Electronic structure of the (undoped and Fe-doped) NiOOH O₂ evolution electrocatalyst

*José C. Conesa**

Instituto de Catálisis y Petroleoquímica, CSIC

Marie Curie 2, Campus de Excelencia Internacional UAM+CSIC, Cantoblanco

28049 Madrid, Spain

Phone number: +34-915854766 Fax Nr. +34-915854760

e-mail: jcconesa@icp.csic.es

J. Phys. Chem. C 120 (2016) 18999–19010 (doi: 10.1021/acs.jpcc.6b06100)

Abstract

A DFT study is carried out on the atomic and electronic structure of bulk β -NiOOH, with or without substitution of Ni by Fe, examining different stackings and proton distributions in the constituent sheets. The energies of different NiOOH configurations, evaluated at the DFT+U level including dispersion interactions, show very similar values for different stackings and proton distributions, justifying the observed fact that NiOOH is usually obtained highly disordered and allowing to presume that local structures may depend on the synthesis method. Ni ions seem to prefer centrosymmetric coordinations, even if this implies inhomogeneous numbers of OH groups around them; these inhomogeneities may even induce disproportionation of Ni^{3+} into Ni^{2+} and Ni^{4+} . The electronic structure, computed with a hybrid DFT functional able to give accurate bandgaps for different materials, shows always semiconducting character, the bandgaps having widths varying in the 0.8-1.5 eV range and edges formed by Ni 3d states. A metallic character, anticipated by some earlier DFT calculations, is never found. Substitution of Ni by Fe seems to be preferred at sites coordinated with lower number of OH groups; this may induce electron transfer from Fe to Ni, i.e. formation of Fe^{4+} and Ni^{2+} , accompanied in some cases by proton jumps across the inter-sheet space. Some local-level environments, the presence of which may depend on the material synthesis method used, may however stabilize Fe^{3+} , explaining conflicting literature data on the preferred redox state of Fe when included in NiOOH. Overall, the system seems to facilitate electron and proton movement across the material, which may help the electrocatalytic O_2 evolution processes.

Introduction

Solar and wind energies constitute a renewable resource which will play an increasingly important role in the coming years. They have however the problem of intermittency, i.e. they are not available continuously, so that the electrical energy provided by them has to be stored in some way if one wants to use it in off-peak production periods. Among the storage means that can be thought of, capturing CO₂ (from atmosphere or from a combustion exhaust gas) or decomposing water following respectively processes such as

or

seem most attractive since the energy is stored in a fuel that can be used later. Consequently a lot of attention and work has been devoted to the implementation of these processes, as described in reviews on this subject^{1,2,3,4,5,6,7}.

In principle, these reactions can be achieved via electrolysis using electrical power generated by a photovoltaic device or a windmill; they can as well result from a photocatalytic or photoelectrochemical process in which current carriers photogenerated in a semiconductor are transferred to a chemical entity at the surface of the photon absorbing material, starting chemical reactions which ultimately yield the products of the reactions above. The efficiency of all these approaches has certain thermodynamic requirements (the energy of the photons used, or the voltage applied in the electrolysis, must be high enough to overcome the free energies per electron of the different redox steps), but is also highly dependent on the energy barriers that must be surmounted in

the chemical processes involved. These barriers are important and make the process unfeasible or energetically disadvantageous unless co-catalysts are used.

Both reactions above have in common the release of O₂ molecules, which requires extracting electrons from water and forming O-O bonds. Although obtaining oxygen would not seem an interesting objective, this release constitutes actually a kinetically difficult chemical process (certainly more difficult than releasing H₂), for which the catalysts traditionally considered to be most efficient, based on Ru or Ir oxides, involve precious metals¹. The cost and scarcity of these have stimulated an intense search for less expensive but efficient catalysts². Some of these efforts try to mimic the enzyme which evolves O₂ in natural photosynthesis and is based on Mn-Ca oxidic clusters^{8,9}, or those which can reduce O₂ all the way to H₂O, like the laccases where the active centers are copper-based clusters¹⁰ and which have shown to work also in the reverse direction¹¹. Most frequently, however, non bioinspired catalysts are explored, as is the case for example of the so-called CoPi (an amorphous Co phosphate), which received much attention in recent years after the work by Kanan and Nocera¹², or those based on nickel hydrous oxide, in particular when including dopants of which the most effective are Fe or Co^{13,14}, others appear to be less active¹⁵.

Concerning the latter system, on which this work is focused, it has been claimed that the good electrocatalytic properties of supposedly pure Ni (hydr)oxide for this process which have been reported in the past may have been actually facilitated by Fe impurities incorporated unintentionally into the electrode structure during its preparation¹⁶. Indeed it has been shown years ago that when used for electrochemical O₂ evolution in alkaline media, in which the solubility of nickel (hydr)oxide is low enough, this type of catalyst can have overpotentials (e.g. 0.23 V for current densities of 10 mA/cm²)¹³ as low as those displayed by good IrO₂ or RuO₂-based systems. It is unfortunate that this nickel

(hydr)oxide catalyst is only stable in strongly alkaline solutions, which poses some difficulties for water (photo)electrolysis since catalysts for the H₂ evolution reaction work best in acidic conditions; in this respect it is interesting to note that recent work¹⁷ claims significant stability of (iron containing) nickel (hydr)oxide in near neutral pH when prepared from a Ni-Mo molecular precursor, which will deserve further theoretical and experimental work.

In spite of the interest of these Ni-based O₂ evolution electrocatalysts a good knowledge of their atomic and electronic structures has not been achieved. A reason for this is that, even though the electrode material may be initially a Ni²⁺ compound like NiO, which in contact with the aqueous electrolyte may transform into the well characterized hydroxide Ni(OH)₂ (normally present in its β crystallographic form, theophraustite¹⁸), in the actual O₂ evolution conditions, i.e. upon application of a positive enough potential, it transforms into a oxy-hydroxide such as NiOOH, which is a layered compound presenting normally stacking disorder and poorly resolved XRD diagrams. Typically two structural modifications of this latter material are reported:

β -NiOOH, again a layered compound (like Ni(OH)₂) which displays however larger disorder. It is normally assumed that Ni is present there in trivalent state, and indeed XANES data in the literature claim this to be the case¹⁹, although it should be remembered that the coexistence in one same material of Ni²⁺ and Ni⁴⁺ is not impossible; it has been in fact experimentally demonstrated to occur in Ni₂O₃H, where Ni³⁺ is not even present²⁰.

γ -NiOOH. This form can be produced by deeper chemical or electrochemical oxidation, starting from β -NiOOH or Ni(OH)₂, and it is normally assumed that the average Ni redox state is ≥ 3.5 , implying that Ni⁴⁺ is present in it. It has a layered structure similar to that of the β form but with a much larger inter-layer distance. This latter effect is

ascribed to the presence in the said inter-layer space of intercalated water and alkaline cations, although variants of it without intercalated cations have been also reported²¹.

For both materials there are conflicting reports concerning the stacking order of the layers and the location of the protons. Furthermore, for the γ phase there is large variability, depending on the preparation, in the amount of cations and water intercalated, which prevents defining a specific stoichiometry and makes much more difficult a good modeling; for this reason the present work addresses only the β -NiOOH phase. The layers stacking order in it has been proposed to be similar to that in $\text{Ni}(\text{OH})_2$ ²², β -CoOOH^{23,24} or different from that²⁵. Also, the protons corresponding to one given layer have been proposed to be distributed between the sheets in different forms^{22,23,24,25,26}. It has been even claimed, on the basis of inelastic neutron scattering spectra, that the protons lie at high symmetry sites instead of being bonded to specific O atoms²⁷, although this is not consistent with the typical concept of hydrogen bond formation. The situation is complicated by the fact that different structures might be obtained depending on the preparation method²⁸.

In the present work sensible models for the β -NiOOH structure will be proposed and analyzed using state-of-the art DFT methods, deriving as well electronic structures for the most likely ones (as judged from their total energies). Finally, a study of the electronic structure and of changes that may appear when Fe is introduced as substituent of Ni in the mentioned oxy-hydroxide phase will be presented.

Theoretical methods

All calculations made in the present work have been carried out using the periodic DFT code VASP²⁹, which expands the electronic functions in plane waves (i.e. as 3-D

Fourier transforms), and representing the core regions and levels of the atoms using the PAW method^{30,31}. The plane wave cutoff used is 500 eV when carrying out geometry relaxations or final energy level calculations, and 550 eV when computing dielectric constants, which are more accuracy demanding. The Brillouin zones are sampled with k meshes having varying numbers of points, chosen depending on the cell dimensions (with 4x4x4 meshes at the very minimum for the largest unit cells used, like the 2X8 models in Table 2), and making tests in a number of cases to verify that the results are reasonably converged in respect to the mesh density.

Depending on the calculation stage the calculations use different theory levels. Initially the ideal models built are relaxed, both in atomic positions and unit cell dimensions, using a DFT functional which includes dispersion interactions (i.e. van der Waals effects). This approach has been chosen since the layers of the structures considered interact among them with forces which are at most of hydrogen bond type, so that other smaller contributions might be nonnegligible to determine the structures. Indeed it has been shown that dispersion interactions, in particular for oxides which have significant ion polarizabilities (as is probably the case here), can be relevant to determine the materials structure and energetics³². The functional used here in these cases is optB88-vdW, which includes the van der Waals functional introduced by Lee et al.³³ and which has been found by Klimeš et al.³⁴ to be most adequate for calculations including dispersion effects. Indeed a previous own work³⁵ has shown that this functional reproduces rather well the geometry of the organohalide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, which involves highly polarizable lead and iodide ions as well as H bonds between the latter anions and organic cations. This functional is supplemented here with a Hubbard term of the rotationally invariant form of Dudarev et al.³⁶ to correct the known deficiencies of standard GGA when describing partially occupied 3d shells; the effective U

parameter chosen here for nickel is $U_{\text{eff}}=5.3$ eV³⁷, and that for iron (when present) is $U_{\text{eff}}=3.0$ eV, close to literature values²⁴. This functional method approach will be termed here DFT+U+vdW, and is used to relax both unit cell dimensions and atomic coordinates. At this calculation stage it is also examined whether same or opposite electronic spin orientations at the Ni atoms (in those cases where there are two Ni atoms per unit cell in the same structure sheet) are preferred.

Once these relaxed geometries are obtained, electronic structures are computed for them using initially a standard GGA functional like PBE, again complemented with the U term; but to get a most accurate value of bandgaps, in the present work it has been chosen to use in the most interesting cases a hybrid functional, and particularly one of the PBE0 type in which the fraction of Hartree-Fock exchange (here named α) is adjusted, following a suggestion based on GW theory (which shows that the exchange fraction α is related to the electronic screening properties of the material)³⁸, to be equal to the inverse of the average value of the high frequency (optical) dielectric constant ϵ_{∞} . Since for NiOOH the value of ϵ_{∞} is not known, it has been determined here via computation of the electric polarization under an external electric field, by means of the Berry phase theory^{39, 40} and using the same VASP code and the same hybrid functional. The ϵ_{∞} value obtained (as one third of the trace of the corresponding tensor) depends on the α value used in the calculation; therefore, following a strategy used in a previous publication⁴¹ different α values were assayed until the condition $\alpha=1/\epsilon_{\infty}$ is met. This self-consistent and fully first principles-based determination of α (called here PBE0 α , as in a preceding work³⁵) has been found subsequently to give bandgap values in rather good agreement with the experimental ones for very different types of semiconductors^{35,42,43}, including nickel oxide for which the normal DFT+U value is significantly less accurate in this respect³⁷. Optimization of geometries using this

functional was however not attempted, since this would be computationally too expensive, in particular if convergence in energy similar to that achievable with DFT+U is desired.

For the Fe-containing systems the procedure is the same: the geometry (unit cell dimensions and atomic positions) is optimized first with the DFT+U+vdW functional, and the PBE0 α method is used finally on the so relaxed atomic structure to get the electronic structure in the most interesting cases. For these systems a new self-consistent determination of α was not carried out, since this part of the calculation requires stringent convergence parameters (for the evaluation of ϵ_∞) which make the calculation too costly for the larger number of atoms involved. Instead, it is assumed that the screening properties of the material will be similar to those of the parent NiOOH phase (since only $\frac{1}{4}$ or less of the Ni atoms are substituted), and consequently the same α value as determined for the mentioned phase is taken.

For all this analysis, assessment of the symmetry of the structures obtained and graphical representation of the different models were carried out with Materials Studio⁴⁴ or VESTA⁴⁵ software codes, the latter being used also to obtain drawings of spin density distributions.

Structural models used

As said above the structure of NiOOH, usually obtained in an ill-crystallized state (and the same can be said of its Fe-doped version), is not well characterized in the literature. Its preparation normally involves the chemical or electrochemical oxidation of Ni(OH)₂. This latter hydroxide has in its usual β phase a brucite-type structure (Fig. S1 in Supporting Information) made of hexagonal OH-Ni-OH trilayer sheets superimposed in

a simple stacking of 1H-type (also called T1) i.e. in an (AB)..(AB)..(AB).. arrangement, where A, B... refers to the position of the anions. The oxidation to NiOOH is assumed to take place with elimination of half of the protons without otherwise major change in the X-Ni-X structure (X representing the O or OH anion) of each sheet, accompanied by ill-defined changes in the sheet stacking sequence so that in many cases only the regular spacing of sheets can be discerned in the XRD diagram. In the present work different possible stackings are considered (as starting structures) for NiOOH:

1- a structure keeping the same stacking type as in β -Ni(OH)₂, proposed by Kazimirov et al.²², with no additional relative parallel displacement of the sheets. The presence of such stacking in a material of essentially NiOOH redox state under certain preparation conditions had been reported previously by Palmqvist et al.²⁸. The structures derived from this stacking will be labeled 1H.

2- A structure with a rhombohedral 3R-type stacking (also called P3), i.e. (AB)..(BC)..(CA)..(AB)... (like in α -CrOOH), proposed by several authors^{23,24}. This will be labeled 3R.

3-A structure with hexagonal 2H stacking, i.e. an (AB)..(BA)..(AB).. arrangement, like in the CoOOH polymorph described by Deliens and Goethals⁴⁶. This will be labeled 2H.

4- The mixed stacking type proposed by Casas-Cabanas et al.²⁵ on the basis of neutron and X-ray diffraction, which took into account also the observation by TEM of a doubled periodicity in the direction perpendicular to the sheets. This stacking may be described as (AB)..(C'A')..(AB).. where the prime superscripts indicate that the second sheet is somewhat displaced laterally from the strict (CA) position. It will be labeled here as 2M.

Besides this, one must choose where to locate the H atoms (protons) forming the OH groups. In principle one may assume that each trilayer sheet keeps the NiOOH stoichiometry and that within it the same amounts of H atoms are located at each side of the sheet, in order to avoid a dipole in it. This implies that the elemental 2D cell, or repeating unit, in each sheet has an even number of NiOOH formula units; this was achieved taking as new in-plane lattice vectors $\mathbf{a}'=\mathbf{a}+\mathbf{b}$ and $\mathbf{b}'=\mathbf{a}-\mathbf{b}$ ($\mathbf{a}$ and $\mathbf{b}$ being those of the simplest hexagonal cell). However, as will be said below, some structures proposed in the literature deviate from these rules. Taking also these latter into account, the following proton arrangements are considered here, which will be distinguished by subscripts appended to the labels mentioned above:

a) All H atoms are located at only one side of the NiOOH sheet, and oriented to the same side in all of them. This arrangement, designated with script S, is that proposed in refs. 22 and 24; it is also designated as *unstaggered* in a recent work by Tkalych et al.⁴⁷

b) 50% of protons are present at each side in all sheets, being arranged in such way that all Ni atoms have a $\text{NiO}_3(\text{OH})_3$ coordination sphere. This arrangement with protons at different sides of the sheets, proposed in ref. 23 and designated as *staggered* by Tkalych et al.⁴⁷, will be designated with subscript D.

c) 50% of protons at each side in all sheets, but arranged so that Ni atoms have centrosymmetric $\text{NiO}_2(\text{OH})_4$ and $\text{NiO}_4(\text{OH})_2$ coordinations in equal amounts (i.e. the OH groups are arranged in respectively equatorial and axial geometries); this will be designated with subscript C.

d) The arrangement which results from the proposal in ref. 25 for a stacking of 2M type if the 90% and 10% populations of H sites given in that work are rounded to 100% and 0% respectively. In this arrangement each NiOOH sheet has all H atoms at only one side, but at difference with the case a) above the sheet side having those atoms

alternates from one sheet to the next so that the inter-sheet spacings are alternately filled or emptied of H atoms. This H atom arrangement, which will be designated with subscript X, will be used only for the said 2M-type stacking

e) The arrangement, more recently proposed for the 2H and 3R stackings by Li and Selloni²⁶ to explain the doubled periodicity reported by Casas-Cabanas et al.²⁵, in which alternating sheets have respectively NiO_2 and Ni(OH)_2 stoichiometries. This arrangement, designated here with subscript W, will be considered only for the two said stackings.

All of these starting structure models are depicted in Fig. S2 of the Supporting Information.

Results & Discussion

1. Structures relaxed at the DFT+U+vdW level: geometry and energetics

All the mentioned structures were relaxed in atomic positions and cell dimensions using the DFT+U+vdW approach described in the Theoretical methods section. It should be mentioned that some of the structures evolved into the same configuration as some other. For example, the 2M_W and 2M_C structures distorted to give the same result as the 3R_W and 3R_C structures, respectively; we will retain only the latter cases in the analysis. More noteworthy is the fact that structure 2H_S evolved spontaneously, with a jump of half of the protons to the opposite side of the inter-sheet space, into the same structure as 2H_W ; this means that having in all sheets all protons at the same side, which implies the presence in each layer a strong dipole with the same sign in all of them (as is assumed in several previous works^{22,24,48}), is not a stable situation, so that the H bridges will try to achieve a better one if their initial configuration makes it possible. The full

set of structural parameters obtained after this relaxation is given in Table S1 of the Supporting Information. From these, the interested reader can compare the c-axis values obtained here for structures 1H_S (or 3R_S) and 1H_D (or 3R_D) with those given in ref. 47 for those called there unstaggered and staggered, which are the closest ones and have inter-sheet distances of 4.544 and 4.741 Å respectively.

Table 1 gives the total energy expressed per NiOOH formula unit, and includes as well the (averaged when necessary) inter-sheet distance, the in-sheet area per NiOOH formula unit and the valence of the Ni atoms obtained from the Ni-O distances using the correlation between valence and average Ni-O distance given by Levi and Aurbach⁴⁹. In nearly all cases valence values corresponding to a Ni³⁺ state are found, as expected. One exception is the 2M_X case, where according to the said correlation surprisingly all Ni ions seem to be present as Ni²⁺. Analysis of the results for this case shows that short O-O bonds (with bond lengths d=1.49 Å, characteristic of peroxide species) across the inter-sheet space have been formed, evidencing that actually a (Ni²⁺)₂(OH)⁻(O₂)²⁻ compound is predicted. In correspondence with this, the (average) intersheet spacing and the area per Ni in each sheet are clearly smaller and larger, respectively, than in all other cases, and differ markedly from all experimental values reported. This structure is unlikely to be realistic and will not be considered further.

Two other cases deviate from the exclusively Ni³⁺ state. On the one hand, the result for both 2H_W and 3R_W displays the coexistence of Ni³⁺ and Ni⁴⁺ in the MO₂ trilayer sheet that contains no protons, and of Ni³⁺ and Ni²⁺ in the Ni(OH)₂ trilayer in which all O atoms contain protons. On the other hand, the initial 2M_D structure rearranges the H atoms in it to produce a 2M_C-type structure, in which the Ni atoms coordinated to only 2 OH groups become mainly Ni⁴⁺ and the others become Ni²⁺. It is noteworthy that, in contrast to this, starting from a 2M_C structure with the initial Ni and O positions as

given in ref. 25 the relaxed structure ends up, as said above, being the same as the $3R_C$ structure, which displays an energy lower by ca. 40 meV/Ni atom than the mentioned $2M_C$ structure derived from $2M_D$ and in which the said valence disproportionation does not occur, all Ni ions remaining as Ni^{3+} species. All this evidences that NiOOH has a significant flexibility in adopting different valence and proton location distributions, explaining that mixing of Ni redox states may appear in some cases²⁰. Except for the mentioned specific cases, all remaining structures show that Ni is present as Ni^{3+} .

Looking in more detail to geometric features, it is observed also that threefold symmetry disappears in the $1H_S$, $2H_S$, $3R_S$, $2H_W$ and $3R_W$ cases which are in principle topologically compatible with it. Examining the coordination environment of the Ni^{3+} species, in all cases one finds that two Ni-O bonds in *trans* position are longer than the other four by 0.1-0.15 Å (see Fig. 1 for an example). This result, which agrees with

Figure 1 Structural view of two of the (relaxed) structures obtained, showing spin density distributions (computed with the PBE0 α hybrid functional) for different Ni redox states (always Ni^{3+} in the $3R_D$ case, as said in the text) and Ni-O distances in one typically distorted Ni^{3+} coordination sphere.

some reported EXAFS data⁵⁰, reflects probably the existence of a Jahn-Teller distortion, which can be expected in these systems since the Ni^{3+} ion (which as explained below has a low spin electronic configuration) has an odd number of electrons and the e_g -type manifold which presumably contains the unpaired electron would be degenerate in a trigonally distorted octahedral coordination. The unpaired electron of Ni^{3+} seems to be present thus in an orbital of $d(z^2)$ type, as can be ascertained from the shape of its spin density distribution shown in Fig. 1. On the other hand, the Ni^{2+} and Ni^{4+} species appearing in the 2H_W and 3R_W cases have a much less distorted geometry, the Ni-O distances varying by not more than 0.035 Å. They also present, as seen in Fig. 1, spin density distributions (here computed with the PBE0 α hybrid functional, as mentioned further below) different from those of the Ni^{3+} ions: the Ni^{2+} case with similar densities along the three Ni-O bonds (reflecting the presence of two unpaired electrons in the two orbitals of the e_g -type manifold) and the Ni^{4+} case with (almost) no spin density at all as expected for a completely filled t_{2g} subshell and an empty e_g subshell. The more spherical electron density distribution resulting in these two cases explains thus the smaller spread in Ni-O distances. Finally, one must note that this distribution of redox states within this proton ordering implies that the NiO_2 sheet is negatively charged (it can be described as $\{[\text{Ni}^{4+}, \text{Ni}^{3+}][\text{O}^{2-}]_4\}^-$) while the other sheet with $[\text{Ni}^{3+}, \text{Ni}^{2+}][(\text{OH})]_4$ composition would be positively charged.

Considering now the energies obtained, it is observed that a range of values appear, spanning an interval of ca. 0.24 eV per NiOOH formula unit. Most notably, different stackings and structures appear with quite similar energy values. In fact, there is not a unique configuration with energy clearly lower than the rest; instead, four of them which correspond to different stackings and proton arrangements have nearly the same minimum energy, the differences between them being much smaller than thermal

energy at ambient temperature ($kT \approx 25$ meV). This explains the high disorder usually found experimentally in NiOOH. Furthermore, this may motivate that depending on the method of preparation the structures obtained in different syntheses have different local-level structures, as proposed in literature²⁸, if these are conditioned by the kinetics of the deprotonation process rather than by thermodynamics.

Still, one can note that those minimum energy configurations ($2H_C$, $2H_W$, $3R_C$ and $3R_W$) share two features: one, that their sheet stackings have all inter-sheet hydrogen bonds perpendicular to the sheet planes; and second, that the Ni atoms in them have in their coordination environment, rather than a composition equal to the stoichiometric one, i.e. $O_3(OH)_3$, even numbers of each of these ligands, so that their configurations have inversion symmetry. This might mean a preference of nickel for a centrosymmetric coordination (which is not possible for an $O_3(OH)_3$ environment), possibly leading to a less distorted arrangement which facilitates a more compact atom packing. Note also that the presence of inversion centers at the Ni atoms implies that there is in them, between the 3d and the empty 4p orbitals (lying higher in energy), no mixing which could transfer electron density from the former to the latter. Calculations with the hybrid PBE0 α functional, to be described below, will be made mainly for those four configurations, adding a few others for the sake of comparison.

2-Electronic structure of the NiOOH models

One first aspect that can be examined is the total spin density on each Ni atom (as projected in the atomic PAW sphere). Here the results obtained with PBE+U or the PBE0 α hybrid functional are considered; those values are given as well in Table 1. In most cases (all those where the valence values, determined as said above, imply a Ni^{3+} redox state) this spin density has an absolute value more or less close to 1.0, implying a

low spin d^7 configuration, i.e. $(t_{2g})^6(e_g)^1$ (with only one unpaired electron in the $3d^7$ shell) as mentioned above and already reported⁴⁷. The values are typically in the 1.05-1.25 range when computed with PBE+U and around 0.85 when computed with PBE0 α . Within this result, configurations having equal spin signs in all Ni atoms have in general energies rather close (higher or lower, but with differences within ca. 20 meV/Ni ion, depending on structure) to others having in the same sheet spins of opposite signs. At ambient or higher temperatures the spin ordering is thus likely to be scarcely relevant for determining the atomic configurational ordering, and may even be subjected to fluctuations so that the relative spin signs will probably have minor influence on the structural and chemical properties. In what follows the comparisons will be made always between structures having in Ni all spins of the same sign, at least within one same sheet. The few cases deviating from the Ni^{+3} state show a spin density close to zero for the Ni^{4+} case and close to 1.8 (when computed with PBE+U) in the Ni^{2+} cases, corresponding respectively to 0 and 2 unpaired electrons on the cation (i.e. low spin $(t_{2g})^6$ and high spin $(t_{2g})^6(e_g)^2$ configurations) in agreement with the spin density distributions shown in Fig. 1.

Next one can consider the bandgaps predicted for these models, which are listed as well in Table 1, including for the most interesting cases also the values obtained with the PBE0 α hybrid functional. First thing to observe is that the bandgaps obtained with PBE0 α are significantly larger than those obtained with PBE+U. Note that the latter method indeed is known to give for NiO a bandgap value $(3.0 \text{ eV})^{37}$ lower, and in significantly worse agreement with the experimental one ($\approx 4.0 \text{ eV}$), than that given by PBE0 α ($E_g=4.11 \text{ eV}^{42}$). Thus one can assume that PBE0 α results are more reliable also for the Ni-containing materials addressed here. From this point of view, the prediction of a metallic character obtained for some of the present models with PBE+U, which was

obtained also in ref. 24, is probably not correct. This was made clear also in ref. 47. Secondly, one can note that in all non-metallic cases the bandgap is indirect, and the first direct gap (which never occurs at the gamma point) can be up to several tenths of eV higher than the indirect one.

Considering therefore only the values obtained with PBE0 α approach, it may be noted that some of them might explain the feature observed at 1.4 eV in the only published UV-Vis-NIR spectrum of NiOOH⁵¹. One should note also the gap value, estimated to be around 1.75 eV (although without discarding that 1.5 eV photons are active also), obtained from the onset of photocurrent observed in some photoelectrochemical measurements⁵². Whether these measurements reflect the direct or the indirect gap is difficult to say, given the quality of the data and the ill-defined structure of the materials considered in those works. Our results can be compared with the value $E_g=1.96$ eV computed in ref. 47 with the G_0W_0 method (based on a PBE+U wavefunction) for a 1H_D-type structure; note that in our calculations this structure has higher bandgap than those giving the lowest energies. But it must be also noted that significantly different bandgap values (in the 0.8-1.3 eV range; 1.05-1.67 eV for the direct gap) are obtained here within the group of four different structures which are predicted as most stable and have very similar total energies. This implies that in the disordered NiOOH materials normally obtained in practice the bandgap can vary largely depending on the preparation, or even be ill defined if different regions of the material have different or irregular stackings and proton distributions. Therefore, trying to obtain a clear-cut picture of the electronic structure of NiOOH with only one model is not well justified.

Still, one can try to ascertain general features of the electronic structure of these materials examining the DOS curves (both total and atom-projected). For this, only the results obtained with the PBE0 α functional for some of the most representative

structures are considered and displayed in Fig. 2. As can be observed from the projected DOS curves, the bandgap edges are generally formed mainly by Ni 3d states of majority spin. In the cases in which Ni^{3+} species with different coordination exist, those with higher number of OH ligands provide a higher VB edge, but the difference is small. On the other hand, in those cases where Ni^{2+} and Ni^{4+} species appear a complex situation

Figure 2. Density of states curves, total and Ni-projected, obtained with the PBE0 α functional for several of the relaxed NiOOH structures.

exists in which after atomic relaxation (which readjusts the O-Ni distances) the occupied majority states of Ni^{2+} contribute to the top of the VB more than Ni^{3+} states, while empty states of the Ni^{4+} ions contribute largely to the bottom of the conduction band. In other words, when disproportionation of Ni^{3+} into Ni^{2+} and Ni^{4+} occurs these latter ions contribute clearly to the top of the valence band and the bottom of the conduction band respectively, as could be expected. It may be noted also that in the structures containing only Ni^{3+} species the oxygen atoms do not contribute largely to the top of the VB, i.e. any additional holes that might be formed in the latter should be in principle described better as Ni^{4+} than as O^- states.

3- Fe-doped NiOOH : energetics and redox states

In several of the structures analyzed above a substitution of one Ni atom by Fe was carried out to give cells with $(\text{Ni}_{n-1}\text{Fe})(\text{OOH})_n$ stoichiometry and several positions for Fe were examined when Ni sites exist having different initial redox states and/or different number of OH groups in the coordination sphere. These structures were relaxed with the DFT+U+vdW functional, leading to rather small overall cell shape changes (which in any case would be scarcely comparable with experimental observations), and the resulting energies were used to compare the different situations. For a first analysis of the electronic structures of the resulting systems the valences of Fe and Ni ions were assessed as well considering the spin densities given by DFT and the Ni-O distances. The resulting data, summarized in Table 2, are discussed in more detail below.

For simplicity the substitution in a structure that contains only one type of Ni is considered first. Thus the case of the 3R_D structure was analyzed. The latter has only one sheet per unit cell, and in a first test 1/8 of Ni atoms in each sheet are replaced. The

supercell is such that the structure contains no Fe-O-Fe links, i.e. Fe is involved only in Fe-O-Ni links (to 6 Ni atoms), and one Ni in each cell is not involved in any Ni-O-Fe link.

Two noteworthy results of the substitution of Ni by Fe in this case were found. The first one is that one of the remaining Ni atoms is transformed in Ni^{2+} , as ascertained from its valence (2.58) computed from the Ni-O distances, which average to 2.02 Å while for the other Ni ions, remaining in Ni^{3+} state, the average is close to 1.97 Å, and from its spin density (1.69 computed with PBE+U; 1.30 with PBE0α), which suggests a high spin $(t_{2g})^6(e_g)^2$ configuration. In line with this change, the differences in Ni-O bond lengths also decrease, as corresponds to the disappearance of the above mentioned Jahn-Teller effect; the same is observed in all the other cases mentioned below in which Ni^{2+} ions are formed. Fe becomes in turn Fe^{4+} , as ascertained by its spin density (-1.98 computed with PBE+U, -1.45 with PBE0α) which suggests an intermediate spin $(t_{2g})^4$ configuration having three electrons with one spin sign and one electron with the opposite one.

The second relevant result is that a jump of protons occurs across the inter-sheet space, away from the Fe atom (Fig. 3). This is obviously connected with the increase in the positive charge of the Fe ion, which will be stabilized better if a higher number of anions with higher charge (oxide instead of hydroxide) are around it. The result is that after this proton jump Fe remains in this structure coordinated to only one OH group, while the Ni atom in the structure that is not involved in Ni-O-Fe links ends up coordinated to 5 OH groups. This almost homogeneous coordination environment of Fe can be related to the observation made with Mössbauer spectroscopy by Axmann et al.⁵³ on anodized Fe:NiOOH systems, where the Fe^{4+} ions detected show no quadrupole splitting suggesting that all neighboring ions are of the same kind, i.e. in that case even

the last proton might have jumped out of the Fe^{4+} coordination sphere. It is noted that even though one would expect that the higher number of OH groups would help stabilizing a lower redox state, the Ni atom coordinated to 5 OH groups is not that which is changed into Ni^{2+} ; it seems that in this structure it is more advantageous to keep the reduced Ni closest to the more highly charged Fe^{4+} cation. In summary: in this structure Ni^{3+} seems to be oxidizing enough that it can draw an electron from Fe^{3+} , producing Ni^{2+} and Fe^{4+} , in a process coupled with the said proton transfer. It is worth noting that this effect of becoming Fe^{4+} and producing proton jump to give an $\text{O}_5(\text{OH})$ coordination around Fe is observed also in structure 1H_D which has initially the same Ni coordination arrangement.

The effect of carrying out the substitution in a structure in which two different Ni coordination types are present has been considered next. Thus the 3R_C case was studied, in which as said above only Ni^{3+} ions are initially present. Also in this case 1/8 of the Ni atoms in each sheet was substituted by Fe, but here the substitution can be made in sites with (initially) $\text{O}_4(\text{OH})_2$ or $\text{O}_2(\text{OH})_4$ coordination. It was found that the second case led

Figure 3. Coupled formation of $\text{Fe}^{4+} + \text{Ni}^{2+}$ and jump of protons across the inter-sheet space produced when Ni is substituted by Fe in the 3R_D structure and the lattice is relaxed.

(after full relaxation) to an energy lower than the first one by ca. 100 meV/cell. Examining the spin densities it was found that Fe and Ni remained trivalent in both cases, and no proton jump occurred. Therefore, although the above mentioned $2H_C$ case could suggest that cation coordinations having 3 OH groups or less could favor that Fe adopts a Fe^{4+} state and one Ni atom becomes Ni^{2+} , this is not a general rule.

Still within the $3R_C$ structure, substitution was made at a higher concentration of Fe per sheet (25% of Ni substituted). Within such $FeNi_3O_4(OH)_4$ stoichiometry it was found that substitution in $O_4(OH)_2$ coordination did lead to a Fe^{4+} state, with generation of one Ni^{2+} , and to an energy lower by ca. 200 meV than when the substitution was made at the site with $O_2(OH)_4$ coordination, in which case Fe remains as Fe^{3+} . Thus, in this case a lower number of OH ligands around Fe leads again to a preference for the Fe^{4+} state. A situation with $3R_C$ structure was tested also in which layers with 25% of Ni substituted alternated with others with no substitution, leading again to $(Ni_7Fe)(OOH)_8$ stoichiometry. In this case substitution of Fe in an $O_4(OH)_2$ coordinated site gave once more lower energy (although by only 23 meV), both sites leading now to a Fe^{4+} state. It is worth noting, however, that in none of these $3R_C$ cases producing Fe^{4+} does a proton jump take place, not even in the case of substitution at a $O_2(OH)_4$ site.

Then the substitution of Ni by Fe was tested in the $2H_C$ structure. Since this stacking has two sheets per unit cell, the $FeNi_7O_8(OH)_8$ stoichiometry was achieved with Fe substituting for 25% of the Ni ions in one sheet (in both $O_4(OH)_2$ and $O_2(OH)_4$ coordinations) and no Fe in the other sheet. In this case the substitution at the site with $O_4(OH)_2$ coordination (but not at the other site) led to a transformation of Fe into Fe^{4+} and of one of the Ni ions in the same sheet into Ni^{2+} , the energy being much lower (by 900 meV) than for substitution at the $O_2(OH)_4$ site. Again no proton jump is produced in any of the two cases. Maybe the centrosymmetric coordination, which as said in the

previous section seems to provide a more stable situation, does not favour the proton jump away from the Fe coordination sphere even when oxidation of the latter cation takes place.

Finally, the substitution of Ni by Fe was studied in the 3R_W case, which as said above contains in each unit cell two sheets having all cations in respectively (OH)₆ and O₆ coordination environments, with the additional particularity that these two situations contain respectively (Ni²⁺)+(Ni³⁺) and (Ni⁴⁺)+(Ni³⁺) mixtures of redox states, so that one can initially locate the Fe atom in four different locations. This was examined with both 8 and 16 cations per unit cell (corresponding to 1/4 and 1/8 of the cations being substituted in the sheet chosen in each case). To tell it short, in most (but not all) of the cases, which included the lowest energy ones, Fe appeared as Fe⁴⁺, leading (when the cation substituted is not already a Ni⁴⁺ ion) to the additional transformation of one Ni³⁺ of the same sheet into a Ni²⁺ state. This supports the idea that in this system Fe has a tendency to appear as Fe⁴⁺ rather than as Fe³⁺. However, in none of these cases a spontaneous proton jump across the inter-sheet space is observed, which agrees with the mentioned hypothesis that the said jump is not favored in centrosymmetric coordinations, which as said above have higher stability.

To summarize, it can be seen that for each cell composition examined those structures which appear with lowest energies have Fe as Fe⁴⁺, although one may find also structures of higher energy stabilizing Fe as Fe³⁺; in particular, this is seen in some of those of 3R type with 1/8 of the Ni atoms per sheet substituted by Fe. Comparing systems with similar stackings and proton distributions but different local concentration of Fe it can be seen that this concentration may affect the preferred redox state of Fe, explaining the fact that new features were observed by Trotochaud et al.¹⁶ in their electrochemical tests when the degree of substitution of Ni by Fe reached the 25% level.

These results also allow understanding that different literature works may give conflicting results concerning whether Fe in NiOOH adopts the Fe^{3+} or Fe^{4+} state. Indeed, as said above, Mössbauer results indicate a Fe^{4+} state⁵³, while recent XANES work⁵⁴ reports a Fe^{3+} state under reaction conditions; note that in the latter case the authors indicate that the retention of a relatively low oxidation state by the material may be due to a very easy transfer of holes to the surface to achieve the final O_2 evolution. Considering the comments given above about the similar energies of different NiOOH configurations, it may well be that whether one obtains mainly one or the other Fe redox state may depend on the preparation method, if the latter also controls the type of stacking and proton distribution in the material.

3- Fe-doped NiOOH: electronic levels

In some of the relevant cases discussed above electronic structures were analyzed with more accuracy using a PBE0 α functional in which the α value adopted was that derived previously for the parent NiOOH structure. Determining α self-consistently in these cases was discarded, because the calculation of ϵ_∞ requires very tight scf convergence criteria which for these larger cells lead to too long calculation times. Since only a fraction of the Ni atoms is replaced, one can expect that the dielectric constant will not change much.

The resulting electronic structures can be visualized with the DOS curves. Characteristic situations are presented in Fig. 4, which shows the DOS obtained with the hybrid functional for several structures which have been pre-relaxed with the PBE+U+vdW functional. Thus Fig. 4 presents two cases in which Fe takes the Fe^{4+} redox state and one Ni^{3+} is reduced to Ni^{2+} (2H_C , with Fe substituting at a position with $\text{O}_4(\text{OH})_2$ coordination, and 3R_D in which proton jump has occurred leaving Fe in $\text{O}_5(\text{OH})$

coordination) and another two cases with iron present as Fe^{3+} and all Ni ions remaining in the trivalent state (2H_C with Fe substituting at a $\text{O}_2(\text{OH})_4$ site and 3R_C with Fe substituting at a $\text{O}_4(\text{OH})_2$ site).

These plots present separately the projection on Fe and the sum of projections on all Ni^{3+} atoms, as well as the projection on the Ni ion identified as Ni^{2+} (from the spin density and the Ni-O distances) when present. As can be seen, the picture is similar to those of the Fe-free cases in that a semiconducting character with bandgaps in the 1-1.5 eV range appears, the bandgap edges being formed mainly by cation-centered orbitals. The most visible difference is that the minority spin (spin down) valence band edge is formed in the first two cases by filled Ni^{2+} states, and in the other two by filled Fe^{3+}

Figure 4. Density of states curves, total and (Ni,Fe)-projected, obtained with the PBE0 α functional for several of the relaxed (Fe,Ni)OOH structures.

states. Integration of this latter feature in the two latter cases shows that it corresponds to two electrons per unit cell; therefore the five 3d electrons in the Fe^{3+} ion are in a low spin state (three electrons with majority spin, two with minority spin), justifying that the total spin density on Fe is close to 1.0.

In the other two cases in which, as said above, iron goes into a Fe^{4+} state while one Ni ion gets an additional electron going into a Ni^{2+} state the projections in the plot show that the electronic states of this latter ion become clearly separated from the Ni^{3+} ions, and actually form a significant part of the top of the valence band, although some overlap with other Ni ions exists so that these latter also contribute to the top of the valence band. These different redox states may be visualized also through the spin density distributions; for example, Fig. 5 shows that distribution for the 1H_D case in which, as said above, Fe^{4+} appears while a Ni^{2+} ion is formed and several protons jump across the inter-sheet space.

Figure 5 Isosurfaces of spin density distribution (yellow, majority spin; blue, minority spin) for $\text{FeNi}_7(\text{OOH})_8$ in 1H_D structure, computed with PBE0 α hybrid functional. Different densities for Ni^{3+} and Ni^{2+} can be distinguished, together with that for Fe^{4+} of opposite spin sign.

Conclusions

After examining a number of different structural NiOOH configurations it becomes clear that in this material different sheet stackings lead to practically indistinguishable energies, which explains that this compound presents almost always a high stacking disorder in the experimental preparations. Furthermore, different proton distributions, leading to different number of OH groups around the Ni ions, appear also with very close energies, so that a high proton disorder can be anticipated as well. One can understand then that, as already claimed in the literature²⁸, the details on the method of preparation may influence strongly the structure finally obtained; and that a single stacking/proton configuration cannot represent faithfully NiOOH. In other words: question 1 in the very recent ref. 55 (What is the crystal structure of NiOOH?) has not a unique answer. And question 3 in the same work (Is density functional theory good for NiOOH?) might have an (dielectric constant-tuned PBE0 is good), but since there is also no unique value for the bandgap with any comparison with experiment is in this case necessarily tricky. Besides this, it is remarkable that some Ni atoms may appear with no OH groups at all in their neighborhood (as already suggested by a recent theoretical modeling²⁶), in which case disproportionation of Ni^{3+} into Ni^{2+} and Ni^{4+} (the latter having been reported in the literature as capable of coexisting²⁰) may occur.

All these results imply that a relatively high mobility of both protons and electrons may occur in NiOOH. The results on the electronic structure, obtained with a highly accurate hybrid functional, reveal on the other hand a semiconducting behavior (not a metal, as may result from a less accurate DFT+U treatment²⁴) but with bandgap significantly varying depending on the specific structure; an ill-defined gap is therefore likely to occur in the disordered materials typically present in the literature in agreement with

some spectral observations^{51,52}. In all cases the band gap edges are formed mainly by 3d levels of the Ni cation; therefore describing the oxidized state in terms of O⁻ ions would be less appropriate than doing it in terms of Ni³⁺ ions.

The effects of inserting Fe in the NiOOH structure are equally complex. Depending on the number of protons remaining in the coordination sphere of the cation, its preferred redox state may be Fe³⁺, which happens mainly, but not always, if that number is higher than 3 (in which case the top of the valence band is made by states of both Ni and Fe ions), or Fe⁴⁺, mainly if the said number is less than 3. Overall, the latter redox state seems to be preferred by Fe in this material, which may give rise to a change of some Ni ions to a (+2) redox state (in which case these Ni ions dominate the top part of the valence band) and to an eventual jump of protons (seemingly favored when the cation environment is not centrosymmetric) to accommodate better the preference of Fe for that higher redox state within an environment having a lower number of protons. The environment preferred by Fe, however, may depend on both its local concentration and the type of sheet stacking and of proton distribution which results from the specific synthesis method used, so that the latter may influence whether mainly Fe³⁺ or Fe⁴⁺ redox states are obtained; this is likely to affect the electrocatalytic activity of the material. Experimental work may determine which preparation method, and consequently which local-level cation environment and redox state, leads to maximum catalytic activity. In any case it is clear that electron transfer between cations, as well as jump of protons between oxygen anions, can take place in this material with minimal energy penalty (even if it seems to have always semiconducting, not metallic, characteristics), which most probably will facilitate the charge transport needed for an efficient O₂ electroevolution. In this respect it is interesting to note that iron

oxyhydroxide, which by itself is not a good oxygen evolution catalyst, may become much more active when its conductivity is raised by applying a larger overpotential⁵⁶.

Supporting information description

Supporting information contains drawings of the starting Ni(OH)₂ and NiOOH structures considered and the crystallographic parameters (cell dimensions, space group and atomic coordinates) of the relaxed NiOOH structures.

Acknowledgements

This work has been carried out under financial support from projects BOOSTER (Plan Estatal de I+D, proj. nr. ENE2013-46624-C4-1-R) and Madrid-PV-CAM (Comunidad de Madrid, program nr. S2013/MAE-2780). Thanks are given as well to computer centers CTI and IFCA for the use of parallel computers *trueno* and *altamira*.

References

-
- ¹ Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering Heterogeneous Semiconductors for Solar Water Splitting. *J. Mater. Chem. A* **2015**, *3*, 2485-2534.
- ² Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729–15735.
- ³ House, R. L.; Iha, N. Y. M.; Coppo, R. L.; Alibabaei, L.; Sherman, B. D.; Kang, P.; Brennaman, M. K. Hoertz, P. G.; Meyer, T. J. Artificial Photosynthesis: Where are

- we now? Where can we go? *J. Photochem. Photobiol. C: Photochem. Rev.* **2015**, *25*, 32–45.
- ⁴ Zou, X.; Zhang, Y. Noble Metal-Free Hydrogen Evolution Catalysts for Water Splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148.
- ⁵ Lewis, N. S. Research Opportunities to Advance Solar Energy Utilization. *Science* **2016**, *351*, 353.
- ⁶ Hansen, J. B. Solid Oxide Electrolysis – a Key Enabling Technology for Sustainable Energy Scenarios. *Faraday Discuss.* **2015**, *182*, 9.
- ⁷ White, J. L.; Baruch, M. F.; Pander III, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao, K.; Gu, J.; Yan, Y. *et al.* Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. *Chem. Rev.* **2015**, *115*, 12888–12935.
- ⁸ Suga, M.; Akita, F.; Hirata, K.; Ueno, G.; Murakami, H.; Nakajima, Y.; Shimizu, T.; Yamashita, K.; Yamamoto, M.; Ago, H. *et al.* Native Structure of Photosystem II at 1.95 Angstrom Resolution Viewed by Femtosecond X-Ray Pulses. *Nature* **2015**, *517*, 99–103.
- ⁹ Wiechen, M.; Najafpour, M. M.; Allakhverdiev, S. I.; Spiccia, L. Water Oxidation Catalysis by Manganese Oxides: Learning from Evolution. *Energy Environ. Sci.* **2014**, *7*, 2203.
- ¹⁰ Thorseth, M. A.; Tornow, C. E.; Tse, E. C. M.; Gewirth, A. A. Cu Complexes that Catalyze the Oxygen Reduction Reaction. *Coord. Chem. Revs.* **2013**, *257*, 130–139.
- ¹¹ Pita, M.; Mate, D. M.; González-Páez, D.; Shleev, S.; Fernández, V. M.; Alcalde, M.; De Lacey, A. L. Bioelectrochemical Oxidation of Water. *J. Am. Chem. Soc.* **2014**, *136*, 5892–5895.

- ¹² Kanan, M. W.; Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+} . *Science* **2008**, *321*, 1072-1075.
- ¹³ Corrigan, D. A. The Catalysis of the Oxygen Evolution Reaction by Iron Impurities in Thin-Film Nickel-Oxide Electrodes. *J. Electrochem. Soc.* **1987**, *134*, 377.
- ¹⁴ Zhang, Y. S.; Cao, X. Y.; Yuan, H. T.; Zhang, W. H.; Zhou, Z. X. Oxygen Evolution Reaction on Ni Hydroxide Film Electrode Containing Various Content of Co. *Int. J. Hydr. Energy* **1999**, *24*, 529-536.
- ¹⁵ Enman, L. J.; Burke, M. S.; Batchellor, A. S.; Boettcher, S. W. Effects of Intentionally Incorporated Metal Cations on the Oxygen Evolution Electrocatalytic Activity of Nickel (Oxy)Hydroxide in Alkaline Media. *ACS Catal.* **2016**, *6*, 2416-2423.
- ¹⁶ Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: the Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **2014**, *136*, 6744-6753.
- ¹⁷ Kuznetsov, D. A.; Konev, D. V.; Komarova, N. S.; Ionov, A. M.; Mozhchil, R. N.; Fedyanin, I. V. Ni-Based Heterogeneous Catalyst From a Designed Molecular Precursor for the Efficient Electrochemical Water Oxidation. *Chem. Commun.* **2016**, *52*, 9255.
- ¹⁸ Szytula, A.; Murasik, A.; Balanda, M. Neutron Diffraction Study of $\text{Ni}(\text{OH})_2$. *Physica Status Solidi B* **1971**, *43*, 125.
- ¹⁹ Bediako, D. K.; Lassalle-Kaiser, B.; Surendranath, Y.; Yano, J.; Yachandra, V. K.; Nocera, D. G. Structure-Activity Correlations in a Nickel-Borate Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 6801.
- ²⁰ Malsbury, A. M.; Greaves, C. The Crystallographic and Magnetic-Structure of $\text{Ni}_2\text{O}_3\text{H}$. *J. Solid St. Chem.* **1987**, *71*, 418-425.

- ²¹ Yang, X.; Takada, K.; Itose, M.; Ebina, Y.; Ma, R.; Fukuda, K.; Sasaki, T. Highly Swollen Layered Nickel Oxide with a Trilayer Hydrate Structure. *Chem. Mater.* **2008**, *20*, 479.
- ²² Kazimirov, V. Yu.; Smirnov, M. B.; Bourgeois, V.; Guerlou-Demourgues, L.; Servant, L.; Balagurov, A. M.; Natkaniec, I.; Khasanova, N. R.; Antipov, E. V. Atomic Structure and Lattice Dynamics of Ni and Mg Hydroxides. *Solid State Ionics* **2010**, *181*, 1764-1770.
- ²³ Van der Ven, A.; Morgan, D.; Meng, Y. S.; Ceder, G. Phase Stability of Nickel Hydroxides and Oxyhydroxides. *J. Electrochem. Soc.* **2006**, *153*, A210-A215.
- ²⁴ Li, Y.-F.; Selloni, A. Mechanism and Activity of Water Oxidation on Selected Surfaces of Pure and Fe-doped NiO_x. *ACS Catal.* **2014**, *4*, 1148-1153.
- ²⁵ Casas-Cabanas, M.; Canales-Vázquez, J.; Rodríguez-Carvajal, J.; Palacín, M. R. Deciphering the Structural Transformations during Nickel Oxyhydroxide Electrode Operation. *J. Am. Chem. Soc.* **2007**, *129*, 5840-5842.
- ²⁶ Li, Y.-F.; Selloni, A. Mosaic Texture and Double C-Axis Periodicity of Beta-NiOOH: Insights from First-Principles and Genetic Algorithm Calculations. *J. Phys. Chem. Lett.* **2014**, *5*, 3981-3985.
- ²⁷ Baddour-Hadjean, R.; Fillaux, F.; Tomkinson, J. Proton Dynamics in Beta-Ni(OH)₂ and Beta-NiOOH. *Physica B* **1995**, *213-214*, 637-639.
- ²⁸ Palmqvist, U.; Eriksson, L.; García-García, J.; Simic, N.; Ahlberg, E.; Sjövall, R. On the Misuse of the Crystal Structure Model of the Ni Electrode Material. *J. Power Sources* **2001**, *99*, 15.
- ²⁹ Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.
- ³⁰ Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953.

- ³¹ Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758.
- ³² Conesa, J. C. The Relevance of Dispersion Interactions for the Stability of Oxide Phases. *J. Phys. Chem. C* **2010**, *114*, 22718-22726.
- ³³ Lee, K.; Murray, E. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-accuracy van der Waals Density Functional. *Phys. Rev. B* **2010**, *82*, 081101.
- ³⁴ Klimeš, J.; Bowler, D. R.; Michaelides, A. Van der Waals Density Functionals Applied to Solids. *Phys. Rev. B* **2011**, *83*, 195131.
- ³⁵ Menéndez-Proupin, E.; Palacios, P.; Wahnón, P.; Conesa, J. C. Self-Consistent Relativistic Band Structure of the CH₃NH₃PbI₃ Perovskite. *Phys. Rev. B* **2014**, *90*, 045207.
- ³⁶ Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: an LSDA+U Study. *Phys. Rev. B* **1998**, *57*, 1505.
- ³⁷ Cinquini, F.; Giordano, L.; Pacchioni, G.; Ferrari, A. M.; Pisani, C.; Roetti, C. Electronic Structure of NiO/Ag(100) Thin Films from DFT+U and Hybrid Functional DFT Approaches. *Phys. Rev. B* **2006**, *74*, 165403.
- ³⁸ Marques, M. A. L.; Vidal, J.; Oliveira, M. J. T.; Reining, L.; Botti, S. Density-based Mixing Parameter for Hybrid Functional. *Phys. Rev. B* **2011**, *83*, 035119.
- ³⁹ Nunes, R. W.; Gonze, X. Berry-Phase Treatment of the Homogeneous Electric Field Perturbation in Insulators. *Phys. Rev. B* **2001**, *63*, 155107.
- ⁴⁰ Souza, I.; Iñiguez, J.; Vanderbilt, D. First-Principles Approach to Insulators in Finite Electric Fields. *Phys. Rev. Lett.* **2002**, *89*, 117602.
- ⁴¹ Conesa, J. C. Band Structures and Nitrogen Doping Effects in Zinc Titanate Photocatalysts. *Catal. Today* **2013**, *208*, 11-18.

- ⁴² Skone, J. H.; Govoni, M.; Galli, G. Self-Consistent Hybrid Functional for Condensed Systems. *Phys. Rev. B* **2014**, *89*, 195112.
- ⁴³ Le Bahers, T.; Rérat, M.; Sautet, P. Semiconductors Used in Photovoltaic and Photocatalytic Devices: Assessing Fundamental Properties from DFT. *J. Phys. Chem. C* **2014**, *118*, 5997.
- ⁴⁴ *Materials Studio* v. 8.0, Dassault Systèmes, 2014.
- ⁴⁵ Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44*, 1272-1276.
- ⁴⁶ Deliens, M.; Goethals, H. Polytypism of Heterogenite. *Miner. Mag.* **1973**, *39*, 152-157.
- ⁴⁷ Tkalych, A. J.; Yu, K.; Carter, E. A. Structural and Electronic Features of Beta-Ni(OH)₂ and Beta-NiOOH from First Principles. *J. Phys. Chem. C* **2015**, *119*, 24315.
- ⁴⁸ Fidelsky, V.; Toroker, M. C. Engineering Band Edge Positions of Nickel Oxyhydroxide through Facet Selection. *J. Phys. Chem. C* **2016**, *120*, 8104-8108.
- ⁴⁹ Levi, E.; Aurbach, D. Crystal Chemistry and Valence Determinations for Mn, Ni and Co Oxides as Cathode Materials in Li Batteries. *Solid St. Ionics* **2014**, *257*, 1-8.
- ⁵⁰ Demourgues, A.; Gautier, L.; Chadwick, A. V.; Delmas, C. EXAFS Study of the Jahn-Teller Distortion in Layered Nickel Oxyhydroxide. *Nucl. Instr. Meth. Phys. Res. B* **1997**, *133*, 39.
- ⁵¹ Varkey, A. J.; Fort, A. F. Solution Growth Technique for Deposition of Nickel-Oxide Thin-Films. *Thin Solid Films* **1993**, *235*, 47.
- ⁵² Carpenter, M. K.; Corrigan, D. A. Photoelectrochemistry of Nickel-Hydroxide Thin-Films. *J. Electrochem. Soc.* **1989**, *136*, 1022.
- ⁵³ Axmann, P.; Freire Erdbrügger, C.; Buss, D. H.; Glemser, O. Formation of Fe-IV and Ni-IV by electrochemical and Chemical Oxidation of an Iron-Substituted Nickel(II)

Hydroxide: the direct Two-Electron Step Ni-II->Ni-IV+2e⁻. *Angew. Chem. Intl. Ed. Eng.* **1996**, *35*, 1115.

- ⁵⁴ Görlin, M.; Chernev, P.; Ferreira de Araújo, J.; Reier, T.; Dresp, S.; Paul, B.; Krähnert, R.; Dau, H.; Strasser, H. Oxygen Evolution Reaction Dynamics, Faradaic Charge Efficiency, and the Active Metal Redox States of Ni-Fe Oxide Water Splitting Electrocatalysts. *J. Am. Chem. Soc.* **2016**, *138*, 5603–5614.
- ⁵⁵ Fidelsky, V.; Butera, V.; Zaffran, J.; Toroker, M. C. Three Fundamental Questions on One of Our Best Water Oxidation Catalysts: a Critical Perspective. *Theor. Chem. Acc.* **2016**, *135*, 162.
- ⁵⁶ Zou, S.; Burke, M. S.; Kast, M. G.; Fan, J.; Danilovic, N.; Boettcher, S. W. Fe (Oxy)hydroxide Oxygen Evolution Reaction Electrocatalysis: Intrinsic Activity and the Roles of Electrical Conductivity, Substrate, and Dissolution. *Chem. Mater.* **2015**, *27*, 8011–8020.

Table 1- Results after structural optimization, using the DFT+U+vdW functional, of the different NiOOH models.

Model	Energy/NiOOH (eV)	Inter-sheet spacing d (Å) ⁺	Sheet area/Ni a _{Ni} (Å ²) ⁺	Valence(s) of Ni atom(s)*	Spin densities on Ni atoms [#]	E _g (PBE+U) [‡] (eV)	E _g (PBE0α) ^{‡,§} (eV)
1H _S	-12.368	4.41	7.48	3.05	1.08	0.265/0.68	n.d.
1H _D	-12.380	4.43	7.49	3.06	1.08 (0.84)	0.322/0.72	1.46/1.90 [0.147]
1H _C	-12.359	4.38	7.48	3.11, 3.02	0.78, 0.79	0.00/0.05	n.d.
2H _S	(after relaxation becomes the same structure as 2H _W)						
2H _D	-12.340	4.49	7.53	3.04	1.24 (0.86)	0.003/0.02	0.44/0.60 [0.149]
2H _C	-12.428	4.57	7.42	3.02, 3.28	1.08, 1.16 (0.84, 0.86)	0.07/0.16	0.94/1.05 [0.12]
2H _W	-12.427	4.57	7.45	2.89, 3.76, 2.65, 3.08	1.13, 0.19, 1.54, 1.57 (0.86, 0.02, 1.27, 1.31)	0.005/0.06	0.81/1.20 [0.15]
2M _S	-12.243	4.45	7.49	3.04, 3.03	1.24, 1.10	0.00/0.23	n.d.
2M _D	-12.392	4.51	7.47	2.39, 3.75	1.73, 1.73, 0.12, 0.12	0.296/0.42	n.d.
2M _C	(after relaxation becomes the same structure as 3R _C)						
2M _W	(after relaxation becomes the same structure as 3R _W)						
2M _X	-12.420	3.97	8.53	3.34	1.75	1.84/2.98	n.d.
3R _S	-12.370	4.42	7.48	3.05	1.09	0.20/0.69	n.d.
3R _D	-12.341	4.48	7.53	3.04	1.25 (0.84)	0.00/0.04	1.42/1.75 [0.157]
3R _C	-12.451	4.56	7.43	3.25, 2.97	1.15, 1.06 (0.89, 0.85)	0.255/0.635	1.28/1.67 [0.135]
3R _W	-12.434	4.55	7.46	3.29, 3.75, 2.86, 2.53	1.08, 0.09, 1.12, 1.74 (0.86, 0.01, 0.89, 1.66)	0.18/0.51	1.07/1.32 [0.145]

⁺Experimental values for d, a_{Ni}: 4.62, 7.13 (ref. 25); 4.84, 6.84 [JCPDS 06-0141]

^{*}Obtained using the formula in ref. 49

[#]From the PBE+U calculation; the PBE0α result, if obtained, is given in parentheses

[‡] Indirect/direct gap values are given separated by a slash

[§] α value is given in square brackets

Table 2 Energetics and Fe redox states for different Fe:NiOOH structures having Fe in different coordination environments

Cell contents	Structure type	Cell dimensions [#]	Fe coordn.	Energy (eV)	Fe redox state
FeNi ₃ (OOH) ₄	1H _D	1X4	O ₃ (OH) ₃	-54.836	Fe ⁴⁺
	3R _C	1X4	O ₄ (OH) ₂	-55.092	Fe ⁴⁺
			O ₂ (OH) ₄	-54.872	Fe ³⁺
FeNi ₇ (OOH) ₈	1H _D	1X8	O ₅ (OH)*	-105.017	Fe ⁴⁺
	3R _D	1X8	O ₅ (OH)*	-104.516	Fe ⁴⁺
	2H _C	2X4	O ₄ (OH) ₂	-105.275	Fe ⁴⁺
			O ₂ (OH) ₄	-104.389	Fe ³⁺
	3R _C	1X8	O ₄ (OH) ₂	-104.774	Fe ³⁺
			O ₂ (OH) ₄	-104.870	Fe ³⁺
		2X4	O ₄ (OH) ₂	-104.526	Fe ⁴⁺
			O ₂ (OH) ₄	-104.503	Fe ⁴⁺
	3R _W	2X4	O ₆ ⁺	-104.706	Fe ⁴⁺
			O ₆ [§]	-104.283	Fe ³⁺
			(OH) ₆ [§]	-104.507	Fe ⁴⁺
			(OH) ₆ [‡]	-104.475	Fe ⁴⁺
FeNi ₁₅ (OOH) ₁₆	3R _W	2X8	O ₆ ⁺	-204.647	Fe ⁴⁺
			O ₆ [§]	-204.198	Fe ³⁺
			(OH) ₆ [§]	-204.440	Fe ⁴⁺
			(OH) ₆ [‡]	-204.277	Fe ⁴⁺

nXm means that the unit cell has n sheets with m cations per sheet

*after proton jump upon relaxation

⁺Fe in Ni⁴⁺ position

[§]Fe in Ni³⁺ position

[‡]Fe in Ni²⁺ position

Table of contents image