Review Article
Emerging trends in metal oxide electrocatalysis: Bifunctional oxygen catalysis, synergies and new insights from *in situ* studies

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Metal oxide electrocatalysts with minimal or no reliance on precious metals can display outstanding activity in oxygen catalysis and thus hold promise as materials for sustainable energy storage/conversion technologies. We review recent progress in the preparation of oxides for bifunctional oxygen reduction/evolution applications (ORR/OER) and include a summary of benchmark performances achieved over the past 3 years. Parallel and complementary progress on development of activity descriptors for the OER in oxides is also covered; special attention is dedicated to synergistic effects and the importance of support choice and oxide/support interactions to maximize activity and ensure stability. Finally, exciting mechanistic insights on OER and bifunctional ORR/OER oxide catalysis gained from recent *in situ* and *operando* X-ray experiments from the recent literature are discussed.

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The oxygen evolution (OER) and the oxygen reduction (ORR) reactions are key processes for the development of alternatives to fossil fuel-based technologies. It is therefore not surprising that the research community has demonstrated increased interest over the last decade in the discovery of new electrocatalysts and electrode design principles to improve the rate of these reactions while using commercially viable materials and/or synthetic routes. Metal oxides have a long history as electrocatalysts for oxygen redox processes in alkaline media, however, interest in understanding and improving their performance in the OER/ORR has significantly increased in the literature over the past 5 years as shown in Figure 1. Progress is critical in several important areas including: synthesis of hybrid/mixed and bifunctional oxide catalysts, low-cost oxides from earth-abundant elements, new mechanistic insights from computational and *operando* characterization methods, and further advances in electrode architecture and electrolyte optimization. In this perspective article, we will focus on recent advances in bifunctional metal oxide electrodes and oxide/support synergistic effects, as these have emerged as areas with significant margin for improvement and development, and with strong potential for gains in performance. The increasing importance of *in situ* and *operando* spectroscopic characterization methods in metal oxide electrocatalysis is illustrated in the last section, including highlights from the recent literature.
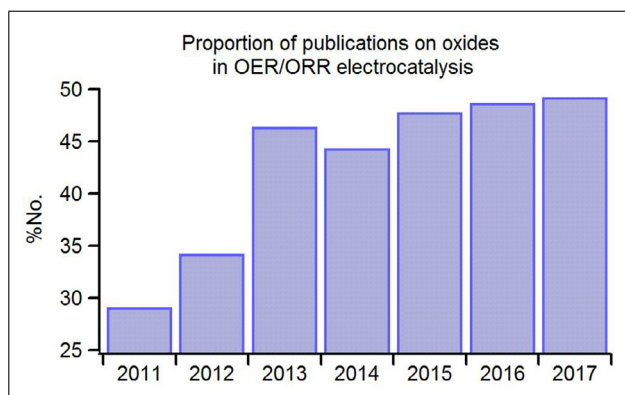
Bifunctional metal oxides
Electrocatalysis for the OER and ORR at a single bifunctional electrode would be greatly desirable for multiple applications that demand both storage and release of energy to take place in the same device, such as fuel cells and metal–air batteries. State-of-the-art catalysts for these two reactions are based on precious metals: Pt-group [1,2] catalysts and IrO_x/RuO_x [3–5] are the most active and stable catalysts for the ORR and OER, respectively. Due to the high cost and scarcity of precious metals, intense activity has been focused on the development of bifunctional electrodes that rely on non-precious metals. In alkaline media, several catalysts based on earth-abundant metals (Co, Ni, Mn, Fe) have been reported to display activity comparable to that of Pt- and Ru/Ir-based catalyst in the ORR [1,6,7] and OER [8,9], respectively. The combination of individual catalysts on the same electrode is a viable route for achieving bifunctionality, however it remains challenging to optimize reaction conditions suitable to both catalysts and/or to avoid inhibiting effects at the two extremes of a charge–discharge cycle. Thus, the identification of materials that integrate stable active sites for both reactions in a single phase remains an important goal in the field to this date.

Non-precious transition metal oxides (TMO) are promising candidates for bifunctional electrodes [10••]; TMOs, in general, show good stability in alkaline media and have been shown to perform well as ORR and OER catalysts. Notably, selected oxides of Mn and Co have been shown to display good activity in both reactions, a rare and

Figure 1

Percent number of publications over the 5 years preceding this manuscript, that focus on oxides, relative to total publications associated to keywords "electrocatalysis" and "OER" or "ORR". Source Web of Science.

Table 1

Catalytic performance of bifunctional materials in alkaline media; values referenced to the RHE.

Catalyst	E_{ORR}/V 1 mA cm^{-2}	E_{OER}/V 10 mA cm^{-2}	Ref.
RuO_2	0.54	1.64	[14•]
IrO_2	0.38	1.55	[14•]
Pt/C	0.96	1.9	[14•]
Mn_xO_y/NC	0.81	1.68	[14•]
Ni_xO_y/NC	0.71	1.64	[14•]
Co_xO_y/NC	0.8	1.66	[14•]
NiFe(OH)C	0.83	1.51	[13••]
$BaTiO_3$[b]	0.73	1.32 (E_{onset})[a]	[18]
Ar-5528[b]	0.65	1.74	[19]
$LaCoO_3$/NC[b]	0.75	1.64	[20]
$LaNi_{0.75}Fe_{0.25}O_3$/NC[b]	0.75	1.68	[20]
$LaNiO_3$/NC[b]	0.74	1.66	[20]
FeCoNi-NGT	0.9	1.55	[17••]
Cs-MnO_x-450	0.91	1.63	[21]
NiFe-LDH/NrGO	0.78	1.47	[22]
$NixCo_yO_4$/Co-NG	0.83	1.63	[23]

a: Only the onset potential (E_{onset}) was available from ref. [18]; b: Perovskites structure.
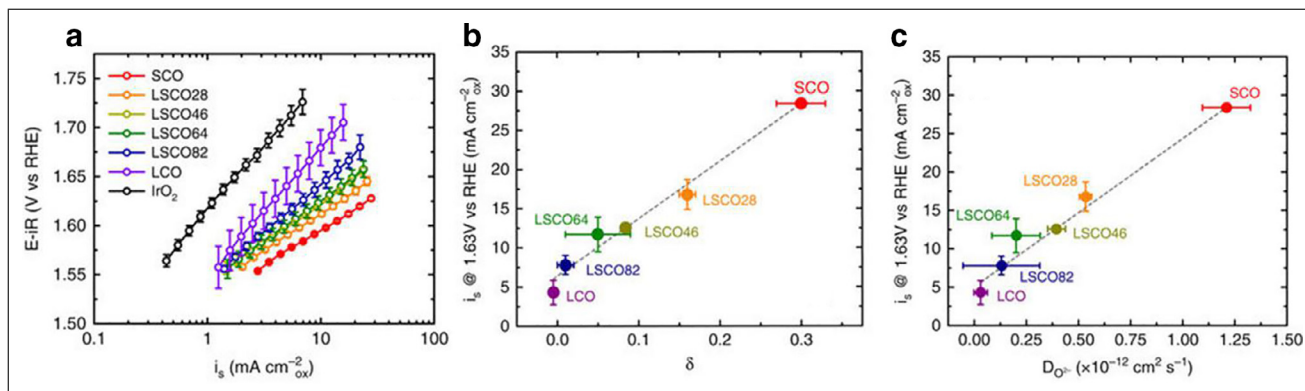
reading on this topic the recent review by Shao *et al*. [1] should be accessed.

Several groups are currently exploring the design of bifunctional TMOs for oxygen electrocatalysis. Despite a fast rise in publication numbers, two major hurdles must still be overcome to enable practical or commercial applications: (i) improving the conductivity of TMO-based electrodes and (ii) increasing catalyst stability in the OER potential region. The most investigated route thus far for addressing both of these challenges consists in preparing composite metal oxide–carbon electrodes [12•–14]. A primary role of the carbon material is to increase electrode conductivity however, the intrinsic ORR catalytic activity of selected carbon materials is also leveraged. A vast combinatorial landscape can thus be explored due to the range of TMOs that have been reported as OER catalysts [15] and the promising ORR activity showed by carbon materials with different compositions and morphology [1]. For instance, Mn_3O_4 and Co_3O_4 nanoparticles embedded in nitrogenated carbon were studied by Masa *et al*. [14•] showing good bifunctional performance, although the stability of the materials was not addressed. Strasser and co-workers [13••] combined the high activity of a double Ni/Fe layered hydroxide for the OER with an ORR-active nitrogenated carbon to prepare a two-phase composite showing the lowest combined OER/ORR overpotential ever recorded. Physical mixing of oxide and carbon phases is often used; however, the preference is to generate the sites once metal precursors to the oxide are intimately mixed with the carbon phase, as reported and discussed in Masa *et al*. [14•] and Andersen *et al*. [12•].

Nonetheless, the use of carbon materials presents significant problems, as the high potentials required for the OER result in carbon oxidation, site poisoning by corrosion byproducts and reduced catalyst stability [10••]. A quick comparison of E_{OER} values in Table 1 against the anodic stability for carbon electrodes in alkali reported by Jaramillo and co-workers [16] highlights this problem. Gupta *et al*. [17••] have recently addressed this by studying different carbon nanomaterials to select for resistance to corrosion. They proposed size-controlled graphene tubes in combination with ternary FeCoNi alloy nanoparticles as active and stable catalysts and suggest that the mitigation of the corrosion is due to the conversion of FeCoNi alloy to its oxides during the OER in bifunctional electrodes.

Finally, the use of oxides based on the perovskite structure in OER/ORR has found renewed impetus. Focus on cation substitution in the bulk structure as a tool for regulating e_g-orbital occupancy has been extensive. More recently, engineering of oxygen defect concentration has gained justified relevance as an important parameter to be leveraged for improving and rationalizing ORR/OER

desirable property that can also be leveraged for the design of bifunctional catalysts [10,11]. In this article, we will highlight recent work in OER/ORR catalysis in base; Table 1 shows a summary of recent reports of ORR/OER activity of various TMO electrodes in terms of potential (vs. RHE) at 1 mA cm^2 and 10 mA cm^{-2} current density for ORR and OER, respectively. Nonetheless, selected oxides also show good stability at low pH and for further

Figure 2

(a) Tafel plots of $La_{1-x}Sr_xCoO_{3-\delta}$ materials for the OER from ref. [24]; (b) Correlation of oxygen evolution activity with the vacancy parameter δ from ref. [24]; and (**c**) Correlation of oxygen evolution activity with the oxygen ion diffusion rate from ref. [24].
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performance, given that vacancies alter electronic properties (e-donors) and oxygen surface mobility in perovskites [24••]. Stevenson and co-workers [24••] showed strong correlation among OER activity, vacancy occupancy and oxygen diffusion rate in $La_{1-x}Sr_xCoO_{3-\delta}$ and proposed that occupancies are diagnostic of M–O covalency and that they play a mechanistic role in the OER cycle, Figure 2(a–c). These insights are relevant to explain the performance of perovskites with outstanding bifunctional performance [20] including some of the newest materials, e.g. the oxygen-deficient t-$BaTiO_{3-x}$ recently reported by Chen *et al.* [18] with ORR/OER activities comparable to state-of-the-art IrO_2 nanoparticles. Interestingly, effects of strain investigated by Petrie *et al.* [25•] in $LaNiO_3$ showed that a compressive strain can also enhance the bifunctional ORR/OER activities, a finding that might be applicable to other TMOs. Nonetheless, conductivity and stability remain important issues for practical applications of perovskites; recent work on degradation pathways under OER conditions emphasizes the need for joint optimization of activity and stability [26].
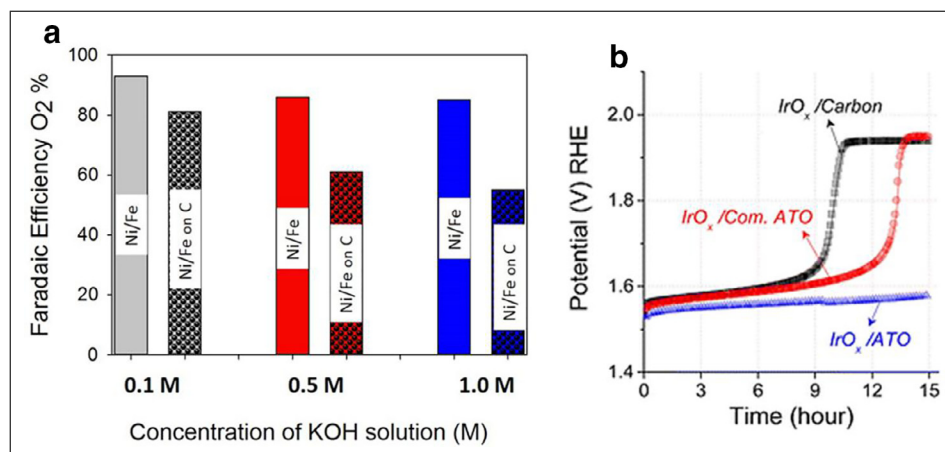
Support-catalyst synergistic effects in the OER

The benefits of synergistic effects between OER-active oxides and the support phase [27–29•], between metal centers in active mixed oxides [11,30–33], and between active oxides and electrolyte impurities or anions have been highlighted in the recent literature [28••,34–36]. Identifying synergies is critical for progress in both precious and non-precious metal oxides for the OER, as such effects can be leveraged to reduce metal load for the former and boost OER activity for the latter. In this opinion article we focus on advances in support optimization although all of the above are known to be paramount for tailoring ultimate OER performance.

Numerous recent reports support a strong link between OER activity of precious and non-precious metal oxides and the chemistry and architecture of the support [37•–41]. Seitz *et al.* [39••] investigated the performance of a MnO_x material as a function of various underlying metals on a GC substrate in 0.1 M KOH electrolyte. The underlying metals, Au, Pd, Pt and Ag, were electrodeposited, then the MnO_x was deposited by the same process on top of the relevant metal. The order of activity for MnO_x/metal followed the trend Au > Pd > Pt > Ag while unsupported MnO_x yielded a significant decrease in performance. X-Ray Absorption Spectroscopy (XAS) after OER was used to determine Mn oxidation states and showed that in MnO_x/metal layers Mn centers oxidize to Mn(IV), while in unsupported MnO_x it remains at Mn(III). Their study indicates that there are strong chemical synergies at play, so that the choice of support offers further degrees of freedom for the optimization of TMO activity in the OER.

Beyond MnO_x, Au-enhanced activities have also been reported by Ng *et al.* [37•] for a Ce-doped NiO_x catalyst, and by Zou *et al.* [40] for FeOOH. Ng *et al.*'s work proposed that NiO_x–Au interactions increase the availability of highly reactive under-coordinated Ni-sites, but we refer to an article in this same issue for a more in-depth discussion. Zou *et al.* [40] found the FeOOH/Au combination to be superior over FeOOH/Pt and attributed this to chemical reactions of Fe ions with Au after cycling, resulting in a larger fraction of the oxide film being accessible to the OER at high potentials. Another study by Wang *et al.* [29•] suggests that by modifying a SnO_2:Sb aerogel support with vanadium improves the OER activity and stability of an IrO_2 catalyst when compared to the same IrO_2 catalyst on an unmodified SnO_2:Sb aerogel support.

Figure 3

(a) Faradaic efficiencies of the OER for unsupported Ni/Fe oxide, and for Ni/Fe oxide supported on Vulcan carbon at different pH values [28••]. (Reprinted (in part) with permission from [28••]. Copyright (2017) American Chemical Society.). (b) Stability tests of IrO₂ on different supports [41]. *Source:* (Reprinted (in part) with permission from [41]. Copyright (2016) American Chemical Society.)

From literature it is evident that the choice of support, among other parameters, is critical for an optimum OER activity and more research in this area is forthcoming. It is worth however to highlight a popular but unconventional OER support, i.e. carbon. Supports should be in the first instance inert toward oxidation in the window of operation for the OER, and we recommend a detailed study of substrate selection reported by Jaramillo and co-workers on this topic [16]. Under high applied potential limits, carbon supports corrode and the associated anodic current can confound the interpretation of OER activity. A good example of problems associated with carbon inertness is Görlin *et al.* [28••] that reports the faradaic efficiencies of a mixed Ni/Fe oxide supported on carbon Vulcan powder and unsupported in three alkaline solutions (Figure 3(a)). The faradaic efficiency of the oxide was found to decrease by up to 35% when supported on Vulcan. The differences observed indicate that carbon corrosion occurs during OER for the Ni/Fe oxide; in the absence of faradaic efficiency tests the anodic currents could have been erroneously attributed entirely to the OER. Also, Oh *et al.* [41] studied the effect of supports on IrO₂ activity, comparing antimony–tin oxide (ATO) and carbon. This study concluded that ATO is more durable than the carbon support in the OER region, Figure 3(b). It remains unclear whether some of the excellent performances in OER reported for selected carbon-supported OER catalysts are affected by corrosion contributions in the absence of reported faradaic efficiencies. To minimize instability and accuracy in OER efficiency determinations, numerous authors are therefore focusing on directly addressing carbon corrosion (see above) or relying on altogether different supports for the oxide-catalyzed OER.
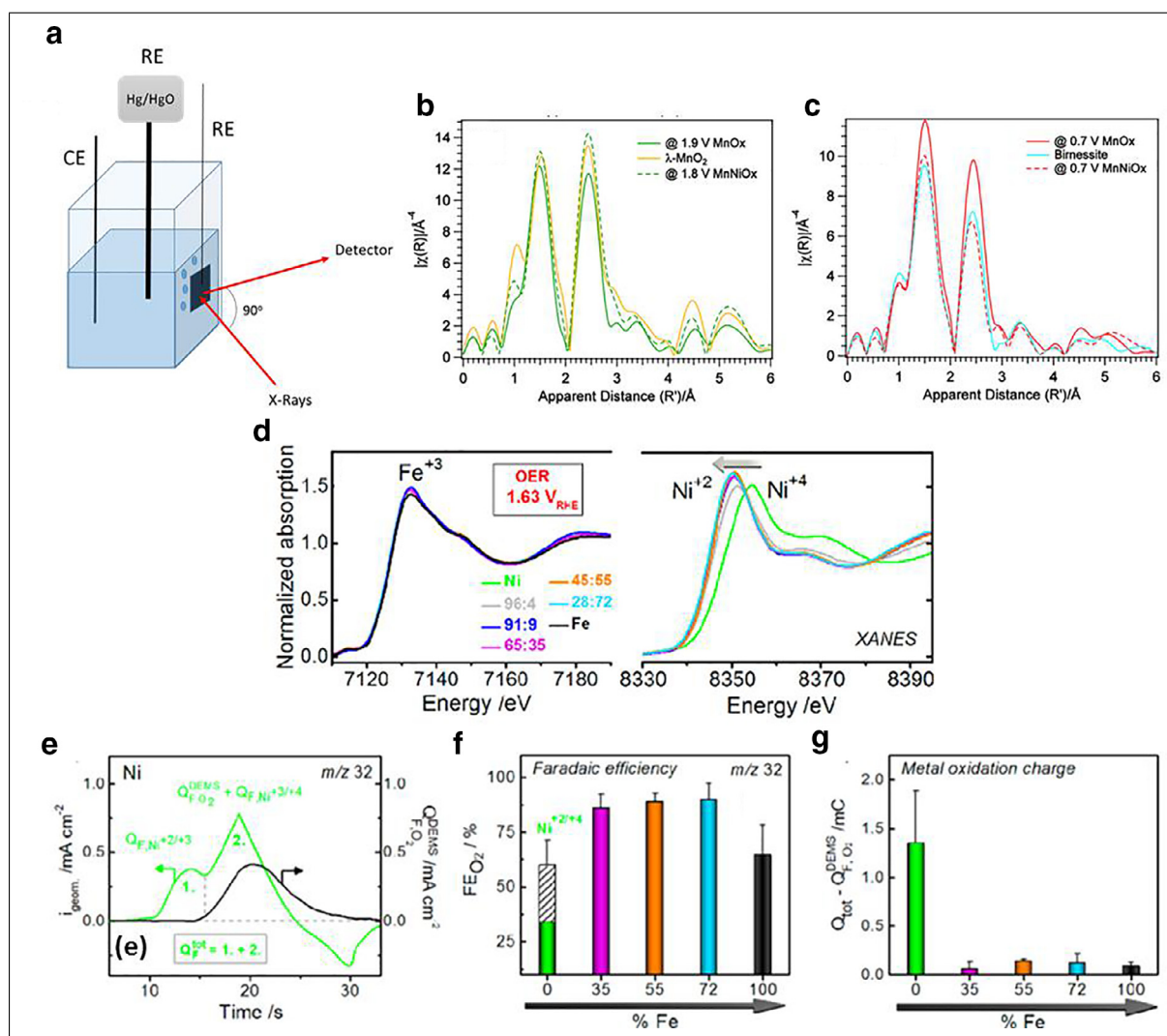
Insights from *in situ* and *operando* studies

Mechanistic understanding of oxygen catalysis at oxides is needed to optimize performance and fully leverage synergies between catalyst and metal centers, host phases and supports. X-ray methods have a stellar record in heterogeneous catalysis and their application to electrocatalysts for the OER has recently seen a remarkable expansion. *In situ* and *operando* X-ray methods play a particularly important role as they can interrogate the catalyst in its functional form and under operating conditions [42].

The best performing oxides in OER/ORR are amorphous or rich in defects and, as discussed above, defect engineering constitutes a tool for tailoring performance; hence, X-ray absorption (XAS) methods sensitive to local structure of metal sites such as extended and near-edge XAS (EXAFS and NEXAFS) are extremely powerful tools. *In situ* XANES and EXAFS at the Mn–K edge was used by Gorlin *et al.* [43] to observe phase changes associated with ORR and OER activity in an electrodeposited bifunctional MnOₓ/Au catalyst. The active phase for both the ORR and the OER in 0.1 M KOH was found to be highly porous and disordered. *In situ* monitoring revealed surprisingly facile structural transformations upon potential changes from an ORR-active disordered Mn₃O₄(II,III) phase to an OER-active MnOₓ(III/IV) layered phase similar to birnessite, Figure 4(b–c).

Mixed metal oxides display some of the best bifunctional performances, however their characterization can benefit from the ability to analyze the local structure of two or more metal centers simultaneously. Wavelength dispersive X-ray emission spectroscopy (XES) [42] can

Figure 4

(a) Schematic of *in situ* XAS conducted in a three electrode electrochemical cell. (b) Mn K-edge EXAFS spectra of MnO_x and $MnNiO_x$ under OER conditions along with a λ-MnO_2 reference pattern [43]. (c) Mn K-edge EXAFS spectra of MnO_x and $MnNiO_x$ under ORR conditions along with a birnessite reference pattern. (Reproduced (in part) from [43] with permission of The Royal Society of Chemistry). (d) Fe and Ni K-edge EXAFS spectra of Mixed Ni–Fe oxides under OER conditions [46•]. (e–g) *In operando* differential electrochemical mass spectrometry (DEMS) of a Ni catalyst [46•]. (e) *In situ* DEMS and CV scan of Ni oxide catalyst. (f) Faradaic O_2 efficiencies from the *in situ* DEMS from ref. [46•] and (g) Faradaic charge needed to change oxidation state from *in situ* DEMS from ref. [46•].
Source: (Reprinted (in part) with permission from [46•]. Copyright (2016) American Chemical Society.)

fulfill this demand for multiplex *in situ* analysis and has interestingly been applied to the study of a Ni/MnO_x bifunctional catalyst by Gul *et al.* [44••]. An analysis of XES spectral differences with respect to a reference potential was used to monitor oxidation states of Mn and Ni simultaneously. In combination with EXAFS and XRD analysis, the method provided a detailed model of phase changes vs. potential and revealed synergies between NiO_x and MnO_x, whereby the presence of NiO_x (i) imparts structural stability compared to pure MnO_x [43] with a likely advantage in terms of catalyst stability,

and (ii) improves OER activity by facilitating oxidation of Mn^{III}-centers to Mn^{IV}.

An improved understanding of synergistic effects has emerged from recent *operando* XAS experiments. In the case of single-metal oxides we note the work by Frydendal *et al.* [38] who investigated the role of Au as a support for MnO_x in OER. On the basis of XANES at the Mn K-edge and Au L_{III}-edge Au was found to facilitate access to high Mn oxidation states under OER; the authors proposed that high density of terrace sites in close interaction

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with MnO_x results in improved OER activity, possibly due to the role of Au–OH_{ads} sites as proton acceptors.

XAS *in situ* methods have recently contributed new insights and further controversy to the debate on the role of Ni- and Fe-centers in (Ni/Fe)OOH catalysts for OER. Friebel *et al.* [45•] studied the structure of mixed oxides over the full range of concentrations and concluded that irrespective of Fe% content, the average oxidation states under OER are +3 and +3.6 for Fe and Ni, respectively. The active phase was identified as Fe-doped NiOOH, with segregation of inactive FeOOH proposed at high Fe%. They observed that while the local structure at Ni-centers during OER was insensitive to Fe-doping and identical to that in OER-inactive NiOOH, the structure at Fe-centers was affected by the NiOOH host matrix. This led to their proposal that Fe cations are the active sites responsible for OER activity. Also, the presence and role of Ni^{IV} at OER catalytic potentials remains a topic of discussion; Görlin *et al.* [46•] combined *quasi in situ* XAS with *operando* differential electrochemical mass spectrometry (DEMS) and demonstrated that Fe-dopants increase the faradaic efficiency of the OER relative to competing metal oxidation to Ni^{IV}, Figure 4(d–g). Their XAS experiments suggest that low Fe% levels (<4%) favor the presence of Ni^{IV} whereas higher Fe% leads to an OER-active $Ni^{II}Fe^{III}OOH$ phase. In contrast with Friebel *et al.* they did not observe formation of separate Ni- and Fe-oxide phases. More recently, Nocera and co-workers [31] confirmed via *in situ* XANES that low Fe% values stabilize Ni^{IV} centers and increase Ni–O covalency; they proposed this favors the oxyl character of Ni–O thus promoting O–O bond formation. As pointed out in Görlin *et al.* at least part of the discrepancies observed in experimental findings and interpretation of results are likely to originate from differences in choice of deposition method/conditions and support electrode materials, which can all affect oxide structure, amorphous character and OER performance. Further clarity on the effect of these parameters on experimentally determined structures under catalytic potentials would be desirable in future work on (Ni/Fe)OOH materials.

Concluding remarks

In this overview of the very recent literature on oxygen electrocatalysis at oxide electrodes we have focused on new developments in bifunctional ORR/OER catalysts and new insights on synergistic effects. There is an active debate in the literature on the role of substrate/support for controlling electrode conductivity, stability and oxide intrinsic activity. We expect to see greater focus in the coming years on the joint optimization of activity and stability, as advocated in recent work. Further discussion of chemical stability toward ageing of many of the oxide materials reported would also be recommended. Most of the highly active oxide materials are disordered, porous and highly defective, therefore chemical ageing effects

are likely to be important; in our own work on MnO_x for the OER we have noted how structural changes in highly disordered phases can lead to activity loss [47]. A better understanding of structural instability and its undesirable but also desirable effects, as outlined in [48], would be thus beneficial.

A robust debate on synergistic effects continues as regards Ni/Fe mixed oxy-hydroxides. The controversies, as mentioned in [46•], are partly fueled by differences in phase segregation and exact conditions of preparation and testing. A better understanding on how these parameters affect activity would help research groups interested in the area of oxy-hydroxides.

Competing interest

The authors declare no competing interest.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • Paper of special interest.
- •• Paper of outstanding interest.

1. Shao M, Chang Q, Dodelet J-P, Chenitz R: *Chem. Rev.* 2016, **116**:3594–3657.

2. Lv H, Li D, Strmcnik D, Paulikas AP, Markovic NM, Stamenkovic VR: *Nano Energy* 2016, **29**:149–165.

3. Frydendal R, Paoli EA, Knudsen BP, Wickman B, Malacrida P, Stephens IEL, Chorkendorff I: *ChemElectroChem* 2014, **1**:2075–2081.

4. Seitz LC, Dickens CF, Nishio K, Hikita Y, Montoya J, Doyle A, Kirk C, Vojvodic A, Hwang HY, Norskov JK, Jaramillo TF: *Science* 2016, **353**:1011–1014.

5. Reier T, Nong HN, Teschner D, Schlögl R, Strasser P: *Adv. Energy Mater.*, vol 7; 2017 1601275–n/a.

6. Domínguez C, Pérez-Alonso FJ, Salam MA, Al-Thabaiti SA, Peña MA, García-García FJ, Barrio L, Rojas S: *Appl. Catal. B* 2016, **183**:185–196.

7. Retuerto M, Pereira AG, Pérez-Alonso FJ, Peña MA, Fierro JLG, Alonso JA, Fernández-Díaz MT, Pascual L, Rojas S: *Appl. Catal. B* 2017, **203**:363–371.

8. Dionigi F, Strasser P: *Adv. Energy Mater.*, vol 6; 2016 1600621.

9. Zhu Y, Zhou W, Chen Y, Yu J, Liu M, Shao Z: *Adv. Mater. (Weinheim, Ger.)* 2015, **27**:7150–7155.

10. Osgood H, Devaguptapu SV, Xu H, Cho J, Wu G: *Nano Today*
•• 2016, **11**:601–625.
This is a highly recommended review article on transition metal oxide catalysts including Fe, Mn, Ni and Co oxides for oxygen electrocatalysis (i.e. OER and ORR). This review discusses the aforementioned metal oxides in terms of fabrication method, physical properties and the OER/ORR performances and the correlations between all three.

11. Wei C, Feng Z, Scherer GG, Barber J, Shao-Horn Y, Xu ZJ: *Adv. Mater. (Weinheim, Ger.)*, vol 29; 2017 1606800–n/a.

12. Andersen NI, Serov A, Atanassov P: *Appl. Catal. B* 2015,
• **163**:623–627.

This manuscript reports a new synthetic method based on the growth of carbon nanotubes (CNTs) on porous supports and subsequent dispersion of non-precious metal oxide catalysts for bifunctional ORR/OER electrodes. The method is attractive as it allows for separate optimization of porosity, CNT network and type of metal oxide catalyst.

13. Dresp S, Luo F, Schmack R, Kuhl S, Gliech M, Strasser P: *Energy*
•• *Environ. Sci.* 2016, **9**:2020–2024.
This paper reports NiFe–LDH–Fe–N–C two-phase bifunctional OER/ORR catalysts fabricated through a one pot microwave assisted fabrication route. The resulting overall OER and ORR overpotential value of 0.747 V at 10 mA cm−2 is extremely encouraging. Furthermore, the catalyst was tested in a reversible electrolyzer which showed rivalling activity to the state of the art material for the OER and ORR. This paper is highly recommend to read if one is researching the OER or ORR, it shows the progression of a catalysts from powder to device and reports Faradaic efficiencies of the materials, which is needed if the catalyst contains a carbon component.

14. Masa J, Xia W, Sinev I, Zhao A, Sun Z, Grützke S, Weide P,
• Muhler M, Schuhmann W: *Angew. Chem.* 2014, **53**:8508–8512.
This manuscript tackles the problem of creating bifunctional ORR/OER catalysts with good conductivity by using a combined pyrolysis/calcination approach to create MnOx/CoOx at nitrogenated carbon supports. The activity of these materials was found to be very competitive. The role of N-sites in the carbon is also discussed and hypothesised to contribute not only to increased conductivity but also to activity via Metal–N residual coordination. The catalysts display relatively low stability due to mechanical spallation however this might be improved via alternative pore architectures.

15. Hong WT, Risch M, Stoerzinger KA, Grimaud A, Suntivich J, Shao-Horn Y: *Energy Environ. Sci.* 2015, **8**:1404–1427.

16. Benck JD, Pinaud BA, Gorlin Y, Jaramillo TF: *PLoS One*, vol 9; 2014 e107942.

17. Gupta S, Qiao L, Zhao S, Xu H, Lin Y, Devaguptapu SV, Wang X,
•• Swihart MT, Wu G: *Adv. Energy Mater.*, vol 6; 2016 1601198.
This article reports the synthesis of bifunctional catalysts based on non-precious FeNiCo nanoparticles and carbon nanomaterials. This article is highly recommended as it demonstrates that it is necessary to carefully select the carbon material to minimise corrosion and maximise catalyst stability. Nonetheless this work shows that carbon materials still hold promise, when suitably selected, for oxygen catalysis, and offers a platform for future design strategies of carbon supports for metal oxide electrocatalysts.

18. Chen C-F, King G, Dickerson RM, Papin PA, Gupta S, Kellogg WR, Wu G: *Nano Energy* 2015, **13**:423–432.

19. Jung J-I, Park S, Kim M-G, Cho J: *Adv. Energy Mater.*, vol 5; 2015 1501560–n/a.

20. Hardin WG, Mefford JT, Slanac DA, Patel BB, Wang X, Dai S, Zhao X, Ruoff RS, Johnston KP, Stevenson KJ: *Chem. Mater.* 2014, **26**:3368–3376.

21. Mosa IM, Biswas S, El-Sawy AM, Botu V, Guild C, Song W, Ramprasad R, Rusling JF, Suib SL: *J. Mater. Chem. A* 2016, **4**:620–631.

22. Zhan T, Liu X, Lu S, Hou W: *Appl. Catal. B* 2017, **205**:551–558.

23. Hao Y, Xu Y, Liu J, Sun X: *J. Mater. Chem. A* 2017, **5**:5594–5600.

24. Mefford JT, Rong X, Abakumov AM, Hardin WG, Dai S, Kolpak AM,
•• Johnston KP, Stevenson KJ: *Nat. Commun.* 2016, **7**:11053.
This article is extremely important for the design of OER catalysts and for explaining performance of bifunctional perovskites. This article shows that O-vacancies in perovskites can alter the electronic structure of the oxide and oxygen diffusion at its surface. This is essential for modulating binding strength at catalysts and explains experimental trends in OER activity.

25. Petrie JR, Cooper VR, Freeland JW, Meyer TL, Zhang Z,
• Lutterman DA, Lee HN: *J. Am. Chem. Soc.* 2016, **138**:2488–2491.
This is a very original article that proposes strain engineering as a mechanism to modulate perovskite activity in the ORR and OER. The authors experimentally show that strain in epitaxially grown LaNiO3 modulates activity in oxygen catalysis and suggest that the effect of strain on eg splitting is responsible for these changes. The use of metal Co-doping to modulate eg-occupancy has been extensively explored in the literature, however, this paper proposes a novel mechanism to

modulate eg orbitals that might find applications in other non-precious metal oxide catalysts.

26. Kim B-J, Abbott DF, Cheng X, Fabbri E, Nachtegaal M, Bozza F, Castelli IE, Lebedev D, Schäublin R, Copéret C, Graule T, Marzari N, Schmidt TJ: *ACS Catal.* 2017, **7**:3245–3256.

27. Browne MP, Nolan H, Duesberg GS, Colavita PE, Lyons MEG: *ACS Catal.* 2016, **6**:2408–2415.

28. Görlin M, Ferreira de Araújo J, Schmies H, Bernsmeier D, Dresp S,
•• Gliech M, Jusys Z, Chernev P, Kraehnert R, Dau H, Strasser P: *J. Am. Chem. Soc.* 2017, **139**:2070–2082.
This article is if outstanding interest as the results highlight the importance of oxygen faradaic efficiency testing for OER catalysts when carbon is used as a support/substrate. Stasser et al., in this article, report that when a NiFe based material is supported on carbon the O2 faradaic efficiency, in various KOH concentration electrolytes, is lower than that of a catalyst not supported at carbon.

29. Wang L, Song F, Ozouf G, Geiger D, Morawietz T, Handl M,
• Gazdzicki P, Beauger C, Kaiser U, Hiesgen R, Gago AS, Friedrich KA: *J. Mater. Chem. A* 2017, **5**:3172–3178.
This study clearly shows the importance of tailoring support/catalyst interactions to modulate OER activity. In this manuscript, vanadium doping of a SnO2:Sb aerogel support was found to enhance the activity of IrO2 catalysts dispersed on the aerogel. Support engineering allows for a reduction of up to 70% in the precious metal loading at the electrode without a decrease in performance.

30. Dai J, Zhu Y, Chen Y, Zhou W, Shao Z: *ACS Appl. Mater. Interfaces* 2017, **9**:21587–21592.

31. Li N, Bediako DK, Hadt RG, Hayes D, Kempa TJ, von Cube F, Bell DC, Chen LX, Nocera DG: *Proc. Natl. Acad. Sci.* 2017, **114**:1486–1491.

32. Bates MK, Jia Q, Doan H, Liang W, Mukerjee S: *ACS Catal.* 2016, **6**:155–161.

33. Carrasco JA, Romero J, Varela M, Hauke F, Abellan G, Hirsch A, Coronado E: *Inorg. Chem. Front.* 2016, **3**:478–487.

34. Browne MP, Stafford S, O'Brien M, Nolan H, Berner NC, Duesberg GS, Colavita PE, Lyons MEG: *J. Mater. Chem. A* 2016, **4**:11397–11407.

35. Gao Q, Ranjan C, Pavlovic Z, Blume R, Schlögl R: *ACS Catal.* 2015, **5**:7265–7275.

36. Klaus S, Cai Y, Louie MW, Trotochaud L, Bell AT: *J. Phys. Chem. C* 2015, **119**:7243–7254.

37. Ng JWD, García-Melchor M, Bajdich M, Chakthranont P, Kirk C,
• Vojvodic A, Jaramillo TF: *Nat. Energy* 2016, **1**:16053.
This article demonstrates the importance of both Co-dopants and support choice in determining OER activity of NiOx catalysts. The authors prepared a Ce-doped NiOx catalyst supported on Au electrodes. A combination of experimental and computation results suggest that both the metal doping and the choice of support are important for establishing the outstanding performance of these catalysts. In particular, results suggest that under-coordinated sites at the oxide-support interface play an important role in OER.

38. Frydendal R, Seitz LC, Sokaras D, Weng T-C, Nordlund D,
• Chorkendorff I, Stephens IEL, Jaramillo TF: *Electrochim. Acta* 2017, **230**:22–28.
This study uses *operando* XAS methods to understand the effect of Au as a support on MnOx catalysis of the OER. The oxidation state of Mn was tracked under OER conditions for samples with different Au nanoparticle contents, which displayed different levels of oxide-support intimate mixing. The authors propose that the oxide–Au interface is important also in the case of MnOx, as shown previously for NiOx, and in particular that Au promotes the higher oxidation states of Mn centers needed for OER catalysis.

39. Seitz LC, Hersbach TJP, Nordlund D, Jaramillo TF: *J. Phys. Chem.*
•• *Lett.* 2015, **6**:4178–4183.
This is an excellent manuscript in which the authors correlate the activity of MnOx catalysts in the OER to the type of metal nanoparticle used to support the oxide. A screening of Au, Pd, Pt, and Ag reveals that increased activity correlates with increased Mn4+ under OER conditions and that Au and Pd are the best supports among those explored.

40. Zou S, Burke MS, Kast MG, Fan J, Danilovic N, Boettcher SW: *Chem. Mater.* 2015, **27**:8011–8020.

41. Oh H-S, Nong HN, Reier T, Bergmann A, Gliech M, Ferreira de Araújo J, Willinger E, Schlögl R, Teschner D, Strasser P: *J. Am. Chem. Soc.* 2016, **138**:12552–12563.

42. Lassalle-Kaiser B, Gul S, Kern J, Yachandra VK, Yano J: *J. Electron. Spectrosc. Relat. Phenom.* 2017. https://doi.org/10.1016/j.elspec.2017.05.001.

43. Gorlin Y, Lassalle-Kaiser B, Benck JD, Gul S, Webb SM, Yachandra VK, Yano J, Jaramillo TF: *J. Am. Chem. Soc.* 2013, **135**:8525–8534.

44. Gul S, Ng JWD, Alonso-Mori R, Kern J, Sokaras D, Anzenberg E,
•• Lassalle-Kaiser B, Gorlin Y, Weng T-C, Zwart PH, Zhang JZ, Bergmann U, Yachandra VK, Jaramillo TF, Yano J: *Phys. Chem. Chem. Phys.* 2015, **17**:8901–8912.
This work demonstrates applications of wavelength-dispersive X-ray emission spectroscopy to *in situ* characterization of electrocatalysts. The technique can be used for multiplex analysis of the coordination environment at two metal centres, in the case of this experiment Mn and Ni, in real time and in the OER region. The application of this method to electrocatalysis is novel and expected to offer new tools for understanding the dynamics of oxygen evolution at oxide electrocatalysts.

45. Friebel D, Louie MW, Bajdich M, Sanwald KE, Cai Y, Wise AM,
• Cheng M-J, Sokaras D, Weng T-C, Alonso-Mori R, Davis RC, Bargar JR, Nørskov JK, Nilsson A, Bell AT: *J. Am. Chem. Soc.* 2015, **137**:1305–1313.
One of the first studies to use DFT and *operando* XAS measurements on the highly active mixed NiFe-based oxides to try and identify the active sites. Phase segregation is proposed to occur on these specific materials as a function of Fe% content and, somewhat controversially, Fe centres are proposed as the active sites rather than Ni centres.

46. Görlin M, Chernev P, Ferreira de Araújo J, Reier T, Dresp S, Paul B,
• Krähnert R, Dau H, Strasser P: *J. Am. Chem. Soc.* 2016, **138**:5603–5614.
This manuscript used *operando* XAS and DEMS methods to study Ni–Fe mixed OER oxide catalysts. The oxidation state of the Ni under OER conditions was found to be highly dependent on the Fe% content in the material. At <4% content, Ni4+ is present in agreement with Li et al. [31]; however it is Ni2+ above 4% (i.e. 9% atomic Fe content). This is a significant result as most papers on NiFe oxides believe the Ni2+ oxidises to Ni3+ under OER conditions. Interestingly, the authors find no evidence of phase segregation but emphasise the importance of deposition and measurement conditions in determining the material evolution with Fe content and ultimate OER activity.

47. Lian S, Browne MP, Dominguez C, Stamatin SN, Nolan H, Duesberg GS, Lyons MEG, Fonda E, Colavita PE: *Sustain. Energy Fuels* 2017, **1**:780–788.

48. Binninger T, Mohamed R, Waltar K, Fabbri E, Levecque P, Kötz R, Schmidt TJ: *Sci. Rep.* 2015, **5**:12167.