used as received. Ultrapure water (18.2 MΩ·cm) was produced by Milli-Q Advantage A10 system (Millipore).

Synthesis of the ferrites

All ferrites, All ferrites, namely, CoFe₂O₄, NiFe₂O₄, ZnFe₂O₄, as well as high-entropy Zn_{0.2}Mn_{0.2}Ni_{0.2}Co_{0.2}Fe_{2.2}O₄ ferrite [4A_{1/4}Fe_{2.2}O₄] were prepared by robust coprecipitation method adapted from elsewhere^[12] using NaOH as a precipitating agent. Typically, the molar ratio of base to metal precursors was fixed to be 10 : 1. The reproducible gram-scale synthesis of the ferrites (>5 g) was achieved using a 2 L automated Atlas Potassium synthesis system (Syrris) equipped with two syringe pumps (Syrris), temperature control system LH85 PLUS (Julabo), overhead stirrer, and a temperature probe. In a typical reaction, 11.0 g of NaOH (0.225 mol) was dissolved in 400 mL of ultrapure water while heating at 80 °C under mechanical stirring of 300 rpm for 30 min. This step was followed by a controlled addition of the metal precursors previously dissolved in 200 mL of ultrapure water at a feeding rate of 5 mL/min. Typically, for two-metal ferrites, 42 mmol of Fe(III) salt and 21 mmol of the corresponding A(II) salt were mixed and used as the precursor solution. For the synthesis of the high-entropy ferrite containing five metals, an aqueous solution was prepared with 42 mmol of Fe(III) salt and 4.2 mmol of each M(II) salt. After complete addition of the precursor solution to the NaOH solution in the 2 L reactor, the reaction mixture was allowed to gradually cool to room temperature. The resulting solid products were either collected magnetically with the aid of a permanent NdFeB magnet for magnetically active products or through centrifugation at 12,000 rpm for 10 min for weakly magnetic products. The resulting ferrites were extensively washed with water and ethanol and dried under vacuum. The obtained powders were calcined at 400 °C under air with a heating rate of 3 °C/min and holding time of 5 h. The calcination products were converted into fine powders through ball milling in an 8000 M high-energy mixer/mill (SPEX) using a zirconia vial and spheres at a sample-to-sphere w/w ratio of 9:1 (1 cycle at 1425 rpm of 30 min).



Characterization

The materials were characterized by powder X-ray diffraction (XRD, X'Pert PRO diffractometer, PANalytical), Raman spectroscopy (alpha300 R confocal microscope, WITec), Mössbauer spectroscopy (MS4 spectrometer, SEE Co.), transmission electron microscopy (TEM, JEM-2100 microscope, Jeol), high-angle annular dark field scanning TEM (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDX) in STEM mode (STEM-EDX, Titan ChemiSTEM microscope at 200 kV; FEI, 0.08 nm point resolution, Super-X EDX System), N₂ physisorption at 77 K (Autosorb IQ2 apparatus, Quantachrome), scanning electron microscopy (SEM, Quanta 650 FEG microscope, FEI), energy dispersive X-ray spectroscopy (EDX, INCA 350 spectrometer, Oxford Instruments), vibrating sample magnetometry (VSM, EV9 instrument, Lot-Oriel), UV/Vis diffuse reflectance spectroscopy (LAMBDA 950 UV/vis/NIR spectrophotometer, PerkinElmer), X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Scientific), and inductively coupled plasma-optical emission spectroscopy (ICP-OES, ICPE-9000 spectrometer (Shimadzu; all powders were digested by concentrated HCl 37% solution. The NiFe₂O₄ nanoparticles were further digested under heat treatment at 170 °C using an autoclave reactor).

Half-cell alkaline OER measurements

The electrochemical OER activity of the synthesized ferrites was studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in a conventional three-electrode glass cell. Before use, the glassware was cleaned following a standard cleaning procedure: First, the glassware was submerged overnight in a saturated KMnO₄ solution. Next, the solution was rinsed with a dilute H₂O₂ solution and then heated to boil three times in ultrapure water (5 minutes each time). The working electrode consisted of a catalyst ink drop-casted on glassy carbon (GC) rotating disk electrode (RDE) (Metrohm, $\varnothing = 3\text{ mm}$, $S = 0.0071\text{ cm}^2$). The counter electrode and reference electrode were a GC rod and a Hg | HgO electrode, respectively. All potentials E in the half-cell study are quoted with respect to reversible hydrogen electrode (RHE), converted via $E_{\text{RHE}} = E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.059 \cdot \text{pH} + E_0(\text{Hg}/\text{HgO}) = E(\text{Hg}/\text{HgO}) + 0.924\text{ V}$.³⁴ The applied potential was controlled by an Autolab PGSTAT302N potentiostat (Metrohm) while the RDE rotation rate was controlled by an Autolab RRDE rotator (Metrohm).

The catalyst ink was prepared by mixing ultrapure water, isopropanol (volume ratio of water/isopropanol = 3:1), Sustainion ionomer solution (5% in solvent, Dioxide Materials) of 5% volume ratio to the overall volume, a physical mixture of the synthesized ferrite powder (8 mg/mL), and conductive carbon black (16 mg/mL). Before drop-casting the catalyst ink, the GC RDE was polished with alumina powder for 5 min, and then rinsed with water and ethanol. This procedure was repeated three times. After ultrasonication treatment for 15 min, the as-formulated catalyst ink was drop-casted on the GC RDE, and then left in a solvent-vapor-saturated water + isopropanol atmosphere overnight for drying. The mass

loading (0.3 mg/cm² ferrite + 0.6 mg/cm² conductive carbon black) was precisely controlled by the volume of the drop-casted ink.

Aqueous 1 M NaOH electrolyte solution was used, and all experiments were performed under N₂-saturated (5.0, LindeGas) conditions at room temperature. Before electrochemical characterization, the working electrode containing the catalyst was carefully rinsed with ultrapure water, followed by electrochemical cleaning for 15 min by performing CV from 0 to 1.2 V_{RHE} at a scan rate of 200 mV/s. All data shown is iR -corrected for a voltage drop of 80%. The electrochemical surface area (ECSA) of the working electrode was determined by double-layer capacitance (C_{dl}) measured at 1 V_{RHE}, assuming a uniform specific double layer of 40 $\mu\text{F}/\text{cm}^2$. OER properties of the synthesized ferrites in KOH electrolyte were also investigated in non-RDE mode at higher catalyst mass loading of 1 mg/cm² on a 1 cm² glassy carbon plate. The catalyst ink was prepared by dispersing a mixture of 4 mg of catalyst and 1 mg of conductive carbon black in a 3:2 ethanol/water solution while adding 60 ml of Nafion ionomer solution (5% in aliphatic alcohols and water, Sigma-Aldrich) as binder; to the total volume of 1 mL.

Full-cell AEMEL testing

Full-cell testing was conducted in an in-house-built AEMEL electrolyzer based on a cell with 4 cm² active area (Fuel Cell Store). The catalyst was coated on the gas diffusion/porous transport layers (GDL/PTL) by the catalyst coated on substrate electrodes (GDE/PTE). The cathode GDE was carbon paper GDL SGL 39BC (Sigracet) loaded with 0.3 mg/cm² of 40%Pt/C catalyst (Premetek), while the anode PTE was nickel PTL 2Ni 18-0.5 (Bekaert) loaded with 3 mg/cm² of the synthesized ferrite catalysts. Proprietary Membrane B 70 μm (HYDROLITE) was employed as the AEM, and PTFE gaskets of 200 μm and 400 μm were used for the sealing of the cathode and the anode, respectively. After the assembly, the AEMEL cell was connected to the electrolyte inlets and outlets, thermocouple, as well as voltage and current sensors in the testing workstation. The 1 M KOH electrolyte was supplied on the OER side at a flow rate of 170 mL/h. Membrane electrode assembly (MEA) activation was performed by gradual voltage increase from 1.4 to 2 V to achieve maximum current density for a cell at a specific temperature. All catalysts were tested at both 60 °C and 80 °C. After the activation, current-voltage (I - V) curve was measured from 1.4 to 2 V and backwards. The short-term durability of the AEMEL cells was evaluated by chronoamperometric measurements under constant current density of 0.5 A/cm² for 20 h.

Results

CoFe₂O₄, NiFe₂O₄, ZnFe₂O₄, and high-entropy Zn_{0.2}Mn_{0.2}Ni_{0.2}Co_{0.2}Fe_{2.2}O₄ were prepared following a straightforward coprecipitation method using NaOH as the precipitating agent. We avoided the use of aqueous ammonia solution for the precipitation because of possible formation of



soluble complexes with several transition metals (*e.g.*, Ni, Zn). An automated benchtop synthesis system was employed, which allows for the synthesis of NPs on a gram scale in a highly controlled and reproducible fashion.^{32, 35} The as-synthesized products were calcined at a moderate temperature to clean the surface of the catalysts from possible synthesis residuals. Finally, the catalysts were subjected to ball milling to decrease their degree of agglomeration to facilitate the formulation of catalytic inks.

Powder XRD patterns collected of the catalysts (Figure S1) evidenced all final products to be single-phase nanocrystalline ferrite powders exhibiting cubic spinel structure (space group *Fd-3m*, no. 227). No diffraction peaks corresponding to secondary phases were detected. The average size of the crystallites and reliable unit cell parameters were estimated from the collected XRD data and are summarized in Table S1. Next, Raman spectra were recorded from the prepared catalysts (Figure S2), which exhibited broad peaks with low signal-to-noise ratio, which is common for nanocrystalline powders. The catalysts displayed typical Raman band profiles associated with the spinel structure of *O^{7h}* (*Fd-3m*) space group while featuring characteristic Raman-active bands arising from A_{1g} ($\gg 690\text{ cm}^{-1}$), T_{2g} ($\gg 470\text{ cm}^{-1}$), and E_g ($\gg 320\text{ cm}^{-1}$) modes.³⁶⁻³⁹ As expected, the different elemental compositions of the prepared ferrites were mostly reflected in the small shifts and splitting of the observed Raman bands.⁴⁰ Based on the XRD and the Raman spectroscopy results, the synthesized catalysts were obtained as phase pure ferrites.

cation distribution in the synthesized catalysts, the products were analyzed by Mössbauer spectroscopy at 6 K (Figure 1). The collected Mössbauer spectra for all four catalysts can be fitted with three magnetically split sextets, Q_1 , Q_2 , and Q_3 , and the extracted Mössbauer parameters, namely, centroid shift, δ , quadrupole shift, ε , magnetic hyperfine field, B_{hf} , magnetic hyperfine field distribution, σ , and intensity, I , for all measurements are summarized in Table S2. Analysis of the Mössbauer data revealed that the cation distribution for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, within the experimental errors, are $[\text{Co}_{0.36}\text{Fe}_{0.64}]^A[\text{Co}_{0.64}\text{Fe}_{1.36}]^B\text{O}_4$, $[\text{Fe}]^A[\text{NiFe}]^B\text{O}_4$, $[\text{Zn}_{0.36}\text{Fe}_{0.64}]^A[\text{Zn}_{0.64}\text{Fe}_{1.36}]^B\text{O}_4$, and $[\text{M}_{0.01}\text{Fe}_{0.99}]^A[\text{M}_{0.79}\text{Fe}_{1.21}]^B\text{O}_4$, respectively (Table S3). These distributions confirm that while CoFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ catalysts are partially inverse ferrites, the NiFe_2O_4 catalyst is an ideal inverse ferrite.

TEM was next employed to gather information on the size of the obtained catalysts. Figure 2 shows representative low-magnification TEM images of the ferrites. The NPs were found to be moderately agglomerated and reasonably polydisperse with average sizes of $20 \pm 7\text{ nm}$, $26 \pm 6\text{ nm}$, $18 \pm 4\text{ nm}$, and $21 \pm 5\text{ nm}$ for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, respectively (Table S1, Figure S3). Notably, the observed nanocrystalline nature of the catalysts gave rise to relatively high specific surface areas, S_{BET} , which were estimated to be 65, 42, 54, and 84 m^2/g for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, respectively (Table S1). Further, SEM-EDX/STEM-EDX was used for the elemental analysis of the catalysts. The obtained data confirmed the chemical composition of the samples (Figures S4 to S6), as well as indicated the elements to be uniformly distributed, even within the high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ ferrite (Figure S6).

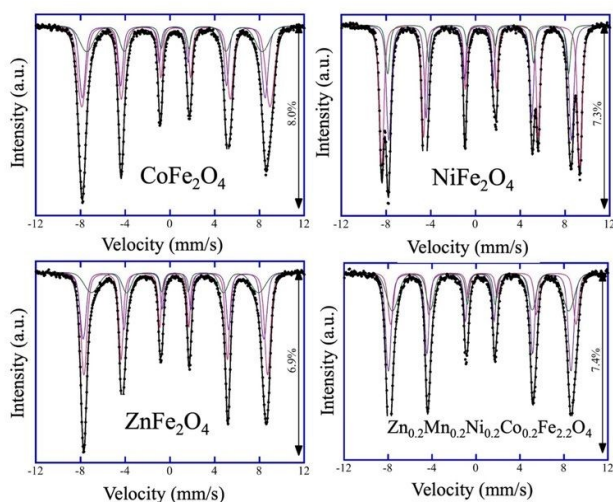


Figure 1. Mössbauer spectra for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ catalysts collected at 6 K. Experimental data: black circles. Calculated spectrum: black line. Q_1 , Q_2 , and Q_3 components: red, violet, and green, respectively.

After confirming the phase composition of the catalysts, the cation distribution within the ferrite catalysts was studied. Notably, the spinel structure $AB_2\text{O}_4$ has tetrahedral (A) and octahedral (B) sites, and for ferrites with normal and inverse spinel crystal structures the compositions $[\text{M}_1]^A[\text{Fe}_2]^B\text{O}_4$ and $[\text{Fe}_1]^A[\text{M}_1\text{Fe}_1]^B\text{O}_4$ are expected, respectively. To estimate the

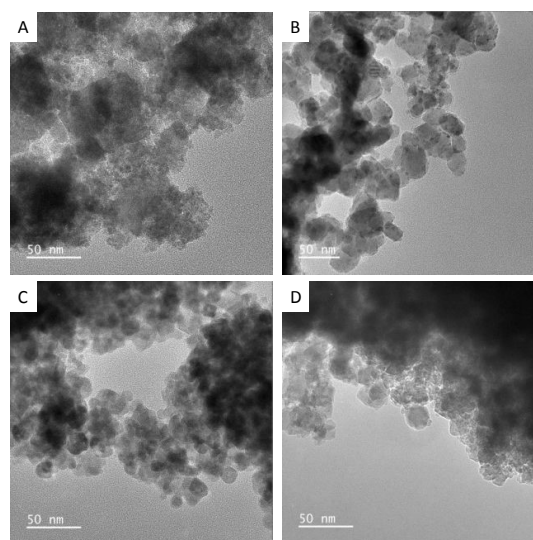


Figure 2. Representative low-magnification TEM images of CoFe_2O_4 (a), NiFe_2O_4 (b), ZnFe_2O_4 (c), and high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ (d) catalysts.



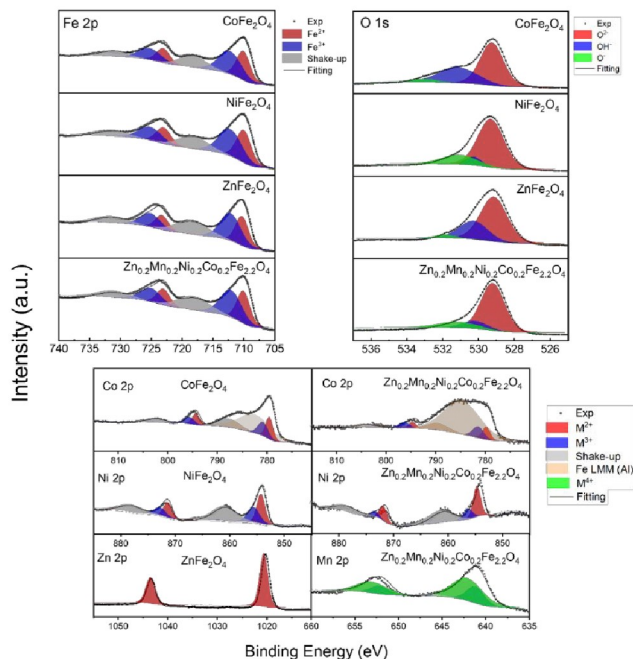


Figure 3. XPS spectra collected from the CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ catalysts synthesized by coprecipitation method followed by calcination and ball milling. High-resolution XPS data for the Fe 2p and O 1s region collected from all studied catalysts (up panel). High-resolution XPS data for the rest metallic element, such as Co 2p, Ni 2p, Zn 2p and Mn 2p for the catalysts.

Since the catalysis taking place at the surface of the materials, X-ray photoelectron spectroscopy (XPS) was used to probe the surface of the catalysts. Figures 3 and S7 show the survey and the high-resolution XPS data for the synthesized CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ materials. The deconvolution of the XPS data revealed that the as-synthesized ferrites display the expected elemental composition at the surface. In the ferrites where Co is present, the detailed XPS peaks (Co $2p_{3/2}$) located at 780.5 eV, 782.1 eV, and 787.5 eV can be attributed to Co^{2+} and Co^{3+} , together with the corresponding shakeup satellites,^{41, 42} which is consistent with the Mössbauer data above. Here the peak located at around 782 eV is attributed to Auger line of Fe LMM (its contribution is much more pronounced in the case of $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, due to higher Fe:Co ratio). The same applies to the other synthesized ferrite catalysts (Figures 3, S7), where the corresponding ionic species were observed, namely, for $\text{Ni}^{2+}/\text{Ni}^{3+}$,^{43, 44} Zn^{2+} ,⁴⁵ and Mn^{2+} .⁴⁶ In the case of the Fe 2p XPS spectra, BEs at 710.5 eV, 712.0 eV, and 716.0 eV can be attributed to Fe^{2+} and Fe^{3+} , together with the corresponding shakeup satellites.^{47, 48} Moreover, the asymmetric nature of the Fe $2p_{3/2}$ bands for all the ferrites further suggests the existence of Fe^{3+} ions in the octahedral and tetrahedral sites of the structures.⁴⁹ In all the catalysts, in the O 1s XPS data, the bands located at around 529.2 eV, 530.4 eV, and 531.5 eV are attributed to O^{2-} (metal oxide), OH^- (metal hydroxide) and O^- (deficiencies, or adsorbed oxygen), confirming the formation of M–O bonds.

Next, the physical properties of the synthesized materials were studied. The magnetization *versus* magnetic field $M(H)$ dependence at 300 K is shown in Figure 4. While NiFe_2O_4 , ZnFe_2O_4 , and high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ samples demonstrate superparamagnetic-like behavior, CoFe_2O_4 features ferromagnetic-like behavior but with rather small coercivity and remanence in the $M(H)$ curve (Table S4). The lowest saturation magnetization $M_s = 15 \text{ emu g}^{-1}$ was expectedly observed for ZnFe_2O_4 . At the same time, CoFe_2O_4 , NiFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ exhibited reasonably high M_s values of 39, 44, and 50 emu g^{-1} . Further, the optical bandgap E_g of the synthesized catalysts was experimentally estimated by means of UV/Vis diffuse reflectance spectroscopy. From the Tauc plots optical bandgap values of 1.48 eV, 1.58 eV, 1.70 eV, and 1.51 eV were obtained for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, respectively (Table S1, Figure S8). Despite the limitation of this method for band gap determination,⁵⁰ the observed results are in line with reported data, wherein the optical band gap of the ferrites is strongly influenced by the preparation method, heat treatment procedures, mean particle size, and the degree of structural disorder in the lattice.^{51–55}

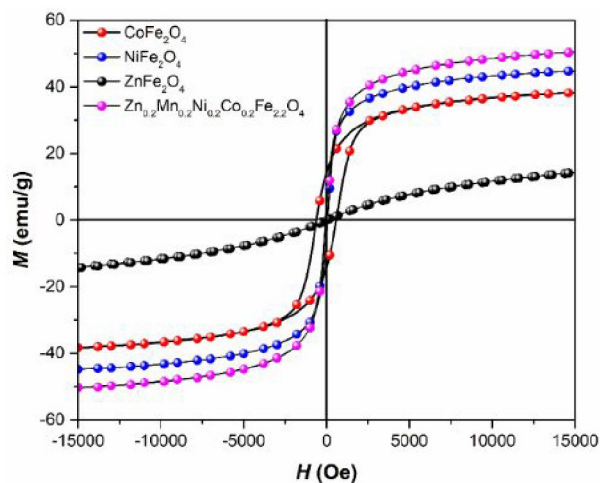


Figure 4. Room temperature $M(H)$ dependence data for the synthesized catalysts.



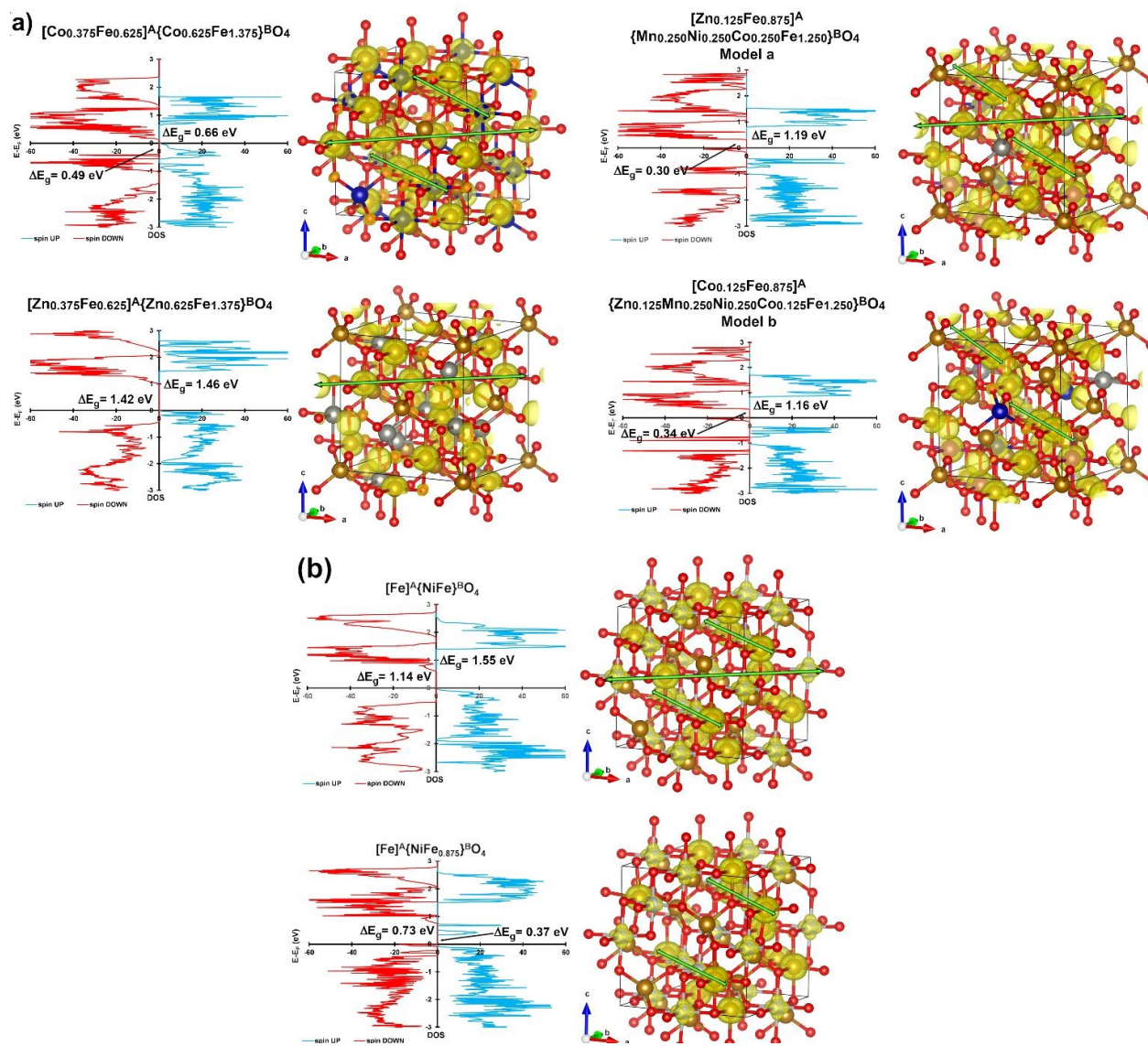


Figure 5. (a) Density of states (DOS, left) and α - β > 0 spin density (spin up, $0.04 \alpha_0^{-3}$, right) for the most stable ground states of partially inverse spinel Model a and Model b of $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, and (b) DOS (left) and α - β > 0 spin density (spin up, $0.04 \alpha_0^{-3}$, right) for the most stable ground states of perfect NiFe_2O_4 and defective $\text{NiFe}_{2-x}\text{O}_4$. Possible spin channels are marked with green arrows.

The magnetic and electronic properties of CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ were also investigated by DFT+U+J method (see section Computational study on spinel ferrites in the ESI for further information). The cation distributions provided by Mössbauer spectroscopy were used as plausible input to build the computational bulk models for all the ferrites under study. Two possible models were constructed in the case of $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ (Figure 5a) and NiFe_2O_4 (Figure 5b). The $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ bulk models were built based on both the cation distribution provided by Mössbauer spectroscopy ($T = 6$ K) and the high-resolution XPS data shown in Figure 3, in which Zn^{2+} and Co^{2+} both can occupy tetrahedral positions. Thus, $[\text{Zn}_{0.125}\text{Fe}_{0.875}]^A[\text{M}_{0.750}\text{Fe}_{1.250}]^B\text{O}_4$ ($M = \text{Co}, \text{Ni}, \text{Mn}$) and $[\text{Co}_{0.125}\text{Fe}_{0.875}]^A[\text{M}_{0.750}\text{Fe}_{1.250}]^B\text{O}_4$ ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$) are Model a and Model b, respectively, for

$\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$. These models agree with the available experimental data on $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, which report a difficult inclusion of Zn^{2+} and Ni^{2+} species into the spinel structure.⁵⁶ Regarding NiFe_2O_4 , Mössbauer spectroscopy showed an intensity of 46% at the B-sites (see the first subspectrum Q_1 in Table S2). This value is slightly smaller than the expected 50%. A possible explanation for the observed small reduction in Q_1 could be the presence of some Fe vacancies ($\approx 12\%$) at the octahedral sites of NiFe_2O_4 . This has been also experimentally suggested in the available literature data, since the cation distribution and the cation occupancy for nickel ferrite depends on several factors, such as the preparation method, calcination temperature, and particle size.⁵⁷ Thus, two computational bulk models for the inverse NiFe_2O_4 ferrite were built, one with no Fe vacancies at the octahedral sites and one



with 15% of Fe vacancies at the *B*-sites (Figure 5b). The calculated lattice parameters at 0 K of all the investigated ferrites are in good agreement with the experimental ones presented in the Table S1. Regarding the magnetic properties, all possible electronic ground states (*i.e.*, ferromagnetic, antiferromagnetic, ferrimagnetic, and non-magnetic) were computationally explored for each ferrite (Tables S8–S13, Figures S9–S20). Calculation data show that all the bulk structures possess ferrimagnetic ordering as the most stable electronic ground state at 0 K. Indeed, all the samples have non-zero magnetization at 300 K (Figure 3, Table S4), suggesting that the blocking temperature is placed between 1–300 K in the case of the superparamagnetic samples. Moreover, the calculated minimum band gaps (Figures 5a,b) show that all the ferrites under study are semiconductors, in good agreement with the experimental optical band gaps estimated by UV/Vis diffuse reflectance spectroscopy, which are known to depend on the particle size.^{58,59}

Regarding conductivity properties (Table S14), defective $\text{NiFe}_{1.875}\text{O}_4$ is the best among the investigated bulk models, exhibiting the smallest minimum band gaps (0.37 and 0.73 eV as spin \uparrow and spin \downarrow band gaps, respectively). While partially inverse $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ (Model a and Model b) and CoFe_2O_4 are the two ferrites displaying the smallest minimum band gaps within the stoichiometric ferrites, demonstrating 1.19–1.16 eV (spin \uparrow)/0.30–0.34 eV (spin \downarrow) and 0.66 eV (spin \uparrow)/0.49 eV (spin \downarrow), respectively.

With phase-pure, nanocrystalline, and chemically uniform ferrite materials in hand, we investigated the anodic OER half-reaction of electrochemical water splitting in alkaline electrolyte at room temperature by half-cell laboratory measurements.

First, we studied the OER properties of the synthesized materials in kinetic regime with low catalyst mass loading (0.3 mg/cm^2) while using RDE testing mode so that the effects of mass transport limitations are minimized.⁶⁰ As shown in the inset of Figure 6a, the basic CV characteristics of all the ferrite catalysts were quite similar: (i) capacitor-like behavior over a wide potential range, which may be ascribed to the capacitance current of both the ferrite catalyst and the conductive carbon additive; (ii) a pair of redox peaks located at $\approx 1.3 \text{ V}_{\text{RHE}}$, which may be ascribed to the redox behavior of metal hydroxide/oxyhydroxide (A^{2+} -to- A^{3+} , *e.g.*, $\text{Ni}(\text{OH})_2$ to NiOOH in the case of NiFe_2O_4) at potentials prior to the OER onset potential.

In Figure 6a, the OER current may be overlapped with the oxidation current of the ferrites, as shown by the redox peaks at $\approx 1.3 \text{ V}_{\text{RHE}}$ (inset in Figure 6a). According to the literature,^{31,61,62} the onset potential for OER over ferrite catalysts (*e.g.*, NiFe_2O_4 , CoFe_2O_4) is expected to be $\approx 1.5 \text{ V}_{\text{RHE}}$. This is also the case with most of our ferrites, with CoFe_2O_4 and ZnFe_2O_4 featuring a slightly earlier onset. Nevertheless, for the precise determination of the OER onset potential (*i.e.*, to track the onset potential for the production of O_2 rather than the anodic current), the application of *in situ* techniques, such as differential electrochemical mass spectrometry^{63,64} is necessary.

The electrochemical activity towards OER was evaluated by comparing the current densities (normalized by electrochemically active surface area) at $1.6 \text{ V}_{\text{RHE}}$ (Figure 6b). Since the measured overall current is $\approx 0.1 \text{ mA}$, the Ohmic drop corrections (*viz.*, we applied 80%) will not make a large difference.⁶⁵ All the synthesized ferrite catalysts have similar OER activities in alkaline media except for CoFe_2O_4 , the activity of which was measured to be about twice that of the others, albeit with significant uncertainty. The observed higher OER activity of CoFe_2O_4 in kinetic regime could originate from the suitable binding strength of the reactive intermediates during OER.⁶⁶

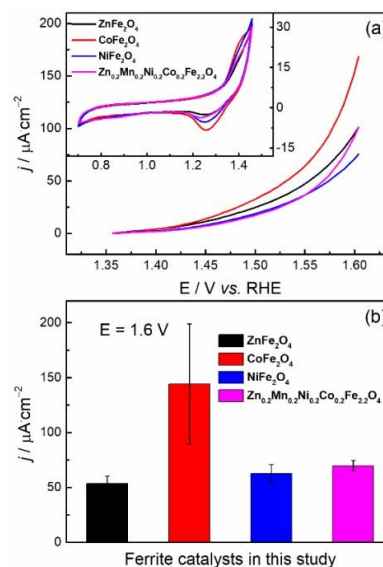


Figure 6. (a) Representative positive going linear sweep voltammograms at OER potentials and (b) the current densities (normalized by ECSA) at $1.6 \text{ V}_{\text{RHE}}$ towards OER for CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$. The corresponding basic cyclic voltammograms are given as the inset in (a).

Second, to be closer to realistic AEMEL conditions, we examined the OER properties of the synthesized ferrites with higher catalyst mass loading of 1 mg/cm^2 on glassy carbon plate to drive higher current densities.⁶⁷ For this purpose, we employed commercially available Ni foam. From the recorded LSV voltammograms (Figure 7a), the OER activity decreases in the order $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4$, with overpotential values at the current density 10 mA/cm^2 of 432, 455, 484, and 500 mV, respectively. Similarly, the Tafel slopes increase in the same trend (Figure 7b). Also, $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ shows a very low charge transfer resistance (0.66 Ohm) in the Nyquist plot (Figure 7c). Figure 7d shows the capacitive current at different scan rates recorded at the non-faradaic potential window, where $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ again shows the highest positive slope, implying the highest roughness factor. From the slope, the calculated roughness values are 61, 47, 37, and 21 for $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, NiFe_2O_4 , CoFe_2O_4 , and ZnFe_2O_4 , respectively.



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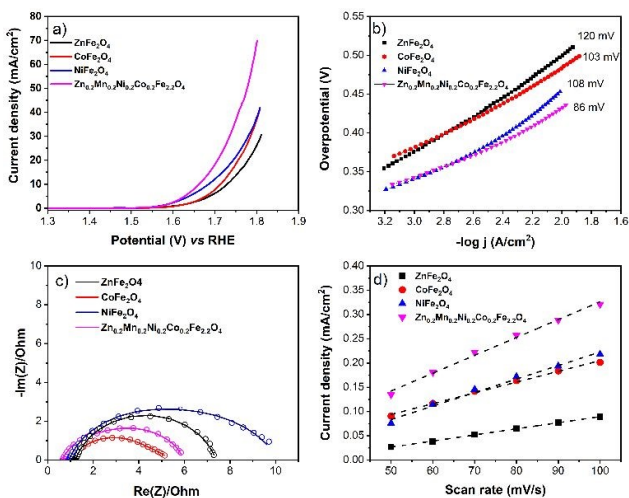


Figure 7. (a) Representative LSV voltammograms recorded at 5 mV/s scan rate and (b) Tafel plots extracted from the respective LSV curves; (c) Nyquist plot; (d) capacitive current density as a function of scan rate for the synthesized ZnFe_2O_4 , CoFe_2O_4 , NiFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ catalysts.

With the promising OER data in hand and to gain insight into structure–property relationships of the synthesized ferrite catalysts, we next implemented the materials in the AEMEL cell to study their system-level performance. Figure 8 shows the polarization curves of AEMEL cells with the four different ferrite anode catalysts, operated at 60 °C (Figure 8a) and 80 °C (Figure 8b). At a cell potential of 2.0 V, the AEMEL cells with ZnFe_2O_4 and CoFe_2O_4 anode catalysts were found to deliver the lowest current densities of ≈ 0.7 and ≈ 1.2 A/cm^2 at 60 and 80 °C, respectively. The AEMEL cells with high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ as anode showed a significantly higher performance, delivering current densities of ≈ 1.0 A/cm^2 (60 °C) and ≈ 1.5 A/cm^2 (80 °C) at a cell potential of 2.0 V. Finally, at the cell potential of 2.0 V, the AEMEL cells with NiFe_2O_4 anode catalyst was established to deliver ≈ 1.3 and ≈ 1.9 A/cm^2 at 60 and 80 °C, respectively.

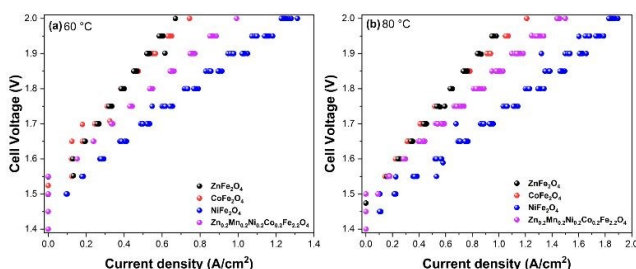


Figure 8. Polarization curves of AEMEL cells with the synthesized CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ anode catalysts recorded at 60 °C (a) and 80 °C (b) under atmospheric pressure in 1 M KOH electrolyte.

After determining the viability of the synthesized ferrites as anode catalysts on a single-cell AEMEL level, we then investigated the short-term durability of the AEMEL cells with different ferrite anodes. Figure 9 shows the cell-voltage changes under a constant current density as a function of time. Notably, the recorded cell voltages demonstrate merely small fluctuations over 20 h of chronoamperometric measurements,

thus evidencing good short-term durability of the AEMEL cells with the ferrite anode catalysts. At a constant current density of 0.5 A/cm^2 , the AEMEL cell performance decreased in the order $\text{NiFe}_2\text{O}_4 > \text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4$, reinforcing the I – V measurement results presented in Figure 8. Overall, from all the prepared ferrites with different chemical compositions and material properties, NiFe_2O_4 showed the topmost performance at the single-cell AEMEL level, affording the highest current density of ≈ 1.9 A/cm^2 with a cell voltage of 2.0 V at 80 °C while demonstrating a high stability.

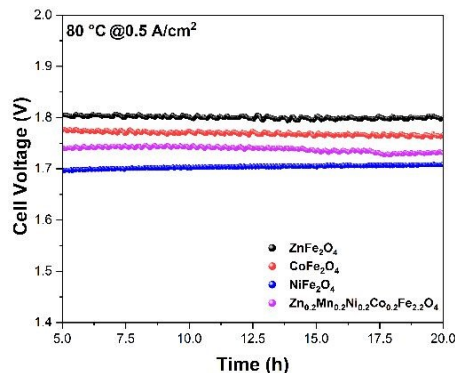


Figure 9. Cell voltage changes at a constant current density of 0.5 A/cm^2 as a function of testing time for the AEMEL cells with the synthesized CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ anode catalysts, recorded at 60 °C under atmospheric pressure in 1 M KOH electrolyte.

Discussion

The spinel ferrites, such as NiFe_2O_4 or CoFe_2O_4 , are among the most explored earth-abundant OER catalysts given their high OER activity.^{31, 43, 68–71} For example, $\text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrites anchored onto S-doped graphitic carbon nitride have been reported to exhibit low overpotential $h_{10} = 250$ mV at current density $j = 10$ mA/cm^2 and good stability.⁷² In another study, doped CoFe_2O_4 -based hollow nanospheres displayed high OER activity due to heteroatomic substitution and vacancy engineering through Cr^{3+} doping and S^{2-} exchange.⁷³ Doping with Cr^{3+} at the octahedral Fe sites induces a Co vacancy that activates the adjacent Fe^{3+} present at the tetrahedral sites. The S^{2-} exchange resulted in a structural distortion of tetrahedral Fe, leading to enhanced adsorption of intermediate $^*\text{OOH}$ species of the OER. Another work described the preparation of mesoporous first-row transition metal ferrites based on Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} ,⁷⁴ and found NiFe_2O_4 to show the highest OER activity with low $h_{10} = 278$ mV. The best OER activity was also found for NiFe_2O_4 in a study of tubular ferrite microstructures ($A\text{Fe}_2\text{O}_4$, $A = \text{Fe}^{2+}$, Co^{2+} , Ni^{2+}),⁷⁵ where the high activity was attributed to the large specific surface area, high active surface area, and low charge-transfer resistance. On that line, MnFe_2O_4 has also been reported as an alternative OER catalyst by fine-tuning the Mn occupancy at the octahedral sites along with the conversion of Mn^{2+} to Mn^{3+} through heat treatment.⁷⁶ The mixed valence of Mn resulted in improved alkaline OER activity, wherein Mn^{3+} was suggested to be more catalytically active than Mn^{2+} .



In this work, we show that the high-quality ferrite nanoparticle catalysts can be prepared at large-scale (5 g) using an automated synthesis system. The magnetic property measurements confirmed that the synthesized materials largely exhibit superparamagnetic state at room temperature as a consequence of the small size of the particles, allowing the spontaneous flip of their magnetization at room temperature. We further found that the OER properties of the synthesized ferrites are quite similar in kinetic regime at low current densities of $\gg 0.1$ mA (Figure 6). At the same time, the alkaline OER measurements with higher catalyst mass loading over glassy carbon plate, *i.e.*, at higher current densities $\gg 0.1$ mA, clearly show that the catalysts demonstrate different performance compared to the kinetic regime. Specifically, the NiFe_2O_4 and CoFe_2O_4 ferrites feature OER activities in the range of the literature data (Table S5), with overpotentials of 455 and 484 mV at 10 mA/cm², respectively. In addition, high-entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ ferrite outperforms the two-metal ferrites showing an overpotential of $\eta_{10} = 432$ mV at $j = 10$ mA/cm². Interestingly, the number of reports regarding the OER activity of high-entropy spinels is still limited as compared to one- or two-metal spinel oxides (Table S5), and the results in Figure 7 highlight the potential of such materials as highly active OER catalysts.^{77, 78}

Previously, many descriptors have been identified for the OER,⁷⁹ such as e_g electrons, M–O–M bond angle, and M–O bond length. The magnetic moment is also considered as one of the descriptors.⁸⁰ In the case of spinel ferrites, therefore, the saturation magnetization can be identified as an important macroscopic experimental descriptor, as anticipated from theory,^{23, 81, 82} as the increase in the saturation magnetization results in an increase in the OER activity in the case of ferrites AFe_2O_4 (A = Mg, Ni, Mn, Co).⁸³ This trend is clearly observed in the current study (Figure 10), with $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$, exhibiting the highest saturation magnetization, showing the highest OER activity at moderated current densities (Figure 6). On the other hand, ZnFe_2O_4 catalyst with the lowest saturation magnetization showed the lowest OER activity among the spinel ferrites (Figure 10). Also, the surface state of the high-entropy ferrite is unique compared to the ferrites with fewer elements. Namely, the presence of a higher number of elements leads to highly dispersed active sites, and may provide various active sites for OER.⁸⁴ In the present case, $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ has very low charge transfer resistance, low overpotential, low Tafel slope, low bandgap, high saturation magnetization, and high roughness factor, leading to the observed highest OER activity in moderate current density range (Figure 7). Interestingly, in full-cell AEMEL testing at high current densities, NiFe_2O_4 outperforms $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ (Figures 8, 9), and the observed AEMEL performance for these two anodes compares favorably with the literature (Table S6). Two explanations can be proposed for the superior activity of NiFe_2O_4 and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ at high current densities. First, the computational calculations revealed that nickel and high-entropy ferrites show the lowest band gaps, *i.e.*, exhibit high conductivity (Figures 5a,b, Table S13), due to the presence of Fe vacancies that help to reduce the band gap and enhance

the electron transfer. Second, after careful examination of the spin polarization of the oxygen atoms along the spin channels (Figures 5a,b), we can suggest that nickel ferrite should advantageously possess more catalytically active centers along the spin channels (*i.e.*, more metal sites with high spin-polarized oxygen atoms) than $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ ferrite, which showed spin polarization on the oxygen atoms only at very few metal sites.

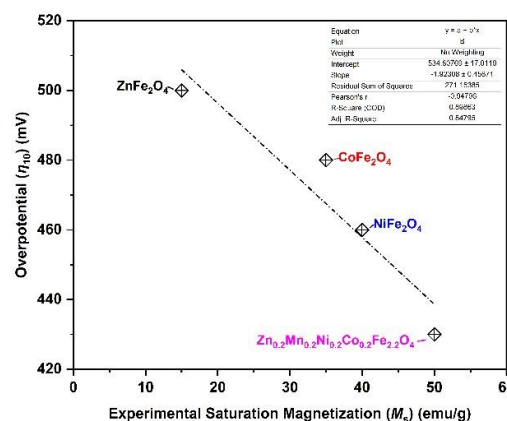


Figure 10. Alkaline OER overpotential η_{10} needed to drive current density $j = 10$ mA/cm² as a function of saturation magnetization of the synthesized ferrite catalysts.

Conclusions

The spinel ferrites, CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , and high entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ are successfully synthesized at large scale by the coprecipitation method. XRD, Mössbauer spectroscopy, and XPS confirmed the mixed spinel compositions of the samples. The magnetic measurements evidenced largely superparamagnetic ground state at room temperature of the synthesized nanocrystalline materials. In kinetic regime at very low current densities, the ferrites demonstrate similar alkaline OER properties, while high entropy $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ ferrite was established to be the best-performing OER catalyst in moderate current density range. An increase in the OER activity was observed with increasing saturation magnetization, indicating that saturation magnetization can be considered a macroscopic experimental descriptor for magnetic spinels. Finally, the AEMEL measurements at high current densities identify NiFe_2O_4 and $\text{Zn}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Fe}_{2.2}\text{O}_4$ as the most promising anode catalysts among the studied spinel ferrites, most likely due to their favorable electronic and magnetic structure, as corroborated theoretically. Future efforts should focus on (i) the electrode level optimization of AEMEL, since this hydrogen generation technology is in the developing stage at present; and (ii) investigation of the OER properties of ferrimagnetic/ferromagnetic counterparts of the ferrites presented in the current study.



Author Contributions

Tiago Fernandes: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Ramsundar Mohan:** Data curation, Investigation, Methodology, Writing – original draft. **Laura Donk:** Investigation, Methodology. **Wei Chen:** Investigation, Methodology, Writing – original draft. **Chiara Biz:** Investigation, Methodology, Writing – original draft. **Mauro Fianchini:** Investigation, Methodology, Writing – original draft. **Anna Kitayev:** Investigation, Writing – review & editing. **Saeed Kamali:** Investigation, Data curation, Writing – review & editing. **Siavash Mohammad Alizadeh:** Data curation. **Aviv Ashdot:** Investigation, Writing – review & editing. **Miles Page:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing. **Laura M. Salonen:** Writing – review & editing. **Sebastian Kopp:** Writing – review & editing. **Ervin Tal Gutelmacher:** Funding acquisition, Resources, Supervision, Validation, Writing – review & editing. **José Gracia:** Funding acquisition, Resources, Supervision, Validation, Writing – review & editing. **Marta Costa Figueiredo:** Funding acquisition, Resources, Supervision, Validation, Writing – review & editing. **Yury V. Kolen'ko:** Funding acquisition, Resources, Supervision, Validation, Writing – review & editing.

Acknowledgements

This work was supported by the European Union's Horizon 2020 research and innovation program through the SpinCat Project under Grant Agreement No. 964972. The authors also thank the feedback provided by Dr. Oleksandr Bondarchuk during XPS analysis of the samples.

Conflicts of interest

There are no conflicts to declare.

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The data supporting this article have been included as part of the Supplementary Information. Data related to materials synthesis and characterization is openly available in a public repository that issues datasets with DOIs.

View Article Online
DOI: 10.1039/D4YA00170B

