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A survey of Earth-abundant metal oxides as oxygen evolution electrocatalysts in acidic media (pH < 1)[†]

Jiahao Yu, ^{ab} Stefano Giancola, ^a Bahareh Khezri, ^{ab} David Nieto-Castro, ^a Jesús Redondo, ^{cd} Frederik Schiller, ^{ei} Sara Barja, ^{cef} Maria Chiara Spadaro, ^g Jordi Arbiol, ^{gh} Felipe A. Garcés-Pineda ^{*a} and José Ramón Galán-Mascarós ^{*ah}

Electrolytic hydrogen appears as one of the most promising options to store renewable energy. In this water splitting process, the sluggish kinetics of the 4-electron oxygen evolution reaction (OER) with its high overpotentials have been widely regarded as the bottleneck to facilitate a fast, energy-efficient process. In alkaline media, numerous earth-abundant metal oxides are efficient OER catalysts, stabilized by the high concentration of hydroxide anions in the electrolyte. However, under acidic conditions, where the hydrogen evolution reaction (HER) is technologically preferred, only noble metal-based oxides (RuO₂ and IrO₂) are suitable OER catalysts, putting into question the scalability to wide-spread applications due to their scarcity and high cost. Most earth abundant metal oxides dissolve at high proton concentrations. A promising strategy to avoid this drawback consists of incorporating these catalysts into partially hydrophobic composite electrodes. Following this strategy, we have been able to conduct an extensive survey of the activity and stability of mono-, bi- and trimetallic earth-abundant transition metal oxides during the electrocatalytic OER under strongly acidic conditions. Our results confirm the general validity of the strategy by using a hydrophobic electrode to confer high stability to common metal oxides under these harsh conditions. Among all OER catalysts investigated, we found that simple manganese oxides appeared as the most active also exhibiting high, long-term stability. In particular, the stability of Mn₂O₃ oxide in the OER in acidic media was well confirmed by post-electrolysis characterization data.

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Broader context

Acidic water electrolysis from electrolytes with high proton concentration has advantages in hydrogen production. However, only noble metals (typically iridium) are viable oxygen evolution (OER) catalysts to promote acidic water oxidation, limiting the techno-economic development of this technology. We are introducing a novel strategy to stabilize OER catalysts from earth abundant transition metals, by blending them into a partially hydrophobic electrode support. Under these conditions, we have investigated a variety of mono-, bi- and trimetallic oxides, to discover that Mn₂O₃ is the most active phase, reaching a competitive performance when compared with IrO₂, with a remarkable performance stability for over 24 h. The implementation of an analogous approach towards real electrolyzers may open promising opportunities for the substitution of noble metals by economic, viable counterparts.

^a Institute of Chemical Research of Catalonia (ICIQ-CERCA), The Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain.
E-mail: jgarcés@icq.es, jrgalan@icq.es

^b Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel··i Domingo 1, 43007 Tarragona, Spain

^c Department of Polymers and Advanced Materials, Centro de Física de Materiales, University of the Basque Country UPV/EHU, 20018 San Sebastián, Spain

^d Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, 18000, Prague 8, Czech Republic

^e Donostia International Physics Center (DIPC), 20018 San Sebastian, Spain

^f IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

^g Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain

^h ICREA, Passeig Lluís Companys, 23, 08010 Barcelona, Spain

ⁱ Centro de Física de Materiales (CSIC-UPV-EHU) and Materials Physics Center (MPC), 20018 San Sebastián, Spain

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by using a GATAN QUANTUM energy filter in order to obtain compositional maps.

Results and discussion

Metal oxide preparation

It has been well documented that catalyst preparation and processing may affect electrochemical performance.^{27–32} To minimize synthetic effects, all oxides for this survey were prepared by the very same combustion methodology.²² We prepared twenty five oxides in total with the following ratio among reagents: MO_x (monometallic); MM'O_x (50 : 50 ratio); and MM'M''O_x (33 : 33 : 33 ratio).

Although this method did not yield completely homogeneous materials for each composition, we chose it as a common method for all materials, to minimize performance differences originated from the use different synthetic preparation methods. The dominant crystalline phases in the products were identified by powder X-ray diffraction (PXRD) and assigned to Powder Diffraction File (PDF) cards (Fig. S2–26, ESI†). According to the structural data, most of the materials contained single crystalline phases (Table 1) with some exceptions. Metal composition was determined by energy-dispersive X-ray (EDX) spectra, and in good agreement with the reagent ratio (Fig. S7–S26 and Table S1, ESI†).

The oxides were mixed with graphite (G) and paraffin oil (PO) in the desired ratio (see the Experimental section) to obtain homogeneous composites (MO_x/GPO, MM'O_x/GPO and MM'M''O_x/GPO) to be inserted into the pocket of a working electrode.

Comparative OER performance

We applied the same experimental protocol to collect the linear sweep voltammetry (LSV) for all of the oxide electrodes in 1 M

H₂SO₄ electrolyte (Fig. 1). In the monometallic series, we observed that MnO_x shows a pre-catalytic, reversible event that we assigned to a Mn³⁺/Mn⁴⁺ oxidation (Fig. 1a). MnO_x/GPO offered the best voltage efficiency, reaching ≈ 50 mA cm^{−2} at 1.73 V although the pre-catalytic event does not allow the onset potential to be directly estimated. All other oxides showed onset potentials > 1.55 V (vs. RHE) with current densities below 20 mA cm^{−2} at 1.73 V vs. RHE (Fig. 1b and Table 2), with decreasing activity as Co > Fe > Zn > Ni. The H₂SO₄ electrolyte used does not contain metallic impurities, precluding Fe uptake, well known to enhance the activity of NiO_x phases.³³

In the bimetallic oxide series, the highest current density was found for the CoNiO_x, reaching 23 mA cm^{−2} at 1.73 V vs. RHE (Fig. 1b), still far from the activity found in MnO_x/GPO electrodes. Meanwhile, pre-catalytic oxidation peaks were found for all Mn-containing catalysts, in which MnFeO_x, MnCo_x, MnNiO_x showed quite similar activities. The rest of the series exhibited lower performance (Table 2). The FeNi oxide, which is regarded as most efficient OER electrocatalyst in alkaline media, appeared to offer the best performance before 1.7 V and then be overpassed by CoNi and MnNi oxides.^{7,34,35}

The trimetallic series (Fig. 1c), follows the same trend with the appearance of a pre-catalytic event in Mn-containing oxides. In this case, the highest activity was found for MnNiZnO_x, reaching 27 mA cm^{−2} at 1.73 V vs. RHE. No material exhibited an electrocatalytic OER performance matching that of MnO_x/GPO electrodes.

Beyond activity, stability is a crucial feature required for OER electrocatalysts. To evaluate this, we used the benchmarking protocol proposed by Jaramillo *et al.*,^{6,36} comparing the evolution of overpotential during a 2 h chronopotentiometry at 10 mA cm^{−2}. The results for the most active electrodes are shown in Fig. S27 (ESI†), with their benchmarking comparison with other electrocatalysts in recent literature (Fig. 2). We found good stability for all oxides examined in this survey, suggesting the validity of the approach: a hydrophobic binder/surface confers great stability to (almost) all metal oxides during the OER under extremely acidic conditions, opening an interesting strategy towards future applications. Some oxides (such as MnZnO_x, CoZnO_x) improved their activity during the tests. We selected MnO_x/GPO as the best performing catalyst for further studies, to better define structure/performance correlations.

OER with Mn oxides in 1 M H₂SO₄

As described before (Table 1 and Fig. S2, ESI†), the MnO_x obtained with our standardized synthetic method was indeed a mixture of two crystalline phases, Mn₂O₃ and Mn₃O₄. We prepared the Mn₂O₃ and Mn₃O₄ single phases to identify their actual OER catalytic activity. We used two different synthetic protocols to obtain pure phases of each. GPO electrodes were prepared and characterized following the same previous protocols.

After 10-cycle CV activation (Fig. S28, ESI†), LSV data of Mn₂O₃/GPO and Mn₃O₄/GPO were measured and collected. The results indicated that Mn₂O₃/GPO offered better OER activity, reaching a current density of 124 mA cm^{−2} at 1.73 V (Fig. 3a). Interestingly, the Mn₃O₄/GPO electrodes offered instead analogous

Table 1 The feeding metal ratio in syntheses and crystalline phases found by X-ray diffraction analysis

Catalyst	Crystalline phases found
MnO _x	Mn ₂ O ₃ , Mn ₃ O ₄
FeO _x	Fe ₂ O ₃
CoO _x	Co ₃ O ₄
NiO _x	NiO
ZnO _x	ZnO
MnFeO _x	(Mn, Fe) ₂ O ₃
MnCoO _x	(Co, Mn) ₃ O ₄
MnNiO _x	Ni ₆ MnO ₈
MnZnO _x	ZnMnO ₃ , ZnMn ₃ O ₄
FeCoO _x	(Co, Fe) ₂ O ₃
FeNiO _x	NiFe ₂ O ₄
FeZnO _x	ZnFe ₂ O ₄ , ZnO
CoNiO _x	(Co, Ni)O
CoZnO _x	ZnCo ₂ O ₄ , ZnO
NiZnO _x	(Ni, Zn)O
MnFeCoO _x	(Mn, Fe, Co) ₃ O ₄
MnFeNiO _x	(Mn, Ni)Fe ₂ O ₄ , (Mn, Fe)Ni ₂ O ₄
MnFeZnO _x	ZnMn ₃ O ₄ , (Fe, Zn) _{0.85} O, MnFe ₂ O ₄
MnCoNiO _x	Ni ₆ MnO ₈ , (Co, Ni)O
MnCoZnO _x	(Mn, Zn)Co ₂ O ₄
MnNiZnO _x	Ni ₆ MnO ₈ , (Ni, Zn)O
FeCoNiO _x	(Co, Ni)Fe ₂ O ₄
FeCoZnO _x	(Fe, Co) ₂ O ₃ , ZnO
FeNiZnO _x	Fe ₃ O ₄ , (Ni, Zn)O
CoNiZnO _x	CoNiO ₂ , ZnCo ₂ O ₄ , ZnO



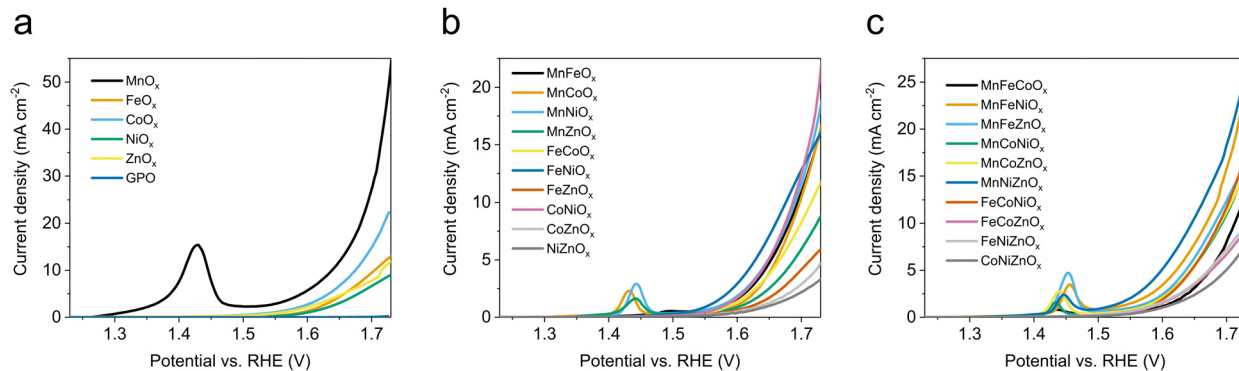


Fig. 1 LSV curves in 1 M H₂SO₄ electrolyte (pH 0.1) with 1 mV s^{−1} scan rate of (a) MO_x/GPO, (b) MM'O_x/GPO, (c) MM'M'O_x/GPO.

Table 2 Electrochemical parameters for metal-oxide/GPO electrodes. From LSV: overpotential (η_{10}) to reach $j = 10 \text{ mA cm}^{-2}$; and current density (j_{500}) at 500 mV overpotential ($\approx 1.73 \text{ V vs. RHE}$). From chronopotentiometry at $j = 10 \text{ mA cm}^{-2}$: initial overpotential ($\eta_{t=0.1}$) and overpotential after 2 h ($\eta_{t=2 \text{ h}}$)

Electrode	$\eta_{10} \text{ (V)}$ $j = 10 \text{ mA cm}^{-2}$	$j_{500} \text{ (mA cm}^{-2}\text{)}$ $\eta = 500 \text{ mV}$	$\eta_{t=0.1} \text{ (V)}$	$\eta_{t=2 \text{ h}} \text{ (V)}$
MnO _x	0.407	52	0.421	0.425
FeO _x	0.473	14	0.544	0.536
CoO _x	0.443	22	0.468	0.466
NiO _x	—	9	0.596	0.604
ZnO _x	0.486	12	0.582	0.591
MnFeO _x	0.465	16	0.485	0.466
MnCoO _x	0.467	16	0.496	0.495
MnNiO _x	0.459	18	0.488	0.480
MnZnO _x	—	9	0.546	0.488
FeCoO _x	0.485	12	0.550	0.537
FeNiO _x	0.448	16	0.537	0.548
FeZnO _x	—	6	0.615	0.588
CoNiO _x	0.454	23	0.496	0.488
CoZnO _x	—	5	0.565	0.528
NiZnO _x	—	3	0.617	0.588
MnFeCoO _x	0.484	14	0.499	0.478
MnFeNiO _x	0.437	25	0.467	0.462
MnFeZnO _x	0.453	17	0.511	0.476
MnCoNiO _x	0.462	16	0.502	0.477
MnCoZnO _x	0.462	17	0.497	0.468
MnNiZnO _x	0.417	27	0.472	0.470
FeCoNiO _x	0.458	17	0.539	0.528
FeCoZnO _x	—	9	0.537	0.518
FeNiZnO _x	—	10	0.568	0.564
CoNiZnO _x	—	8	0.558	0.533
Mn ₂ O ₃	0.328	124	0.358	0.365
Mn ₃ O ₄	0.282	74	0.438	0.432

performance to the original MnO_x/GPO electrodes. The electrochemical double-layer capacitance (EDLC) data, which are proportional to the electrochemically active area, were estimated at 29 and 10 mF cm^{−2} for Mn₂O₃/GPO and Mn₃O₄/GPO respectively (Fig. S29, ESI†). This larger EDLC may contribute to the higher electrochemical activity observed. However, this should not be the only significant effect, since other parameters point also towards a genuine better catalytic performance for Mn₂O₃/GPO.

The total density of active centers can be estimated from the Mn⁴⁺/Mn³⁺ quasi-reversible redox pair observed in the CV data (Fig. S30, ESI†). The measurements at different scan rates

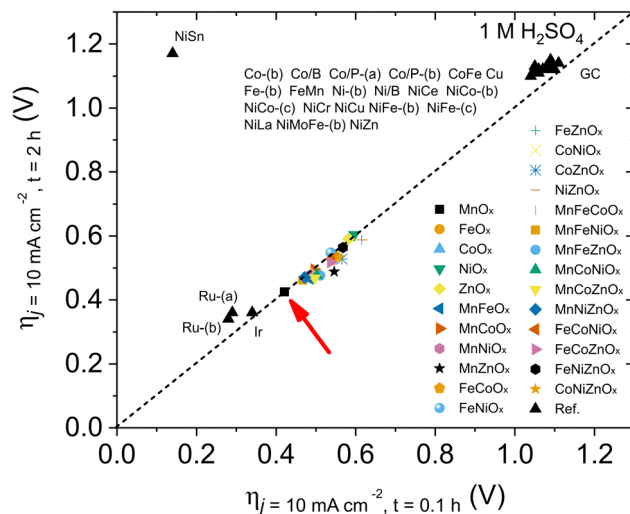


Fig. 2 Benchmarking of the activity/stability features for OER electrocatalysts in acidic media following the protocol by Jaramillo *et al.*⁶

allowed us to estimate a 172 nmol cm^{−2} density for Mn₂O₃/GPO and 100 nmol cm^{−2} density for Mn₃O₄/GPO, respectively. Besides, a higher TOF value was found for Mn₂O₃/GPO (0.0013 s^{−1}) compared to that of Mn₃O₄/GPO (0.00071 s^{−1}) under a 500 mV overpotential. In addition to the larger density of active Mn³⁺/Mn⁴⁺ centers and turnover frequency per active site, the smaller Nyquist semicircle diameter in the electrochemical impedance spectroscopy (Fig. S31, ESI†) showed a faster charge transfer for Mn₂O₃/GPO with a lower R_{ct} value of 10 Ω compared to 17 Ω of Mn₃O₄/GPO. This suggests a faster reaction mechanism also supported by the Tafel analysis: a distinct Tafel slope of 158 mV dec^{−1} was found for Mn₂O₃/GPO, much lower than the 287 mV dec^{−1} found for Mn₃O₄ (Fig. S32, ESI†). The Tafel slope is directly dependent on the kinetics of the rate-limiting step, and not on the total number of available active sites.³⁷ MnO_x/GPO electrodes showed a quite similar Tafel slope (157 mV dec^{−1}) to that of Mn₂O₃/GPO, showing the dominant contribution of the Mn₂O₃ active phase. The previous benchmarking protocol applied to Mn₂O₃/GPO showed a stable, low overpotential of $\leq 365 \text{ mV}$, to maintain

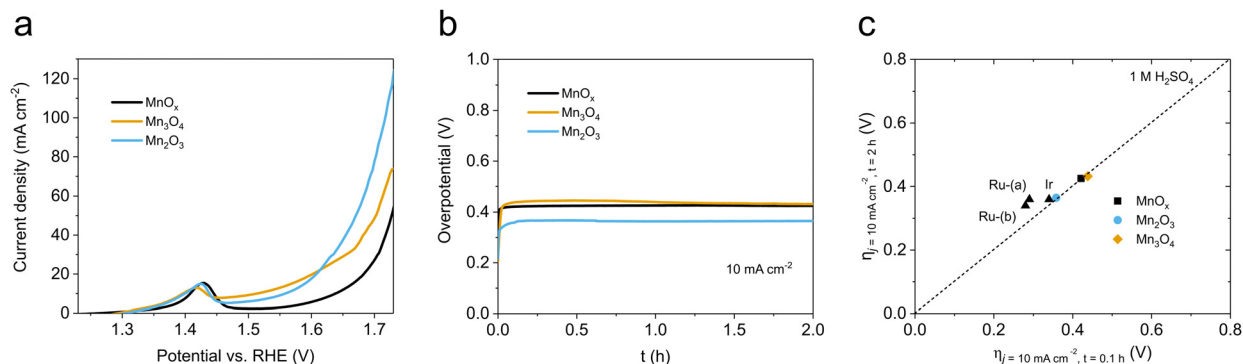


Fig. 3 (a) electrocatalytic activity of MnO_x/GPO, Mn₃O₄/GPO and Mn₂O₃/GPO; (b) stability tests of MnO_x/GPO, Mn₃O₄/GPO and Mn₂O₃/GPO in chronopotentiometry measurements at 10 mA cm⁻²; (c) benchmarking of the activity/stability features between our Mn-based oxide and noble metal-based electrocatalysts according to the study of Jaramillo *et al.*⁶

a comparable performance of noble metal (Fig. 3b and c). The long-term stability of this catalyst was also confirmed during a 24 h chronopotentiometry at 10 mA cm⁻² (Fig. S33, ESI†). Besides, this excellent stability was much better than that of other Mn-based materials towards OER in acid (Table S2, ESI†). After the benchmarking experiment, we analyzed the electrolyte content to check for any Mn leaching (Table S3, ESI†). We found the presence of Mn just at the ppb level, accounting for a maximum leaching of ≈ 0.38% of the total. With these data, we can estimate a stability number³⁸ of 130, and an activity-stability factor³⁹ of 52. An estimated lifetime of 3914 h is comparable and competitive to that of noble metal-based catalysts under analogous conditions. This is a promising performance/stability matching for noble metal oxide catalysts under acidic conditions.

To confirm the critical role of the hydrophobic binder, we performed analogous experiments with Mn₂O₃ on glassy carbon electrodes (Mn₂O₃/GC), without the addition of paraffin oil. The electrochemistry of this electrode differed significantly from that observed for the related Mn₂O₃/GPO electrode. Lower currents were reached, below 1.5 mA cm⁻² at a 500 mV overpotential (Fig. S34A, ESI†). Moreover, the Mn₂O₃/GC electrodes completely lost activity after just ~15 minutes under a 2 mA cm⁻² density (current (Fig. S34B, ESI†). This fast deactivation in the absence of the paraffin oil supports its active protective role in the GPO binder.^{19,21,22}

Finally, we measured anodic oxygen evolution during chronopotentiometry experiments with Mn₂O₃/GPO electrodes at a constant current density of 10 mA cm⁻² (Fig. S35, ESI†). >99% faradaic efficiency was obtained, confirming that the dominant catalysis process was the OER under these conditions.

Post-electrolysis Mn₂O₃/GPO characterization

We characterized the structural and chemical evolution of the Mn₂O₃/GPO electrodes after these 2 h electrolysis at 10 mA cm⁻² in 1 M H₂SO₄, further confirming the stability of Mn₂O₃ as a genuine OER catalyst. The PXRD patterns confirm the presence and stability of the Mn₂O₃ phase as no significant change nor shift were found in the observed peaks (Fig. S36, ESI†).

This suggests no evident structural changes are occurring in the bulk of the material Mn₂O₃.

We also investigated the Mn₂O₃/GPO composite after 2 h electrolysis at 10 mA cm⁻² by means of HRTEM (Fig. 4). The HRTEM images and STEM-EELS analyses also confirmed a high structural and chemical stability (Fig. S37–S41, ESI†). As we can observe in Fig. 4a, the NPs still have the orthorhombic Pbcu α-Mn₂O₃ atomic structure (S.G.: 61) imaged along its [101] zone axis. The presence of crystalline graphite has been also evidenced with the 2H oriented structure along its [0001] zone axis. In Fig. 4b both top and side views are reported and highlighted in the frequency filtered map, in red and yellow respectively. In Fig. 4c the STEM-HAADF image and STEM-EELS analysis is reported observing that the elements are homogeneously distributed confirming the atomic ratio evaluated from the HRTEM analysis. The crystalline nature of the graphite is also evidenced as it has been possible to extrapolate its contribution from the amorphous C arising from the TEM grid support. For STEM-EELS the C K edge at 284 eV (blue for amorphous and orange for graphite), O K edge at 532 eV (green) and Mn L edge at 640 eV (red) have been used. On the right side of Fig. 4c the relative composition analysis of Mn and O is also reported, to evaluate the atomic ratio of the investigated NPs. By comparing the HRTEM and STEM-EELS analysis from all the investigated samples we can observe that neither crystallinity nor particle size are affected by the electrochemical process.

We employed X-ray photoemission spectroscopy to determine the surface chemical composition of the electrodes before and after the electrocatalytic process. Fig. 5a shows the Mn 2p core-level of the Mn₂O₃/GPO composite before (ii) and after (iii) the electrochemical test. The spectra of Mn₂O₃ without the binder (i) are provided for reference.

The two main emission peaks correspond to the 2p_{3/2} and 2p_{1/2} components arising from the spin-orbit splitting. The different possible oxidation states of a transition metal in an oxide contribute to the 2p core level line shape. In this considered Mn case, this involves Mn²⁺, Mn³⁺ and Mn⁴⁺ oxidation states, which challenges the unambiguous assignment of the oxide formed (Fig. S42, ESI†). Still, the absence of satellites peaks at about 6 eV higher binding energies from 2p_{1/2} and 2p_{3/2}



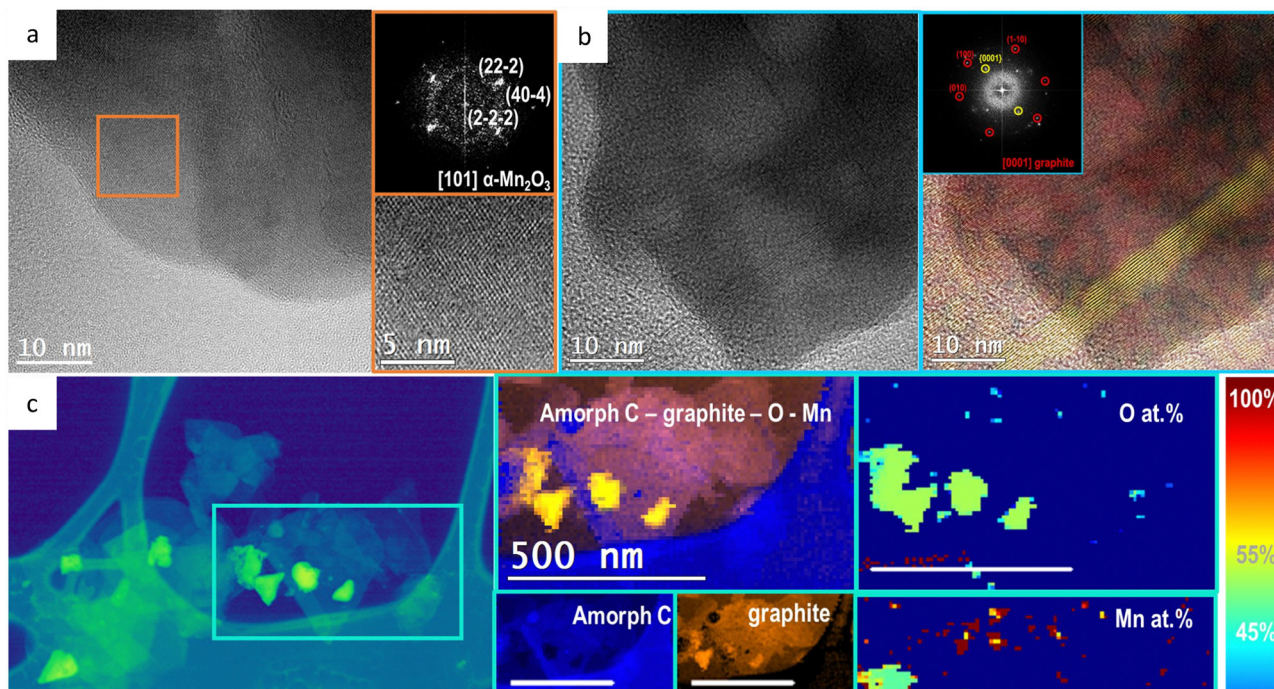


Fig. 4 (a) HRTEM general image of a Mn_2O_3 nanocrystal, with a magnified view on the bottom right and its corresponding indexed power spectrum. (b) HRTEM image showing the lattice fringes corresponding to the graphite-like structures. On the right side we present an indexed power spectrum from the same area, superposed to the obtained frequency filtered image where the found graphitic structures are shown in red and yellow, respectively. (c) False color HAADF STEM general view and the corresponding EELS composition, from relative composition analysis, for both Mn and O. (All scale bars correspond to 500 nm).

components fairly allows us to exclude the MnO phase,⁴⁰ while the observance of the Mn $2p_{1/2}$ satellite structure ($\Delta E_{2p_{1/2}\text{-sat}} \approx 10.1$ eV) supports the presence of the Mn_2O_3 phase^{41,42} identified by HRTEM analysis. Note that the apparent attenuation of the described satellite in the $\text{Mn}_2\text{O}_3/\text{GPO}$ samples is related to the

overlap with the In $3p_{3/2}$ photoemission peak from the In foil used as a sample plate (see the Experimental section).

Relevantly, we do not observe a variation of the Mn 2p line shape, nor energy shift in the binding energy of the 2p components, from the electrode after the OER compared to the as-synthesized electrode. In addition to the line shape of the Mn 2p spectra, analysis of the energy separation of the two peaks characteristics of the Mn 3s core-level has been used to identify the Mn oxidation state. Fig. 5b shows the Mn 3s spectra of the $\text{Mn}_2\text{O}_3/\text{GPO}$ composite before (ii) and after (iii) the electrochemical test, as well as the Mn_2O_3 reference (i). The energy peak separation of the Mn 3s multiplet splitting $\Delta E_{3s} \approx 5.5$ eV, constant across the three compounds, additionally supports the absence of significant changes in the oxidation state of the catalyst due to the electrochemical performance.^{41,42}

These experiments showed the bulk and functional stability of $\text{Mn}_2\text{O}_3/\text{GPO}$ electrodes during acidic OER electrocatalysis. Nevertheless, we cannot discard surface reconstruction occurring under operation conditions. This is a challenging task that will be worth investigating using appropriate techniques.⁴³

Conclusions

In summary, we have carried out a survey of earth abundant transition metal oxides as oxygen evolution electrocatalysts under acidic conditions using a conductive and partially hydrophobic support to confer on them good stability. This reliable

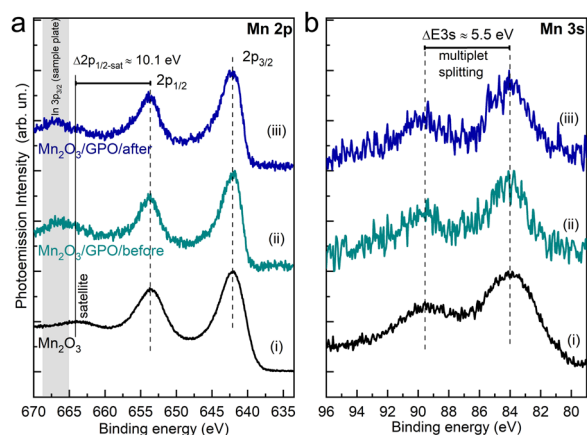


Fig. 5 XPS spectra of (a) Mn-2p and (b) Mn-3s regions of the Mn_2O_3 electrodes before (ii) and after (iii) the electrochemical performance. The spectra of the Mn oxide prior to be mixed with the graphite powder is provided as reference (i). The relative energy position of the $2p_{1/2}$ satellite and the constant magnitude of multiplet splitting in the 3s component supports the existence of a stable Mn^{3+} oxide.

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There are no conflicts to declare.

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