Co-doped $FeNbO_4$: Simple synthesis, DFT calculations and electrocatalytic performance for the hydrogen evolution reaction in alkaline medium

Raí F. Jucá[1,9*], Diego S. Evaristo[2], Francisco G. S. Oliveira[2], Luís P. M. Santos[3], Gilberto D. Saraiva[2], Antonio J. R. Castro[4], Nilson S. Ferreira[1,9], Luis F. Lobato[5], João M. Soares[6], Anna Luiza B. Brito[7], Rui Fausto[7,8], Marcelo A. Macêdo[1] and Benilde F.O. Costa[9]

[1]Departamento de Física, Universidade Federal de Sergipe, São Cristóvão 49100-000, Sergipe, Brazil.

[2]Faculdade de Educação Ciências e Letras do Sertão Central, Universidade Estadual do Ceará, Quixadá – CE, 62902-098 , Brazil.

[3]Programa de Pós-Graduação em Engenharia e Ciência de Materiais, Centro de Tecnologia, Universidade Federal do Ceará, Campus do Pici, Bloco 729, 60440-900, Fortaleza, CE, Brazil.

[4]Universidade Federal do Ceará, Campus Quixadá, 63902-580, Quixadá, CE, Brazil.

[5] Institute of Criminalistics, Scientific Police of Pará, Marabá, PA 68507-000, Brazil.

[6]Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59610-210, Mossoró, RN, Brazil.

[7] University of Coimbra, CQC-IMS, Department of Chemistry, P-3004-535 Coimbra, Portugal.

[8] Istanbul Kultur University, Spectroscopy@IKU, Faculty of Sciences and Letters, Department of Physics, Bakirkoy, Istanbul 34158, Türkiye.

[9]University of Coimbra, CFisUC, Department of Physics, P-3004-516 Coimbra, Portugal

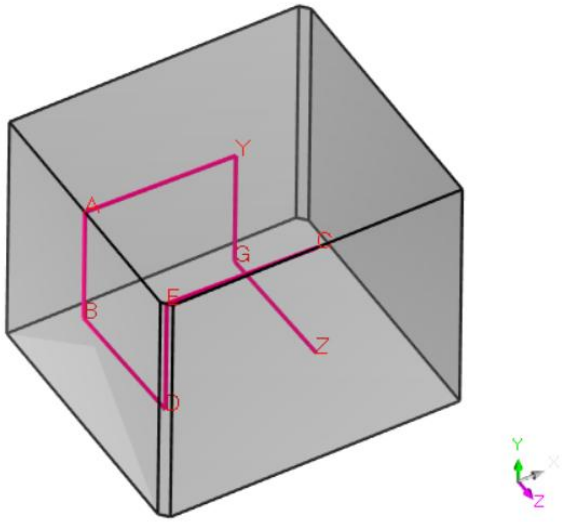

Fig. S1: reciprocal lattice of $FeNbO_4$ illustrating the high symmetry path used in this calculation.

Table S1. *Lattice parameters (a, b, c), angles (α = γ, β), unit Cell Volume (V), weighted profile factor (R_{wp}), and chi (χ^2), estimated from the XRD pattern Rietveld refinement for $Fe_{(1-x)}Co_xNbO_4$ ($0.0 \leq x \leq 0.20$).*

Co Content	*a (Å)*	*b (Å)*	*c (Å)*	*α = γ (°)*	*β (°)*	*V (Å³)*	*R_{wp} (%)*	*χ^2*
0.00	*4.6463*	*5.6137*	*4.9940*	*90.00*	*90.046*	*130.26*	*16.54*	*1.51*
0.05	*4.6468*	*5.6175*	*4.9978*	*90.00*	*90.024*	*130.46*	*16.34*	*1.32*
0.10	*4.6486*	*5.6209*	*5.0019*	*90.00*	*90.046*	*130.70*	*17.79*	*1.44*
0.15	*4.6491*	*5.6223*	*5.0029*	*90.00*	*89.962*	*130.54*	*16.77*	*1.23*
0.20	*4.6601*	*5.6364*	*5.0161*	*90.00*	*89.931*	*131.75*	*16.33*	*1.69*

Table S2. *Bond length and Angles for $Fe_{(1-x)}Co_xNbO_4$ ($0.0 \leq x \leq 0.20$) structure.*

		Co^{+2} content				
	Type	*0.00*	*0.05*	*0.10*	*0.15*	*0.20*
Bond length (Å)	*(Fe/Co)-O1*	*1.949*	*1.981*	*2.001*	*2.120*	*2.282*
	(Fe/Co)-O2	*1.969*	*1.975*	*1.968*	*1.961*	*1.965*
	(Fe/Co)-O2	*2.111*	*2.259*	*2.262*	*2.275*	*2.291*
	Nb-O1	*1.976*	*1.981*	*1.978*	*1.971*	*1.968*
	Nb-O1	*2.136*	*2.034*	*1.998*	*2.001*	*2.005*
	Nb-O2	*1.893*	*1.891*	*1.875*	*1.883*	*1.862*
Bond Angle (°)	*(Fe/Co)-O-(Fe/Co)*	*99.97*	*100.60*	*99.99*	*98.61*	*97.72*
	Nb-O-(Fe/Co)	*127.38*	*126.14*	*125.10*	*124.24*	*122.76*

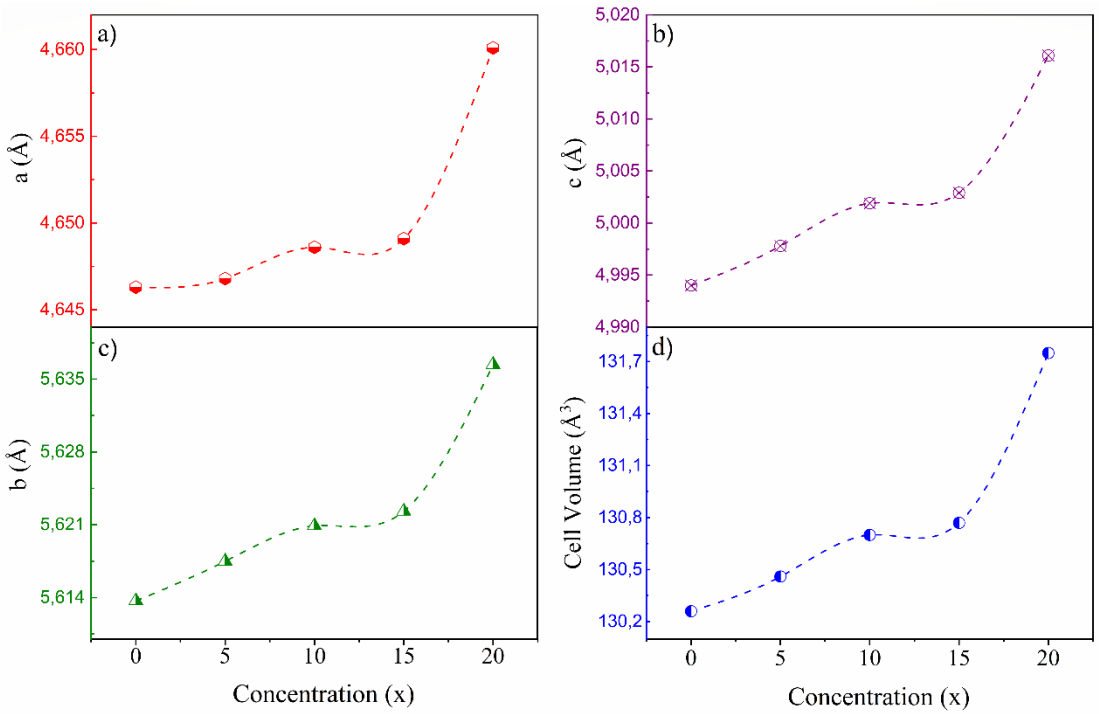

Fig. S2: (a-c) Plot of lattice parameters (a, b, c) and (d) volume as a function of increasing Co content.

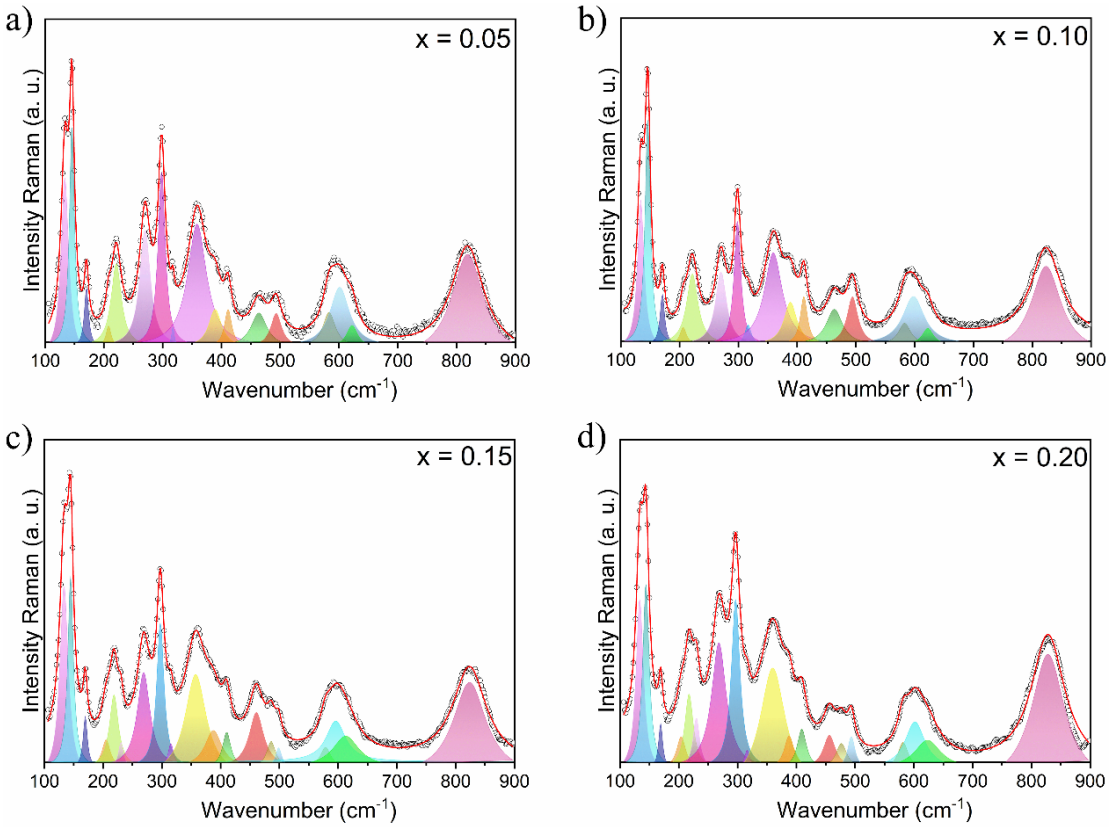

Fig. S3: Deconvolution profile of the Raman modes for $Fe_{(1-x)}Co_xNbO_4$ samples ($0.05 \leq x \leq 0.20$). (a) x = 0.05, (b) x = 0.10, (c) x = 0.15, (d) x = 0.20.

Table S3. *Raman shift modes of $Fe_{(1-x)}Co_xNbO_4$ ($0.0 \leq x \leq 0.20$) samples.*

ω_{obs} (cm^{-1})				
0	***0.05***	***0.10***	***0.15***	***0.20***
133.72	*133.73*	*134.04*	*134.07*	*134.17*
146.60	*146.01*	*145.86*	*144.77*	*144.15*
172.01	*171.04*	*170.42*	*169.95*	*169.33*
209.16	*208.20*	*206.64*	*205.09*	*204.46*
222.06	*221.25*	*222.19*	*218.77*	*217.68*
271.96	*270.22*	*271.16*	*268.98*	*268.36*
299.83	*298.52*	*298.13*	*297.43*	*296.96*
318.92	*317.64*	*316.86*	*315.62*	*315.55*
359.41	*358.68*	*359.61*	*357.59*	*359.93*
389.71	*389.62*	*388.69*	*387.91*	*387.75*
412.62	*411.69*	*411.54*	*410.76*	*409.52*
464.28	*463.63*	*463.77*	*460.82*	*456.31*
494.61	*494.71*	*494.24*	*496.46*	*489.07*
583.64	*583.67*	*583.86*	*578.35*	*581.61*
599.26	*601.36*	*597.48*	*596.50*	*601.67*
622.30	*622.50*	*622.50*	*616.95*	*623.43*
814.51	*818.69*	*823.97*	*824.63*	*829.61*

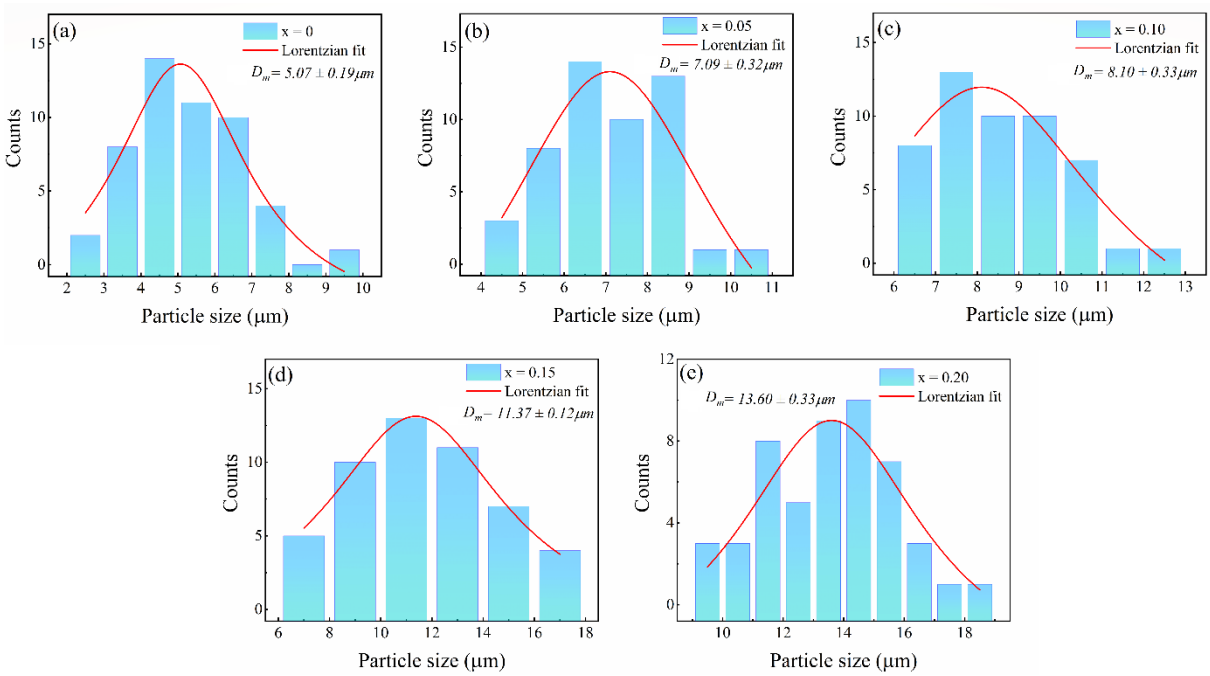

Fig. S4: Size distribution histograms obtained from SEM images for $Fe_{(1-x)}Co_xNbO_4$ samples ($0.05 \leq x \leq 0.20$). (a) x = 0, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15 and (e) x = 0.20.

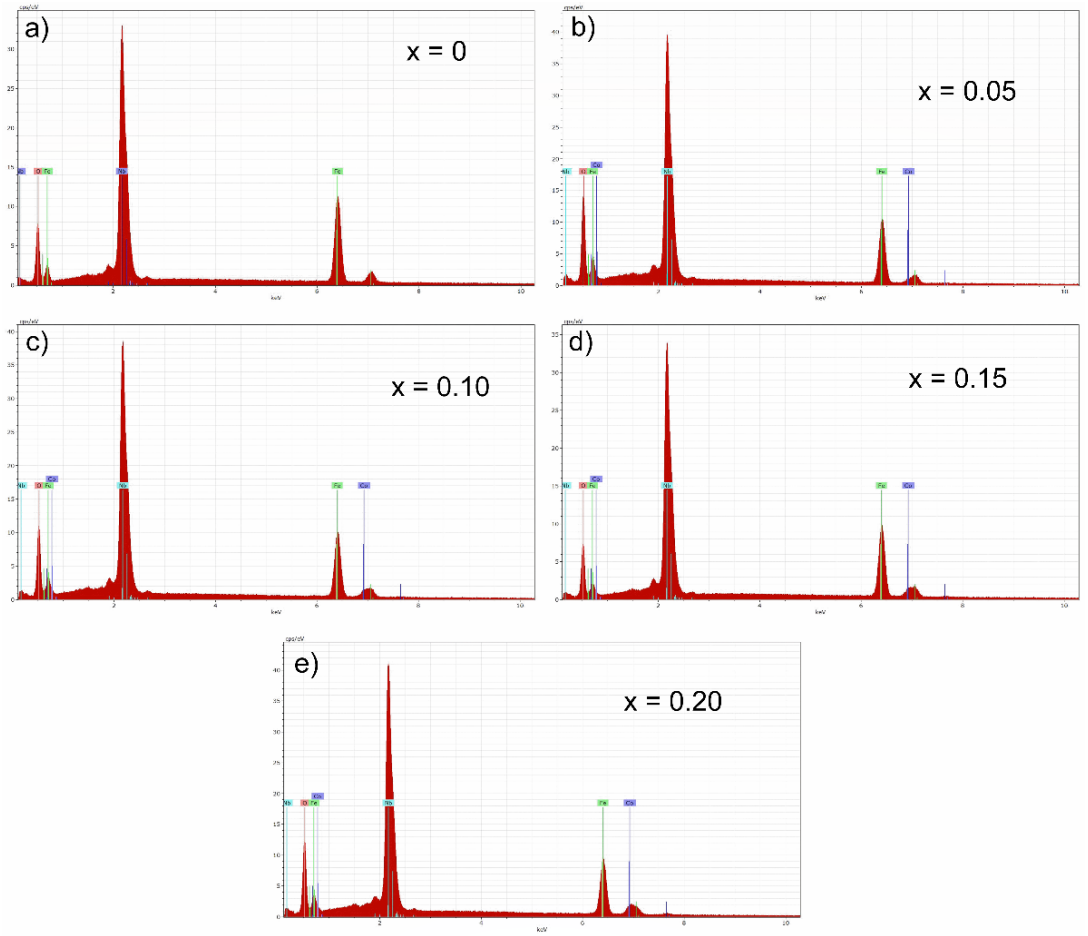

Fig. S5: EDS spectra for $Fe_{(1-x)}Co_xNbO_4$ polycrystalline. (a) x = 0.0, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15 and (e) x = 0.20.