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# ChemNanoMat

Supporting Information

## Efficient Electrocatalysts for Alkaline Oxygen Evolution Reaction from Wolframite Derived Heteroatom Materials

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**Table S1.** Chemical composition by EDX of the  $Ni_xMn_{1-x}WO_4$  series.

Element	Atomic percentage						
	Formula	$Ni_{0.9}Mn_{0.1}WO_4$	$Ni_{0.75}Mn_{0.25}WO_4$	$Ni_{0.6}Mn_{0.4}WO_4$	$Ni_{0.5}Mn_{0.5}WO_4$	$Ni_{0.4}Mn_{0.6}WO_4$	$Ni_{0.25}Mn_{0.75}WO_4$
Ni		91,45	78,99	62,31	50,61	42,18	20,11
Mn		8,55	21,01	37,69	49,39	57,82	79,89
$\Delta\%$		1,45	3,99	2,31	0,61	2,18	4,89

EDX measurements of Ni and Mn composition for samples of different formula content x (0.9 to 0.25). The results are averaged values from spectra done on 1 to 3 area of each sample. The quantification was done using the Phi-Rho-Z model without standard. The samples surfaces were not flat surface as expected by the model but a layer of nanosized particles. For such surface and without standard, significant experimental error on the quantification have been observed in the literature.<sup>[1]</sup> We considered a conservative absolute experimental error of 5 %. The observed differences between the measured and theoretical compositions ( $\Delta\%$ ) of the samples ranged from 0.61 % to 4.89 % which is within the 5 % experimental error.

**Table S2.** Chemical composition by EDX of the  $Ni_xMn_{1-x}WO_4$  series.

Element	Atomic percentage						
	Formula	$Ni_{0.9}Mn_{0.1}WO_4$	$Ni_{0.75}Mn_{0.25}WO_4$	$Ni_{0.6}Mn_{0.4}WO_4$	$Ni_{0.5}Mn_{0.5}WO_4$	$Ni_{0.4}Mn_{0.6}WO_4$	$Ni_{0.25}Mn_{0.75}WO_4$
Ni		91,45	78,99	62,31	50,61	42,18	20,11
Mn		8,55	21,01	37,69	49,39	57,82	79,89
$\Delta\%$		1,45	3,99	2,31	0,61	2,18	4,89

**Table S3.** The overpotential value of  $M1_xM2_{(1-x)}WO_4$  at different current densities.

Samples	Overpotential (v vs. RHE) at 1 mA·cm <sup>-2</sup>	Overpotential (v vs. RHE) at 5 mA·cm <sup>-2</sup>	Overpotential (v vs. RHE) at 10 mA·cm <sup>-2</sup>
$Fe_{0.5}Ni_{0.5}WO_4$	1.71	2.35	2.42
$Co_{0.5}Mn_{0.5}WO_4$	1.94	2.31	2.79
$Fe_{0.5}Co_{0.5}WO_4$	1.75	2.03	2.48
$Ni_{0.5}Mn_{0.5}WO_4$	1.63	1.75	1.83

**Table S4.** The overpotential value of  $Ni_xMn_{1-x}WO_4$  at different current densities.

Samples	Overpotential (v vs. RHE) at 1 mA·cm <sup>-2</sup>	Overpotential (v vs. RHE) at 5 mA·cm <sup>-2</sup>	Overpotential (v vs. RHE) at 10 mA·cm <sup>-2</sup>
$NiWO_4$	1.85	2.58	2.68
$Ni_{0.9}Mn_{0.1}WO_4$	2.19	2.61	2.71
$Ni_{0.75}Mn_{0.25}WO_4$	2.26	2.74	2.87
$Ni_{0.6}Mn_{0.4}WO_4$	1.75	2.23	2.29
$Ni_{0.5}Mn_{0.5}WO_4$	1.61	1.76	1.83
$Ni_{0.4}Mn_{0.6}WO_4$	1.61	2.14	2.25
$Ni_{0.25}Mn_{0.75}WO_4$	1.97	2.60	2.76
$MnWO_4$	2.02	2.60	2.71

**Table S5.** Comparison of the onset potential, overpotential and Tafel plot of samples

Samples	Overpotential (v vs. RHE) at 10 mA·cm <sup>-2</sup>	Tafel plot (mv·dec <sup>-1</sup> )
$NiWO_4$	2.68	399
$Ni_{0.9}Mn_{0.1}WO_4$	2.71	380
$Ni_{0.75}Mn_{0.25}WO_4$	2.87	322
$Ni_{0.6}Mn_{0.4}WO_4$	2.29	264
$Ni_{0.5}Mn_{0.5}WO_4$	1.83	247
$Ni_{0.4}Mn_{0.6}WO_4$	2.25	252
$Ni_{0.25}Mn_{0.75}WO_4$	2.76	379
$MnWO_4$	2.71	373

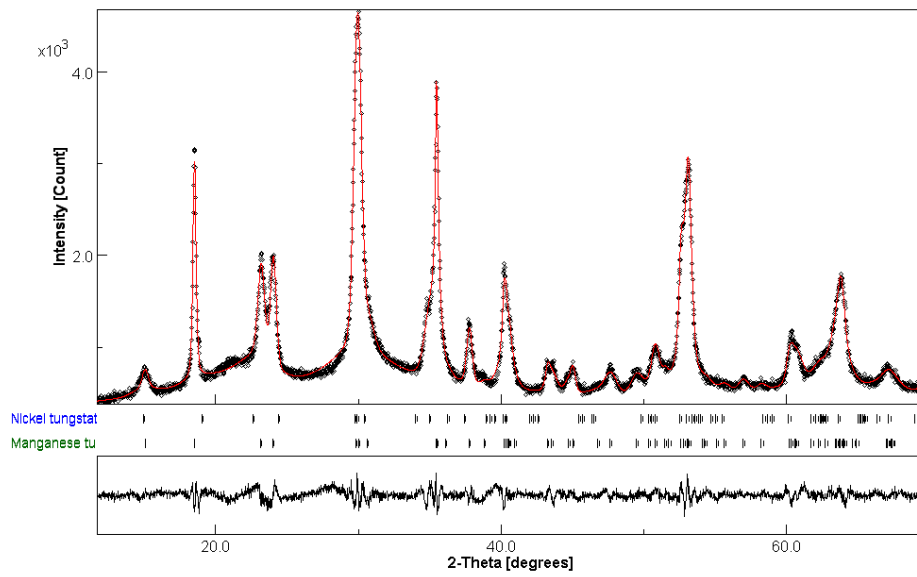


Figure S1. Rietveld plot for  $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{WO}_4$  sample.

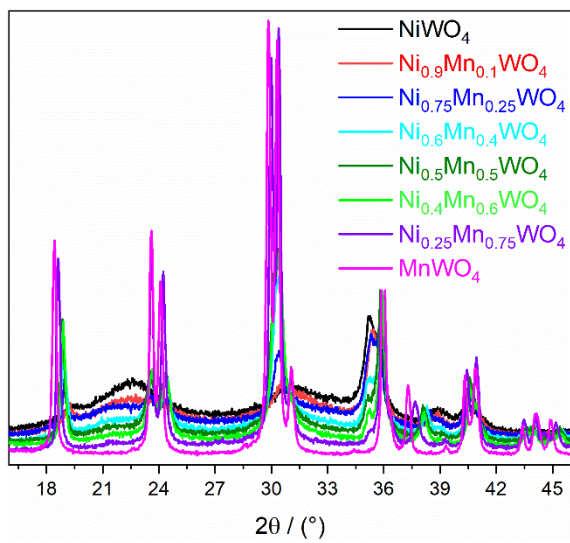
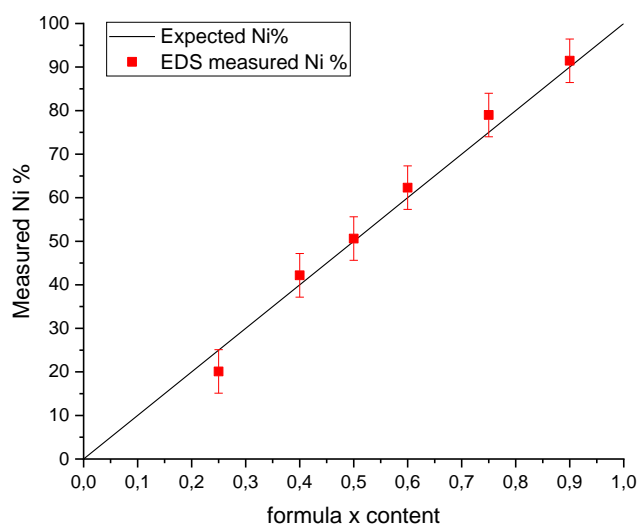


Figure S2. XRD patterns for selected  $\text{Ni}_x\text{Mn}_{1-x}\text{WO}_4$  samples



**Figure S3.** Chemical composition by EDX of the  $\text{Ni}_x\text{Mn}_{1-x}\text{WO}_4$  series. Comparison of theoretical (black line) and measured (red square) nickel proportion for  $\text{Ni}_x\text{Mn}_{1-x}\text{WO}_4$  series. The experimental error bar is represented by the red line.

## References

- [1] Shirley, B., Jarochowska, E. Chemical characterisation is rough: the impact of topography and measurement parameters on energy-dispersive X-ray spectroscopy in biominerals. *Facies* **68**, 7 (2022). <https://doi.org/10.1007/s10347-022-00645-4>