Partially substituted magnetic ferrites as Pt-free catalysts for hydrogen evolution from water photo-electrolysis

Luana De Pasquale,[a,†] Tatiana Rodriguez-Flores,[b,†] Daniele Valenzisi,[b] Falak Shafiq,[b] Roberto Scotti,[b] Francesco Tavella,[a] Matteo Cantoni,[c] Maria Vittoria Dozzi,[d] Chiara Genovese,[a,*] Roberto Nisticò [b,*]

[a]University of Messina, Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFaram), Viale F.S.D'Alcontres 31, 98166 Messina, Italy.
[b]University of Milano-Bicocca, Department of Materials Science, U5, INSTM, Via R. Cozzi 55, 20125 Milano, Italy.
[c]Politecnico di Milano, Department of Physics, Via G. Colombo 81, 20133 Milano, Italy.
[d]Università degli studi di Milano, Dipartimento di Chimica, Via C. Golgi 19, 20133 Milano, Italy.
[†]Both authors contributed equally to this work.
*Corresponding authors. E-mails: chiara.genovese@unime.it (C.G.); roberto.nistico@unimib.it (R.N.).

Supporting Information (SI)

Table S1. Samples synthesized and compositional parameters.

Sample	**Precursors molar ratio Cu:Co:Zn:Fe**	**Nominal chemical composition (description)**
Cu100Fe	1.00:0.00:0.00:2.00	$CuFe_2O_4$ (bare Cu ferrite)
Co100Fe	0.00:1.00:0.00:2.00	$CoFe_2O_4$ (bare Co ferrite)
Zn100Fe	0.00:0.00:1.00:2.00	$ZnFe_2O_4$ (bare Zn ferrite)
Cu95Co5Fe	0.95:0.05:0.00:2.00	$Cu_{0.95}Co_{0.05}Fe_2O_4$ (5% Co substituted Cu ferrite)
Cu90Co10Fe	0.90:0.10:0.00:2.00	$Cu_{0.90}Co_{0.10}Fe_2O_4$ (10% Co substituted Cu ferrite
Cu75Co25Fe	0.75:0.25:0.00:2.00	$Cu_{0.75}Co_{0.25}Fe_2O_4$ (25% Co substituted Cu ferrite)
Cu50Co50Fe	0.50:0.50:0.00:2.00	$Cu_{0.50}Co_{0.50}Fe_2O_4$ (50% Co substituted Cu ferrite)
Cu95Zn5Fe	0.95:0.00:0.05:2.00	$Cu_{0.95}Zn_{0.05}Fe_2O_4$ (5% Zn substituted Cu ferrite)
Cu90Zn10Fe	0.90:0.00:0.10:2.00	$Cu_{0.90}Zn_{0.10}Fe_2O_4$ (10% Zn substituted Cu ferrite
Cu75Zn25Fe	0.75:0.00:0.25:2.00	$Cu_{0.75}Zn_{0.25}Fe_2O_4$ (25% Zn substituted Cu ferrite)
Cu50Zn50Fe	0.50:0.00:0.50:2.00	$Cu_{0.50}Zn_{0.50}Fe_2O_4$ (50% Zn substituted Cu ferrite)

Table S2. Lattice parameters calculation from the instrumental software, and crystallite average sizes estimated by means of the Scherrer Eq. (**1**) for both bare and substituted magnetic ferrite systems.

Sample	**Lattice parameter a=b=c (Å)**	**Volume ($Å^3$)**	**Crystallite average size (nm)**
Cu100Fe	8.34	580	17
Co100Fe	8.35	582	15
Zn100Fe	8.42	596	17
Cu95Co5Fe	8.41	595	22
Cu90Co10Fe	8.40	592	20
Cu75Co25Fe	8.39	591	20
Cu50Co50Fe	8.37	587	26
Cu95Zn5Fe	8.35	582	12
Cu90Zn10Fe	8.38	588	22
Cu75Zn25Fe	8.40	593	55
Cu50Zn50Fe	8.37	585	23

Electrode preparation

The ferrite powder was preliminarily milled and then dispersed in isopropanol using a solid-to-solvent ratio of 1 mg mL^{-1}. The resulting dispersion was sonicated for 30 minutes to obtain a homogeneous suspension, without any binder. The suspension was drop-cast onto FTO-coated glass electrodes while maintaining the substrate on a hot plate set at 85 °C, and then dried overnight in an oven at 120 °C. This procedure resulted in a catalyst loading of 1 mg cm^{-2}, which was determined after the drying step.

Table S3. Current density percentage increase attained by each sample after its exposure to different light irradiation conditions.

Sample	Open spectrum	AM1.5G	UVC cut off	UVB/C cut off
Cu100Fe	17%	8%	12%	1%
Co100Fe	23%	9%	13%	2%
Zn100Fe	23%	11%	18%	3%
Cu95Co5Fe	23%	13%	20%	3%
Cu90Co10Fe	62%	26%	45%	3%
Cu75Co25Fe	40%	17%	27%	1%
Cu50Co50Fe	47%	24%	34%	2%
Cu95Zn5Fe	116%	48%	77%	29%
Cu90Zn10Fe	51%	29%	39%	16%
Cu75Zn25Fe	49%	31%	26%	19%
Cu50Zn50Fe	45%	31%	19%	19%

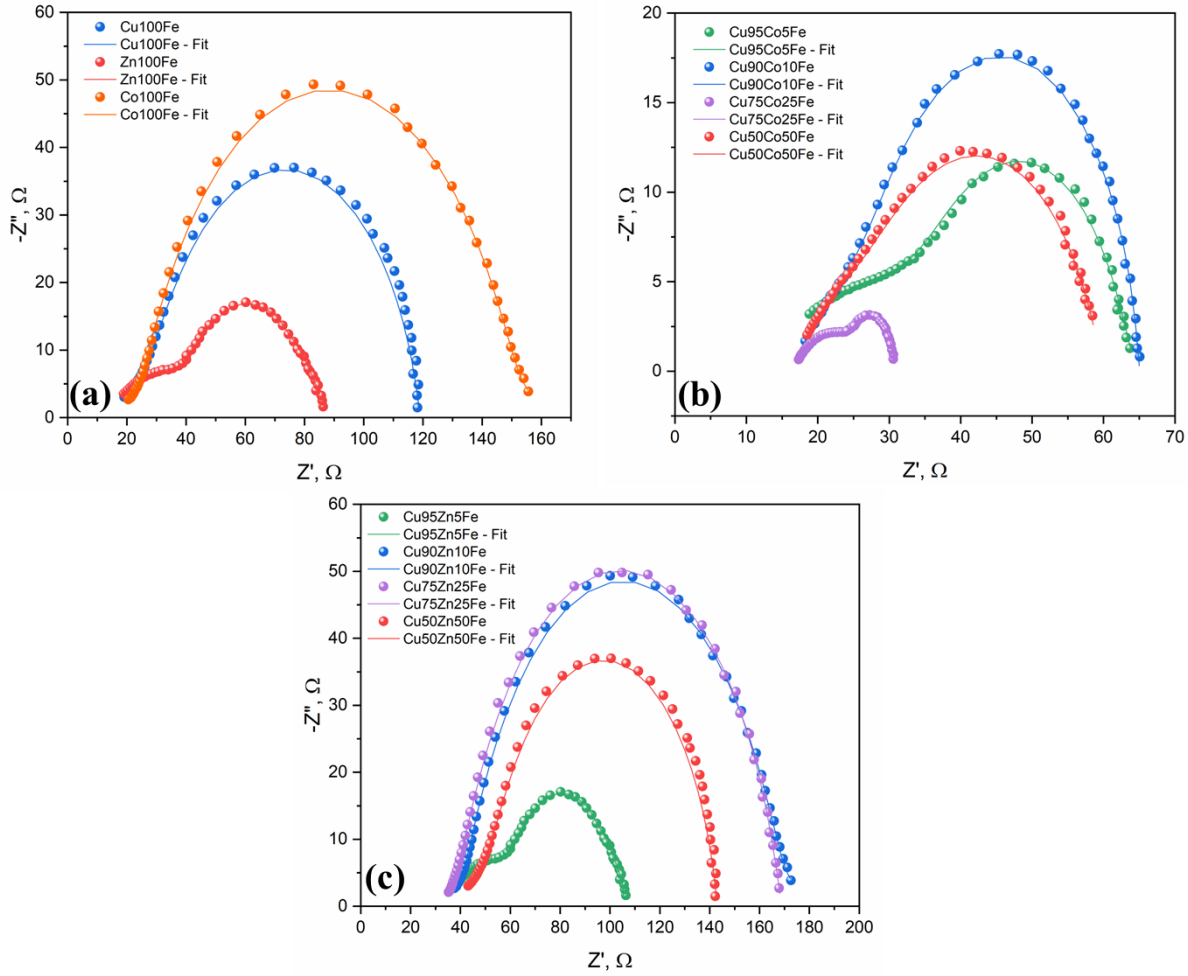

Figure S1. Nyquist plots measured in dark conditions for the bare ferrite systems (a), Co substituted Cu ferrite systems (b), Zn substituted Cu ferrite systems (c), with the dots representing the raw data (recorded applying -0.68 V vs. RHE, frequency range from 10000 Hz to 0.1 Hz, with an amplitude of 0.01 V_{rms} in dark conditions) and the lines representing the fitting.

Table S4. Resistance (in Ω) values of each sample measured by EIS fitting of the data recorded at -0.68 V vs. RHE, frequency range from 10000 Hz to 0.1 Hz, with an amplitude of 0.01 V_{rms} and with the application of light.

Sample	Rs (Ω)	CPE1-T	CPE1-P	CPE' (F)	Rp1(Ω)	CPE2-T	CPE2-P	CPE (F)	Rp2(Ω)
Cu100Fe	16.5	6.69E-05	0.57114	3.28E-07	12.5	6.73E-04	0.78252	0.000229	30.7
Co100Fe	21.7	0.000047597	0.70126	1.5E-06	6.3	1.13E-04	0.81551	3.87E-05	78.8
Zn100Fe	18.2	6.54E-04	0.50219	3.77E-06	8.4	1.25E-04	0.84781	5.03E-05	49.7
Cu95Co5Fe	16.2	1.33E-03	0.41533	1.98E-05	10.6	3.89E-03	1.083	0.004723	30.9
Cu90Co10Fe	18.6	5.80E-04	0.34932	1.76E-07	11.3	2.18E-04	0.82159	9.57E-05	17.7
Cu75Co25Fe	16.9	3.42E-03	0.42947	0.000194	6.1	2.76E-04	0.90411	0.000183	6.1
Cu50Co50Fe	17.2	3.79E-03	0.30831	4.26E-05	10.4	5.14E-04	0.89303	0.000335	15.8
Cu95Zn5Fe	30.1	5.89E-05	0.72967	3.82E-06	37.8	2.58E-03	0.61301	0.000521	20.5
Cu90Zn10Fe	23.6	1.75E-03	0.59961	0.000127	22.2	1.01E-03	0.99413	0.000983	102.4
Cu75Zn25Fe	33.2	2.04E-03	0.55516	6.08E-05	33.7	1.01E-02	0.93554	0.008301	76.1
Cu50Zn50Fe	44.1	2.28E-03	0.44712	2.23E-05	35.6	2.04E-03	0.77462	0.000751	54.6

Table S5. V_{onset} for the Hydrogen Evolution Reaction (HER) calculated with the tangent method from the CV curves**.**

Sample	**V_{onset} (V vs. RHE)**
Cu100Fe	-0.58
Co100Fe	-0.61
Zn100Fe	-0.62
Cu95Co5Fe	-0.63
Cu90Co10Fe	-0.66
Cu75Co25Fe	-0.64
Cu50Co50Fe	-0.67
Cu95Zn5Fe	-0.59
Cu90Zn10Fe	-0.45
Cu75Zn25Fe	-0.62
Cu50Zn50Fe	-0.62

Table S6. Tafel slope obtained from CV curve in mV dec^{-1}.

Sample	**Tafel slope ($mV\ dec^{-1}$)**
Cu95Co5Fe	40.50
Cu90Co10Fe	39.99
Cu75Co25Fe	43.68
Cu50Co50Fe	40.98
Cu95Zn5Fe	78.20
Cu90Zn10Fe	96.70
Cu75Zn25Fe	53.24
Cu50Zn50Fe	53.11

Evaluation of the Electrochemically Active Surface Area (ECSA)

The ECSA was evaluated by calculating the Cdl with cyclic voltammetry (CV) at a non-Faradaic potential window, starting from the OCP of the system at different scan rates (2, 5,10, 20, 30, 40, 50 mV s^{-1}). The current densities at V_{OCP} were plotted against the scan rates, resulting in a linear trend. The linear slope, representing the double-layer capacitance, C_{dl}, was divided by the specific capacitance, C_s, as follows:
ECSA = C_{dl}/C_s, where C_s is the specific capacitance for a flat surface (40 μF cm^{-2}).[S1]

Table S7. ECSA values for all the ferrite systems, reported in cm^2.

Sample	**ECSA (cm^2)**
Cu100Fe	2.16
Co100Fe	1.48
Zn100Fe	1.85
Cu95Co5Fe	1.53
Cu90Co10Fe	1.59
Cu75Co25Fe	2.06
Cu50Co50Fe	1.61
Cu95Zn5Fe	2.49
Cu90Zn10Fe	1.87
Cu75Zn25Fe	1.79
Cu50Zn50Fe	1.59

Table S8. Average current density normalized by ECSA, hydrogen production and F.E. of the PEC (bias +light) and EC (bias only) water splitting for the bare ferrite systems, Co substituted Cu ferrite systems, Zn substituted Cu ferrite systems**.**

Samples	PEC test			EC test		
	Average current density ($mA\ cm^{-2}$)	H_2 production ($mmol\ g^{-1}$)	F.E. (%)	Average current density ($mA\ cm^{-2}$)	H_2 production ($mmol\ g^{-1}$)	F.E. (%)
Cu100Fe	-2.5	227.4	81	-4.5	161.6	64
Co100Fe	-3.0	70.9	39	-3.7	51.6	27
Zn100Fe	-2.2	266.8	83	-3.3	93.0	45
Cu95Co5Fe	-3.8	164.0	49	-4.7	147.8	67
Cu90Co10Fe	-4.0	189.0	74	-3.8	83.3	66
Cu75Co25Fe	-3.3	248.7	97	-4.9	114.4	63
Cu50Co50Fe	-3.2	144.5	79	-3.6	57.8	46
Cu95Zn5Fe	-1.6	304.3	94	-2.3	152.3	71
Cu90Zn10Fe	-2.0	278.4	80	-2.9	177.1	76
Cu75Zn25Fe	-1.9	212.4	87	-2.1	91.1	70
Cu50Zn50Fe	-1.8	187.8	72	-1.3	57.7	63

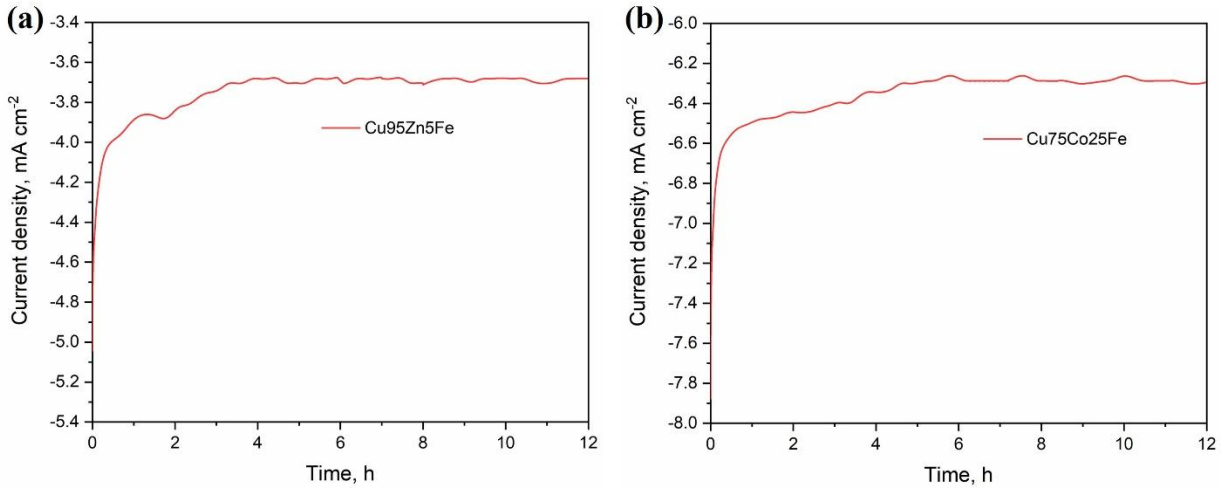

Figure S2. Chronoamperometric response of the Cu95Zn5Fe (a) and Cu75Co25Fe (b) photoelectrodes during 12 h stability tests. Reaction conditions: 0.1M Na_2SO_4, -0.68 V vs RHE, time: 12 hours, full spectrum light irradiation (385 mW cm^{-2}).

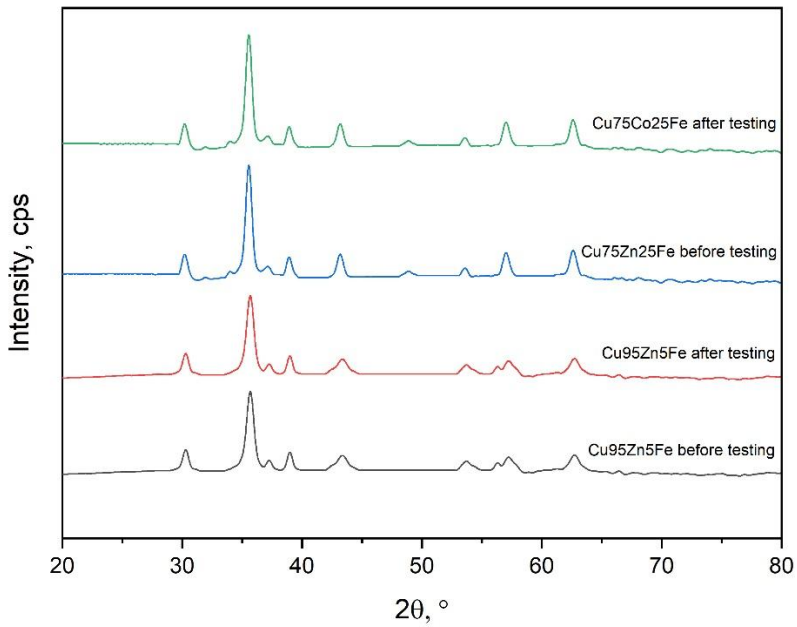

Figure S3. XRPD patterns of Cu95Zn5Fe and Cu75Co25Fe photoelectrodes before and after 12 h stability tests.

References

S1 L. Wu, L. Yu, Q. Zhu, B. McElhenny, F. Zhang, C. Wu, X. Xing, J. Bao, S. Chen and Z. Ren, Boron-modified cobalt iron layered double hydroxides for high efficiency seawater oxidation, *Nano Energy*, 2021, **83**, 105838. https://doi.org/10.1016/j.nanoen.2021.105838.