NiFe-Based (Oxy)hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes

Fabio Dionigi and Peter Strasser*

NiFe-based (oxy)hydroxides are highly active catalysts for the oxygen evolution reaction in alkaline electrolyte solutions. These catalysts can be synthesized in different ways leading to nanomaterials and thin films with distinct morphologies, stoichiometries and long-range order. Notably, their structure evolves under oxygen evolution operating conditions with respect to the as-synthesized state. Therefore, many researchers have dedicated their efforts on the identification of the catalytically active sites employing in operando experimental methods and theoretical calculations. These investigations are pivotal to rationally design materials with outstanding performances that will constitute the anodes of practical commercial alkaline electrolysers. The family of NiFe-based oxyhydroxide catalysts reported in recent years is addressed and the actual state of the research with special focus on the understanding of the oxygen-evolution-reaction active sites and phase is described. Finally, an overview of the proposed oxygen-evolution-reaction mechanisms occurring on NiFe-based oxyhydroxide electrocatalysts is provided.

1. Introduction

The transition to a society where large part of the world energy demand is provided by renewable energy requires storage solutions due to the intermittency nature of renewable energy resources, either wind or sunlight. When the demand matches the supply from these sources, the energy can be captured and directly converted into electrical energy for example by solar cells or wind turbines. But excess electricity that is not immediately utilized should be stored to compensate future temporary decrease of energy supply. A promising strategy to address this issue consists in storing the excess of electrical energy in the form of chemical energy by splitting the water in hydrogen and oxygen. Following this process, electrical energy can be re-obtained when needed by, for example, fuel cell technologies.

The efficiency of the electrolysis process depends on several factors, among which the sluggish kinetic of water oxidation to oxygen, presents a considerable challenge. This reaction is central in natural photosynthesis, where it occurs at the oxygen-evolving center (OEC).

The OEC unit is driven by the light absorbed by photosystem II (PSII) and oxidizes water into oxygen and reducing equivalents. The OEC shows high efficiencies for water oxidation and an excellent estimated turnover frequency. Achieving such desirable performances outside the protein environment that surrounds the OEC is difficult, due to the harsh oxidizing conditions and the complicated mechanism of the oxygen evolution reaction (OER) which makes the optimization of the catalyst problematic (see section 6 for further discussion). Several catalysts have been proposed to reduce the overpotential losses for OER and investigated in different pH conditions, from acid to alkaline and in neutral pHs with buffer addition. Among them, transition-metal oxides and hydroxides have proven so far to be the class of materials that show the best performances for OER. For example, IrO2 is often considered the benchmark catalyst for OER thanks to its superior stability and excellent activity both in acid and basic pH. However, IrO2 still shows a considerable OER overpotential when compared to the overpotential required by the best catalysts to achieve similar currents for the other half cell reaction, the hydrogen evolution. Furthermore, due to the Ir limited resources and its high price several researchers are looking for strategies to reduce its amount without losing performances (alloy, core/shell particles) or alternative catalysts based on earth abundant elements. In alkaline and near neutral electrolytes, oxides and hydroxides of late first row transition metals (Mn, Fe, Co, Ni) show promising performances and so they are the subject of deep investigation.

In particular, hydroxides incorporating both Ni and Fe together are reported to show the lowest overpotential for OER in alkaline conditions (pH 13 and 14) and be active also at near neutral pH in borate buffer. In addition, it has recently been shown that they can be employed as precursors to derive other NiFe-based oxides, nitrides and sulfides with interesting electrocatalytic performances for hydrogen evolution reaction or overall water splitting. Thanks to their high OER activity, NiFe-based hydroxides are investigated also as surface modification of photoanodes for photoelectrochemical water splitting and for seawater oxidation. Corrigan firstly investigated their...
2. The Structure of NiFe-Layered Double Hydroxide

2.1. Crystal Structure and Phase Transformations of Ni(OH)₂

The structure and surface electrochemical redox behavior of Ni-Fe mixed hydroxides can be conveniently understood by introducing Fe-free Nickel hydroxides. Nickel hydroxide, Ni(OH)₂, where Ni is in his most common oxidation state of +2, is a stable compound in alkaline conditions in the pH range between ≈9 and ≈13 when considering the potential window of hydrogen-reduction/water-oxidation according to Pourbaix diagram and consistent with recent density functional theory calculations. Therefore, we will focus our review on (oxy)hydroxides containing both Ni and Fe and the recent insights obtained in the last five years about the active state of these catalysts during the oxygen evolution reaction (Figure 1).

![Image](www.MaterialsViews.com)

**Peter Strasser** is the chaired professor of “Electrochemistry and Electrocatalysis” in the Chemical Engineering Division of the Department of Chemistry at the Technical University Berlin. He was Assistant Professor at the Department of Chemical and Biomolecular Engineering at the University of Houston, after he served as Senior Member of staff at Symyx Technologies, Inc. He earned his PhD in Physical Chemistry and Electrochemistry from the ‘Fritz-Haber-Institute’ of the Max-Planck-Society in Berlin under the direction of Gerhard Ertl. He studied chemistry at Stanford University, USA, the University of Tuebingen, Germany, and the University of Pisa, Italy.

**Fabio Dionigi** completed his PhD in Physics in 2012 at Danmarks Tekniske Universitet (DTU), Denmark. Then he continued in the same university as a postdoc at DTU Nanotech, Department of Micro- and Nanotechnology, till November 2013. Since then he has joined “The electrochemical energy, catalysis, and materials science group” in the Department of Chemical engineering at Technische Universität Berlin, Germany. His work is focused on photocatalytic water splitting and more recently on non-noble metal based catalysts for the oxygen evolution reaction.
three corners (T1 oxygen stacking). Brucite-like $\beta$-Ni(OH)$_2$ has a trigonal crystal symmetry with hexagonal lattice and space group P-3m1. The layers in $\beta$-Ni(OH)$_2$ are held together by van der Waals forces and no hydrogen bonds are observed, while hydrogen bonds are observed for the other phases. The structure of the oxidized phases, $\beta$-NiOOH and $\gamma$-NiOOH, are subject to debate. Van der Ven et al. proposed for the $\beta$-NiOOH a trigonal prismatic arrangement of the oxygen ions between two adjacent layer (P3 oxygen stacking) in contrast with the tetrahedral arrangement of the $\beta$-Ni(OH)$_2$ (Figure 3). In this configuration hydrogen bonds can form connecting the layers. Following this work, Casas-Cabanas et al. performed a high-resolution transmission electron microscopy (HRTEM) study on a chemically oxidized $\beta$-NiOOH. They observed doubling of the c-axis respect to $\beta$-Ni(OH)$_2$ and confirmed an irreversible formation of slightly misoriented crystalline domains. Based on their observation, they proposed that layer shearing is occurring in the transition to $\beta$-NiOOH that this is resulting in a structure with ABCA oxygen stacking and a C2/m space group. The monoclinic structure was also considered by Kazimirov et al., who proposed two models for the $\beta$-NiOOH, with P3m1 space group and monoclinic Cm group, respectively. On the other hand, the ABCA stacking was predicted to be unstable by Li et al. In addition, they proposed formation of tunnel structures at the edge of the domains using genetic algorithm based calculations and suggested that disproportionation of half of the Ni$^{3+}$ into Ni$^{2+}$ and Ni$^{4+}$ could occur in $\beta$-NiOOH. Recently, Tkalych et al. proposed based on density functional theory calculations that $\beta$-NiOOH has a structure with a staggered arrangement of protons (protons are present on both sides of each layer) and that the Jahn-Teller distortion of the low spin Ni$^{3+}$ centered octahedral might be the explanation for two different Ni-O bond distances experimentally observed for this phase. In conclusion, there is not a general agreement on the structure of $\beta$-NiOOH. Similarly controversial is the structure of $\gamma$-NiOOH. For example, Van der Ven et al. proposed a monoclinic unit cell with C2/m space group or a structure with R-3m space group symmetry as possible candidates. In both cases the oxygen
stacking is of P3 type, forming trigonal prismatic structure in the interlayer gap. Contrasting experimental results based on γ-NiOOH obtained by chemical methods from NaNiO₂ precursors support either one or the other structure.⁴³,⁴⁴ Among the four phases described by Bode et al., two distinct redox transformations are obtained by potential cycling across the Ni(II)/(III,IV) redox potential: the charge/discharge cycle between α-Ni(OH)₂ and γ-NiOOH (α/γ) and between β-Ni(OH)₂ and β-NiOOH (β/β). The oxidation of α to γ is reported to occur at lower potential than the one from β(II) to β(III).³⁰,³¹ Departures from these two distinct transformations have been reported by aging and overcharging. Aging, especially in electrolyte with high alkaline pH values, has been found to allow the transformation of α-Ni(OH)₂ to β-Ni(OH)₂. Increasing the potential above the charging of β-Ni(OH)₂ to β-NiOOH leads to the transformation of β-NiOOH to γ-NiOOH (overcharging). This model is broadly accepted and has been recently demonstrated to hold in the case of electrodeposited Ni(OH)₂ on Au electrode that was aged in rigorous Fe-free purified KOH electrolyte.³¹ In contrast, it was found that aging in unpurified electrolyte (containing traces of Fe) leads to Fe incorporation and inhibitions of the two transformations caused by aging and overcharging. In addition to this effect, the incorporation of Fe has been shown to improve dramatically the activity of Ni(OH)₂ and the surface redox chemistry.²⁵,⁴⁵

2.2. Crystal Structure of NiFe-Layered Double Hydroxide

Incorporation of Fe³⁺ in the neutral layers of Ni(OH)₂ leads to positive charged layers that are charge-compensated by anion intercalation in the interlayer region. For example, carbonate anions will be present in half the amount of the incorporated Fe³⁺ due to their double negative charge. Water also intercalates in the structure forming hydrogen bonds with the hydroxide groups. The compound can be expressed with the formula

$$\left[\text{Ni}^{2+},\text{Fe}^{3+}(\text{OH})_2\right]^{x+}(\text{A}^{x-})_n\cdot y(\text{H}_2\text{O})$$

where x is the molar ratio of Fe that is incorporated, A is the anion, n is the charge of the anions and y the amount of water that is intercalated.

The crystal structure formed is the same as in the mineral hydrotalcite and is often denoted in the literature as layered double hydroxide (LDH). Figure 3 shows a comparison between the crystal structure of β-Ni(OH)₂, that is isostructural with brucite, Mg(OH)₂, and the structure of NiFe LDH, isostructural with hydrotalcite, where Al³⁺ substitute Mg²⁺ in layers. For NiFe LDH, Mössbauer spectroscopy and extended X-ray absorption fine structure (EXAFS) indicate that Fe is indeed substitutionally incorporated in the Ni host lattice, due to strong correlation between Ni and Fe features. The maximum amount of Fe that can be incorporated while preserving the LDH structure is not clear. The comparison with other hydrotalcite-like compounds suggests that the Fe content of ≈33%, corresponding to Ni/Fe ratio of 2:1, is the highest limit, after which the unavoidable formation of near neighbor Fe octahedral becomes the basis for the formation of FeOxHy phases.⁴⁷ For this specific ratio between the divalent and trivalent cations, direct nearest neighboring of the trivalent cation, i.e., Fe³⁺, is avoided for a perfect orderly distributed LDH, as discussed by Ma et al. for CoFe LDH.⁴⁸ A previous work by Sideris et al. demonstrated ordering of the cations in a honeycomb arrangement for Mg₂Al₁ LDH therefore excluding random cations.

Figure 3. As-prepared crystal structures. The unit cell (black lines) and layers with four metal atoms each are shown for the fully protonated form of (a) Brucite-like β-Ni(OH)₂ and (b) hydrotalcite-like NiFe LDH with intercalated water and carbonate anions (randomly distributed). The respective oxygen stacking across the interlayer region is shown in (c) and (d). In (e) the top-view along the c-axis of NiFe LDH shows three kinds of OH sites.
arrangement, with only a minor presence of misplaced cationic defects, that are OH surrounded by three Mg cations, of <3%. Cadars et al. later confirmed the presence of this small amount of defects and found a corresponding low amount of trivalent Al-Al clustering. Recently, Abellán et al. also excluded a completely random distribution of cations in NiFe LDH that was synthesized by homogeneous precipitation and found evidence of increasing Fe-Fe clustering with increasing iron content. The arrangement of the cations is important because it determines the kind of hydroxide (or oxygen) sites that might act as the active site for the oxygen evolution reaction. In LDH structure we can distinguish 3 kinds of hydroxides sites, bounded respectively to 3, 2 and 1 metal centers and denoted as μ3, μ2 and μ1 (Figure 3e). We notice that the μ3 site is present only at the central area of the layers, while the μ2 and μ1 are located on the edges. Considering two different metal cations, Fe and Ni, we obtain a maximum of four sites of the kind μ3 (Mg3-OH, Fe3-OH, Mg2Fe-OH, MgFe2-OH), three sites of μ2 (Mg2-OH, Fe2-OH, MgFe-OH) and two μ1 sites (Mg-OH, Fe-OH), if we exclude influence of superior order coordination shells. Therefore the absence (or presence) of Fe-Fe neighbor atoms has a dramatic effect on the kind of hydroxides sites allowed. In general, increasing Fe content in the catalyst preparation often leads to formation of FeOxHy domains or small FeOxHy nanoparticles that are difficult to detect by XRD methods available in standard laboratories. These phases are experimentally observed to start forming at Fe content lower than 33% and shown to cause decrease in OER activity. The different values estimated from the experiments for the solubility limit of Fe in the Ni(OH)2 host might imply its dependence on the preparation method. Besides cations arrangement, the incorporation of Fe and the concomitant intercalation of water and anions also affects the stacking of the layers respect to the brucite-like Ni(OH)2. Every layer of the NiFe LDH is shifted in the plane that is normal to the stacking direction respect to adjacent layers in a way that the oxygen atoms facing the interlayer gallery from two neighboring layers occupy the corners of a trigonal prismatic structure connecting the two layers. This is in contrast with the tetrahedral structure of the brucite β-Ni(OH)2. In this trigonal configuration the hydroxyl groups of adjacent layers that are pointing in the same interlayer gallery are aligned on top of each other and the unit cell contains atoms from 3 layers. This particular stacking is called polytype 3R and the layers are translationally equivalent (in contrast to 2H polytype that consist in a two-layer structure obtained by rotation of 180 degree of each layer and have space group symmetry P63/mmc). It has been noted that the O-H bond are not necessary perfectly aligned with the c-axis, but are slightly tilted. The stacking configuration of the LDH is thought to be originated by the necessity to accommodate anions and water and optimize the hydrogen bonding of the OH groups of the layers with the intercalated water. In this configuration the oxygen of the intercalated water as well as the one of the carbonate anions is envisaged to be randomly distributed between the 6 equivalent positions around the OH group alignment axis. This stacking configuration results in different unit cell respect to brucite and labeling of the X-ray diffraction (XRD) reflections between the two materials. More specifically, hydrogencarbonate-like NiFe LDH has trigonal crystal symmetry with rhombohedral lattice (3R polytype) and space group R-3m. Due to the 3-layer structure of the LDH, the reflection corresponding to the separation of adjacent layers and occurring at low 2θ angles in XRD pattern is indexed as (003) (Figure 4a), while (001) is used for brucite. The separation between the layers is affected by the nature of the intercalated anions which can widely vary including organic and inorganic anions. The anions can be chemically exchanged and in particular carbonate, CO3²⁻, was found to be not easily anion exchanged due to stronger electrostatic interaction with the layers respect to other anions and so it is considered one of the most stable anion for NiFe LDH. A method based on a acid-salt mixed solution was developed by Iyi et al. to anion exchange carbonate intercalated LDH and further successfully used also for NiFe LDH. The anion exchange of NiFe LDH with anions of larger size than carbonate (i.e., ClO4⁻ or NO3⁻) weakens the interlayer interaction and allows for delamination of the LDH into single layers via

Figure 4. Structure characterization and morphology of NiFe LDH and NiFe oxyhydroxides obtained from different synthesis. a) X-ray diffraction patterns of well crystallized NiFe LDH with intercalated CO3²⁻ (pattern a), Cl⁻ (pattern b) and ClO4⁻ (pattern c). Reproduced with permission. Copyright 2008, American Chemical Society. b) TEM image of hexagonal NiFe LDH nanoplates; Reproduced with permission. Copyright 2008, American Chemical Society. c) SEM image of NiFe LDH flowers; Reproduced with permission. Copyright 2009, IOP Publishing. d) SEM image of NiFe flakes grown on Ni foam. Reproduced with permission. Copyright 2016, Royal Society of Chemistry. e) SEM image of a cathodically electrodeposited NiFe (oxy)hydroxide film. Reproduced with permission. Copyright 2014, American Chemical Society.
a liquid phase exfoliation process typically performed in formamide.\(^{[51,57]}\) Another proposed method for delamination of NiFe LDH is based on intercalation of aminoundecanocanoic acid and on following protonation of the amine group in acid aqueous environment to produce electrostatic repulsion between the layers and the cationic amino group of the intercalated molecules.\(^{[56]}\)

As in the case of \(\alpha\text{-Ni(OH)}_2\) and \(\beta\text{-Ni(OH)}_2\), the (electro) chemical oxidation of NiFe LDH is expected to have influence on the crystal and electronic structure. The determination of the structure obtained by increasing the potential more anodically than the Ni redox transition and under OER conditions is not easy due to the instability of the Ni\(^{3+}\) species and the requirement of in situ and in operando methods. This topic will be discussed in section 5.

### 3. Synthesis of NiFe-Based Oxy(hydroxide) Catalysts

NiFe LDH or more generally NiFe-based (oxy)hydroxides can be synthesized with several methods. Different methods produce materials that vary largely in crystal sizes, long-range order and morphology and might present concomitant undesired phases and different electrochemical behavior.

#### 3.1. Co-Precipitation at Constant pH

One of the most used methods consists in the co-precipitation of the metal precursors. In particular, in the “co-precipitation at constant pH”, an aqueous solution of Ni(II) and Fe(III) metal salts is added to a second water solution that is kept under stirring and at a certain mild basic pH (for example 9 or 11) by addition of a base or carbonate (i.e., KOH, \(\text{Na}_2\text{CO}_3\),..).\(^{[60,61]}\) A variation of this method consists in quickly mixing a solution (H\(_2\)O)\(_5\) followed by adsorption of cationic complexes like \(\text{Ni(OH)}_2^+\) or \(\text{Fe(OH)}_2^+\) that further evolve in molecular clusters by increasing pH. Ultimately, the LDH is formed by iron diffusion from the ferric oxyhydroxide phase into the \(\alpha\text{-Ni(OH)}_2\) phase and anion intercalation. The particles formed by this method often show nanoplate morphology with the dimension along the layers stacking direction much shorter than the inplane dimensions. Samples with low crystallinity appear to have nanoparticles more corrugated while high crystallinity samples have large and flat nanoparticles that have the tendency to stack on top of each other as playing cards on a table.

#### 3.2. Homogeneous Precipitation

In the homogeneous precipitation method, often referred to as solvothermal method or hydrothermal method, a hydrolysis agent is mixed with water and the metal salts precursors and by progressive hydrolysis provides a weak base (amines or ammonia) that is responsible for the precipitation of NiFe LDH. Urea, dimethylformamide (DMF) and hexamethylenetramine (HMT) are typical hydrolysis agents used.\(^{[16,51,58,64–68]}\) This method requires a certain temperature to start the hydrolysis process and is performed in autoclaves. Well crystallized NiFe LDH nanoplates are obtained with this process, showing a hexagonal shape that reflects the layer symmetry (Figure 4b). In addition to this standard morphology, a flower-like morphology has also been obtained using ethylene glycol (EG) as chelating agent and urea (Figure 4c).\(^{[67]}\) Other chelating agents have also been proposed. For example, trisodium citrate (TSC) has been proposed as chelating agent during urea hydrolysis in order to reduce the amount of amorphous FeOxH\(_y\) particles.\(^{[58,69]}\) Triethanolamine (TEA) is reported as another chelating agent in combination with a Fe\(^{2+}\) salt or a Fe\(^{3+}\) salt to better match the precipitation of Fe and Ni hydroxides and avoid nonsoluble metallic oxide.\(^{[51,65]}\) The homogeneous precipitation method allows to grow the NiFe LDH catalyst on different substrates. For example, Liu et al. were able to grow highly oriented flakes arrays of NiFe LDH in vertical contact with the Ni foam substrate using a homogeneous precipitation method based on urea and assisted with \(\text{NH}_4\text{F}\) as directing agent (Figure 4d).\(^{[70]}\) Regarding photoelectrochemical applications, Wang et al. showed that homogeneous precipitation using DMF as hydrolysis agent is suitable for direct growth of NiFe LDH catalyst on Ta\(_3\)N\(_5\) photoanode.\(^{[72]}\) More recently, a similar method using urea applied to Ta\(_3\)N\(_5\) photocatalyst powder provided also enhanced photocatalytic OER activity in the presence of an electron scavenger.\(^{[71]}\)

#### 3.3. Cathodic and Anodic Electrodeposition

Another common method consists in the electrodeposition of NiFe hydroxides thin films. The cathodic electrodeposition at constant current is the most used method and results in the formation on the cathode of NiFe-based hydroxides upon reduction reaction in aqueous solution that contains the metal precursors.\(^{[45,72–75]}\) The pH of the deposition bath is either adjusted to acid values (i.e., pH 2) or slightly acid (pH between 2 and 6) or left unadjusted. Basic pH values are not used in order to avoid unintentional precipitation of Ni hydroxide particles in solution. A proposed formation mechanism is based on catalyst precipitation due to local basic pH created upon reduction reaction of the anions (nitrate, sulfate), even though other reductions (nickel and iron plating, hydrogen evolution) are thermodynamically possible and difficult to distinguish.\(^{[72]}\) The film obtained often shows a rough surface (Figure 4e) and is XRD amorphous or poorly crystallized. However, Trotchoud et al. showed that it is possible to increase the crystallinity and form NiFe LDH by aging in alkaline solution a cathodically electrodeposited NiFe oxyhydroxide film.\(^{[45]}\) A recent variation of the cathodic electrodeposition method consists in using pulsed instead of continuous electrodeposition.\(^{[74]}\) This method is particularly effective for thicker films and is able to produce denser films that are better electrically connected and have a more homogeneous Fe distribution. In contrast to the vast use of cathodic electrodeposition, the anodic variant is more rarely used. Recently, an anodic deposition method has been
developed by Morales-Guio et al. that allowed the deposition of Fe rich FeNiO\textsubscript{x} catalyst on FTO and Au electrode.\cite{31} The exact structure and phase of the FeNiO\textsubscript{x} catalyst is still under investigation. The method was also applied by the authors using a hematite photoanode in replacement of FTO with deposition performed under irradiation. Finally, in contrast to the majority of the electrodeposition methods that are carried out in aqueous solvent, a method to electrodeposit NiFe alloy in an ionic liquid has been recently reported by Lo et al.\cite{45} In this work, the film was deposited at constant potential on a Cu substrate and later converted in hydroxides by cycling in 0.1 m NaOH.

### 3.4. Alternative Synthetic Routes: Phase Transformations and Fe Impurity Uptake

In this section we include alternative methods of preparation of NiFe oxyhydroxides that often involve a transformation from a preliminary solid-state phase containing Ni, Fe or both. Indeed, besides direct formation methods of mixed NiFe hydroxides explained so far, other indirect routes are possible: phase transformation by either electrochemical conditioning or chimie douche, Fe impurity uptake using a Ni oxide/hydroxide electrode and pulsed-laser ablation in liquid (PLAL). For example, Trotochaud et al. reported that thin film of thermal oxide of NiO was deposited at constant potential on a Cu substrate and later annealed at low temperature in a furnace (i.e., 100 °C).

#### 4. Electrochemistry in Alkaline Conditions

##### 4.1. Surface Redox Chemistry

The surface redox chemistry of NiFe LDH is studied with cyclic voltammetry. Cyclic voltammograms are usually reported between 1–1.2 V vs RHE and 1.7 V vs RHE. No feature in the voltammograms is associated with change in oxidation state of Fe. On the other hand, an anodic and a cathodic wave is observed and assigned to oxidation of Ni(II) to an higher oxidation state (III, IV) and to the reverse reduction to Ni(II), respectively (Figure 5a). This change in oxidation state is

**Figure 5.** Effect on surface redox chemistry and OER activity of Fe content in NiFe (oxy)hydroxide. a) CV scans in 1 m KOH electrolyte solutions for electrodeposited Fe-free Ni (green) and NiFe oxyhydroxides film with different Fe content (blue, orange, red). Reproduced with permission.\cite{25} Copyright 2014, American Chemical Society. b) Comparison of reported OER overpotential trends as a function of Fe content in NiFe (oxy)hydroxide catalysts. Measurements obtained in different conditions and overpotentials evaluated at different current densities. Therefore, the overpotential difference is plotted with respect to the minimum overpotential reported in each study. The numbers were manually extracted from the published graphs if not stated in tables. Data in black \( \square \) reproduced with permission.\cite{31} Copyright 1987, The Electrochemical Society. Data in red \( \bullet \) and blue \( \Delta \) reproduced with permission.\cite{25} Copyright 2013, American Chemical Society. Data in pink \( \nabla \) reproduced with permission.\cite{46} Copyright 2011, The Royal Society of Chemistry. Data in green \( \circ \) reproduced with permission.\cite{45} Copyright 2015, American Chemical Society.
accompanied by (de)protonation, similarly to the Ni(OH)$_2$/NiOOH redox process in Fe free samples. At higher potential than the Ni(II) oxidation wave an increase in current is observed and assigned to OER. Both redox waves shift anodically and decrease in magnitude with increasing Fe content (Figure 5a). At certain Fe contents the anodic wave disappears due to overlapping with the OER current. Friebel et al. proposed an explanation for this anodic shift based on the results of their density functional theory calculation. The presence of Fe decreases the affinity to oxygen of the Ni surface sites and so rises the potential for the Fe$_x$Ni(OH)$_2$/FeNiOOH transformation to higher values. Chen et al. rationalized this shift in terms of destabilization of Ni$^{3+}$ species in the presence of Fe$^{3+}$ in the second coordination sphere. The Fe$^{3+}$ species makes the bridging oxygen/hydroxide ligands less electron-donating towards the Ni d-orbitals and so the higher formal redox potential increases. In general the complete understanding of the redox behavior is complicated due to possible appearance of multiple peaks and the fact that the anodic and cathodic waves usually evolve upon cycling, both in terms of magnitude as well as shift in potential. Multiple anodic waves could be assigned to different Ni sites, while growing and shift of the waves might be due to more accessibility of the “bulk” sites that could be due to the hydrated nature of this material. Formation of electrically disconnected domains upon cycling due to the different conductivity of the oxidized and reduced phase is also thought to affect the intensity of the redox peaks. The redox behavior is still under debate also for the case of Fe free Ni(OH)$_2$. For example, in the Fe free Ni(OH)$_2$ additional peaks are visible in the CV in the potential range between the main anodic wave and the OER onset potential that are not easy to assign. Efforts in explaining the redox behavior of rigorous Fe free Ni(OH)$_2$ will probably help the understanding of the redox features in NiFe LDH.

4.2. OER Activity: Overpotential, Turnover Frequency and Tafel Slope

NiFe LDH and amorphous NiFe (oxy)hydroxides catalysts show high activity for OER. In this paragraph, we first give an overview of both the most used activity metrics and the related values reported in the literature of recent years. At the end of the paragraph, we discuss in more details the findings related to the various parameters that affect the activity of these catalysts. Among the wide range of possibilities for activity metrics, we have found that the overpotentials at fixed geometric current densities, Tafel slopes and turnover frequencies (TOF) at fixed overpotentials are the most common and are normally used for expressing the catalytic activity of these materials (Table 1). In particular, the overpotential at the current density of 10 mA cm$^{-2}$ is often reported, due to its relevance for integrated photoelectrochemical water splitting devices operating at 1 sun where the photoabsorber is covered by the catalyst. Higher current densities ≥ 500 mA cm$^{-2}$ and closer to industrial electrolyzer conditions are more seldom considered even though equally relevant. The overview in Table 1 shows that in 0.1 m KOH electrolyte the overpotential at 10 mA cm$^{-2}$ varies in general for the best catalysts on flat substrate between values slightly below 300 mV vs RHE and ≈350 mV, apart some exceptions. The overpotential is further decreased by using porous substrate, like Nickel foam, of ≈50 mV vs RHE respect to typically reported and optimized values for flat substrates. In 1 m KOH electrolyte the overpotential at 10 mA cm$^{-2}$ is lower than in 0.1 m KOH for similar catalysts tested in both electrolytes and varies typically between ≈260 mV vs RHE and ≈340 mV vs RHE, with further improvement of the low limit value of ≈40–60 mV with porous substrates (Ni foam, carbon fiber paper). As mentioned in the introduction, these values are among the highest ever reported for OER and show that these catalysts can achieve high current densities at moderate overpotentials. In this metric, there is no indication of how active a specific active site is, since it is not normalized by amount of material or type of sites. To address this important question, the TOF is often used, being a relevant metric for the comparison of intrinsic activity. However, the determination of the TOF per active sites for NiFe (oxy)hydroxides is controversial, mainly due to the unclear nature of the active sites (i.e., Ni or Fe, bridge µ2-OH or on top µ1-OH) and lack of reliable methods to determine them. In general, the TOF calculated by averaging over the total number of moles of metal ions (i.e., determined by inductively coupled spectroscopy) is the more practical and widely accepted method, even though it can only provide an underestimation of the real TOF. Therefore we consider this definition in our review and reported the TOF calculated at the overpotential of 300 mV in Table 1. It has been noted that higher TOF are calculated with low catalyst loading, so the loading should always be indicated. The TOF vary widely among the catalysts. The best TOF approach =0.5 s$^{-1}$ in 0.1 m KOH and =1.5 s$^{-1}$ in 1 m KOH, even so the reported values span the same range for both electrolytes. At the present understanding of the catalyst, further discussion and comparison of the TOF is particularly difficult, in part for the limited data and the above mentioned problems related to the real active sites. In addition to the TOF, another figure of merit for assessing the intrinsic activity is the specific current density, where the current is normalized by the active surface area. This figure is particularly relevant for nonflat electrodes. However, several complications arise in determining the electrochemically active surface area via standard methods. Most of these complications originate from the differences between the more investigated thermal metal oxides, that are conductive and compact, and these hydrated materials, that are poor conductors in the reduced form and have bulk sites that are accessible to intercalated ions and possibly OH$^-$. Therefore calculations and comparisons among different catalysts of electrochemically active surface area (ECSA) and specific current densities must be done with care. Recently, Batchelor and Boettcher have shown that a meaningful estimation of the ECSA is possible by impedance spectroscopy of NiFe oxyhydroxide catalyst in the oxidized phase, that is when is conductive. Due to the complications mentioned, we have chosen to not report and discuss specific current densities. Finally, the analysis of Tafel plots is often carried out both as a comparative metric of activity as well as for elucidating rate limiting steps and the reaction mechanism. In particular, the exchange current density extrapolated from Tafel plots in conjunction with the Butler-Volmer equation is in
general not reported for the OER reaction, due to the reaction complexity and large errors associated with their estimation.[8] Tafel slopes on the other hand are usually estimated from Tafel plots and reported. Despite they can provide a comparison of surface kinetics and can be very useful for elucidating reaction mechanisms, their analysis is particularly difficult in the case of multiple electron-proton transfer reactions, as it is the case for OER. For example, often a potential dependency of the Tafel slope is observed resulting in two or more “Tafel slopes” with a non-linear transition between them.[8] In addition, the application of Butler–Volmer equation in conjunction with Tafel equation is questionable in the case of OER.[85] Therefore we limit ourselves to report absolute values of Tafel slopes as metric to describe electrocatalytic kinetics in term of the dependence of the current on potential (Table 1).

### Table 1. Comparison of catalyst activity from works published in recent years.

<table>
<thead>
<tr>
<th>Catalyst Synthesis Method</th>
<th>Ni:Fe ratio</th>
<th>Substrate</th>
<th>Catalyst loading [μg cm⁻²]</th>
<th>Thin film thickness [nm]</th>
<th>Electrolyte</th>
<th>η [mV] @ Jgeo = 10 mA cm⁻²</th>
<th>TOF [s⁻¹] @ η = 0.3 V (total metals)</th>
<th>Tafel slope [mV dec⁻¹]</th>
<th>Ref. (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Fe film e.d.</td>
<td>60:40</td>
<td>Au</td>
<td>≈26.74** / 70</td>
<td>1 μ KOH</td>
<td>280</td>
<td>≈0.3**</td>
<td>40</td>
<td>[72] (2013)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH-NO₃⁻</td>
<td>3:1</td>
<td>GC</td>
<td>100</td>
<td>1 μ KOH</td>
<td>275°</td>
<td>–</td>
<td>33.6</td>
<td>[55] (2016)</td>
<td></td>
</tr>
<tr>
<td>NiFeO₅ /C (Vulcan XC-72R)</td>
<td>62:38</td>
<td>GC</td>
<td>8 (only metals)</td>
<td>1 μ KOH</td>
<td>290°</td>
<td>0.45</td>
<td>–</td>
<td>[15] (2015)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH/oGSH hybrid</td>
<td>2.9:1</td>
<td>GC</td>
<td>250</td>
<td>1 μ KOH</td>
<td>350</td>
<td>–</td>
<td>54</td>
<td>[108] (2015)</td>
<td></td>
</tr>
<tr>
<td>RGO-Ni-Fe LDH composite</td>
<td>5:1 (†)</td>
<td>GC</td>
<td>200</td>
<td>1 μ KOH</td>
<td>250</td>
<td>–</td>
<td>33</td>
<td>[103] (2015)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH/C (Vulcan XC-72R)</td>
<td>87:13</td>
<td>GC</td>
<td>100 (7:9 only metals)</td>
<td>1 μ KOH</td>
<td>360</td>
<td>0.03</td>
<td>50</td>
<td>[16] (2016)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH/CNT hybrid</td>
<td>5:1</td>
<td>CFP</td>
<td>250</td>
<td>1 μ KOH</td>
<td>308</td>
<td>–</td>
<td>35</td>
<td>[66] (2013)</td>
<td></td>
</tr>
<tr>
<td>NiFe/NF e.d.</td>
<td>3:1</td>
<td>NF</td>
<td>32 (†)</td>
<td>1 μ KOH</td>
<td>240</td>
<td>–</td>
<td>33</td>
<td>[83] (2016)</td>
<td></td>
</tr>
<tr>
<td>3D NiFe LDH</td>
<td>3:1</td>
<td>NF</td>
<td>1000</td>
<td>1 μ KOH</td>
<td>250°</td>
<td>–</td>
<td>50</td>
<td>[64] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>5:1</td>
<td>CFP</td>
<td>250</td>
<td>1 μ KOH</td>
<td>308</td>
<td>–</td>
<td>35</td>
<td>[66] (2013)</td>
<td></td>
</tr>
<tr>
<td>NiFe/NF e.d.</td>
<td>3:1</td>
<td>NF</td>
<td>32 (†)</td>
<td>1 μ KOH</td>
<td>240</td>
<td>–</td>
<td>33</td>
<td>[83] (2016)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>3:1</td>
<td>NF</td>
<td>1000</td>
<td>1 μ KOH</td>
<td>250°</td>
<td>–</td>
<td>50</td>
<td>[64] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFeO₅ film sol. c+ an.</td>
<td>9:1</td>
<td>Au/Ti QCM crystal</td>
<td>1.17 / 2</td>
<td>1 μ KOH</td>
<td>336</td>
<td>0.21</td>
<td>30</td>
<td>[77] (2013)</td>
<td></td>
</tr>
<tr>
<td>Fe: Ni(OH)₂ film Fe i.</td>
<td>88-83:12-17</td>
<td>Au</td>
<td>... / 30</td>
<td>1 μ KOH</td>
<td>280</td>
<td>1.5</td>
<td>40</td>
<td>[31] (2015)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>3:1</td>
<td>GC</td>
<td>70</td>
<td>1 μ KOH</td>
<td>347</td>
<td>0.01</td>
<td>67</td>
<td>[57] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>3:1</td>
<td>GC</td>
<td>70</td>
<td>1 μ KOH</td>
<td>302</td>
<td>0.05</td>
<td>40</td>
<td>[57] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>3:1</td>
<td>GC</td>
<td>70</td>
<td>1 μ KOH</td>
<td>302</td>
<td>0.05</td>
<td>40</td>
<td>[57] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>80:20</td>
<td>GC</td>
<td>50</td>
<td>1 μ NaOH</td>
<td>260</td>
<td>–</td>
<td>21</td>
<td>[107] (2016)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH-MoO₄²⁻ /C (Ketjen black)</td>
<td>9:1</td>
<td>GC</td>
<td>280</td>
<td>1 μ KOH</td>
<td>280</td>
<td>–</td>
<td>40</td>
<td>[116] (2015)</td>
<td></td>
</tr>
<tr>
<td>Ni–Fe/3D-ErGO</td>
<td>4:1</td>
<td>Au</td>
<td>140</td>
<td>1 μ KOH</td>
<td>259</td>
<td>–</td>
<td>33</td>
<td>[104] (2015)</td>
<td></td>
</tr>
<tr>
<td>Ni-Fe</td>
<td>4:1</td>
<td>Au</td>
<td>140 (†)</td>
<td>1 μ KOH</td>
<td>331</td>
<td>–</td>
<td>58</td>
<td>[104] (2015)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>78:22</td>
<td>HOPG</td>
<td>≈444 **</td>
<td>1 μ KOH</td>
<td>280</td>
<td>–</td>
<td>47.6</td>
<td>[79] (2014)</td>
<td></td>
</tr>
<tr>
<td>NiFe LDH/CNT hybrid</td>
<td>5:1</td>
<td>CFP</td>
<td>250</td>
<td>1 μ KOH</td>
<td>247</td>
<td>0.56</td>
<td>31</td>
<td>[66] (2013)</td>
<td></td>
</tr>
<tr>
<td>FeNi LDH</td>
<td>3:1 (†)</td>
<td>NF</td>
<td>250</td>
<td>1 μ KOH</td>
<td>232</td>
<td>0.028</td>
<td>48</td>
<td>[100] (2014)</td>
<td></td>
</tr>
<tr>
<td>FeNi–GO LDH hybrid</td>
<td>3:1 (†)</td>
<td>NF</td>
<td>250</td>
<td>1 μ KOH</td>
<td>206</td>
<td>0.987</td>
<td>39</td>
<td>[100] (2014)</td>
<td></td>
</tr>
</tbody>
</table>
The extraordinary activity of NiFe (oxy)hydroxides is dependent on many parameters. The most common factors that influence the activity of NiFe (oxy)hydroxide and have been studied in the literature are: a) Fe content, b) the pH of the electrolyte, c) different substrate, d) different size/crystallinity, e) the nature of intercalated anions and f) the incorporation of a third metal.

### 4.2.1. Fe Content

Activity trends as a function of iron content have been investigated with the aim of determining the amount of incorporated iron that maximizes the activity.\[25,46,72,86\] Louie et al. found that the activity reaches a broad maximum across Fe compositions in the range of Fe content ≈15%–50% for electrodeposited films evaluated in 0.1 M KOH.\[72\] This is in agreement with Corrigan et al. who found that the lowest overpotential at 50% Fe content was not much different than the value at 10%.\[25\] On the other hand, Li et al. reported the optimum composition at a value ≈10% Fe for electrodeposited NiFe-based film.\[87\] Klaus et al. also measured the maximum OER activity at moderate Fe content of ≈12–17% in Fe incorporated Ni oxyhydroxides film on Au substrate.\[31\] The identification of the optimal composition is difficult, probably due to formation of inactive Fe oxides/oxyhydroxide phases starting at a Fe content that is dependent on the preparation method. However, it is generally accepted that the OER overpotential decreases dramatically for increase in Fe content from 0 to 10%, reaches a minimum at some concentrations in the range between 10% and 50% and further increases for Fe content higher than 50% (Figure 5b). Fe-free Ni hydroxides and Fe (oxy)hydroxides correspond to the two limiting compositions 5.3 and 5.5.\[31,99\] The interaction of NiFe LDH nanoplates with or supported on graphene with various degree of oxidation,\[100–105\] carbon nanoparticles (i.e., Vulcan XC-72R or Ketjen Black),\[15,80\] carbon quantum dots\[106\] and carbon nanotubes (Figure 6).\[66,107–109\] In particular, Gong et al. showed that direct nucleation and growth of NiFe LDH nanotubes on carbon nanotubes resulted in catalyst with higher activity than NiFe LDH mixed with carbon black or with the carbon nanotubes.\[96\] This improvement was investigated by performing x-ray absorption at the carbon k-edge which showed evidence for strong interaction between the NiFe LDH and the carbon nanotubes. Finally, Bates et al. discussed charge transfer resistance in the case of Raney-Ni support by electrochemical impedance spectroscopy analysis and found conductivity comparable with standard Ir black catalyst.\[80\]

### 4.2.2. pH of the Electrolyte

Another parameter affecting the OER activity is pH. It has been shown that the OER activity and the redox features shift as a function of pH with super-nernstian behavior on the NHE scale.\[10,66\] Therefore is important to specify at what pH is the activity reported, even when the RHE scale is used. Both pH 13 and pH 14 are commonly used alkaline pH conditions so we will report the activity for these two pH values.

### 4.2.3. Substrate

In addition, the substrate has been found to have an effect on the activity. This interaction has been studied by many authors by using different substrates for growing NiFe oxyhydroxide thin films or different supports for NiFe LDH nanoparticles. In the case of thin films, in particular the effect of noble metal substrates respect to glassy carbon (GC) was investigated, following previous works on Ni(OH)\(_2\).\[89,90,98\] Trotochaud et al. compared the dependence of the TOF on the thickness of a thin film of NiFe oxyhydroxide and found that is stronger on Au substrate than on GC.\[45\] Furthermore, the TOF values for the catalyst on Au were higher than the one on GC, especially for low thickness. Not a big difference in TOF was observed when a Pt substrate was used instead of Au.\[94\] In the case of Au, the possibility of formation of mixed Au-Ni(Fe) (oxy)hydroxides has been considered.\[31,45,80\] Interestingly the Au substrate has been found to affect not only the TOF but also the transition of NiFe hydroxide to NiFe oxyhydroxide (see later sections 5.3 and 5.5).\[31,99\] The interaction of NiFe LDH nanoplates and nanocarbon based materials has been explored in order to improve the electrical conductivity and the weak interaction of the catalyst with the conductive support. The reported materials vary from hybrid catalysts consisting of NiFe-based nanoplates combined with or supported on graphene with various degree of oxidation,\[100–105\] carbon nanoparticles (i.e., Vulcan XC-72R or Ketjen Black),\[15,80\] carbon quantum dots\[106\] and carbon nanotubes (Figure 6).\[66,107–109\] In particular, Gong et al. showed that direct nucleation and growth of NiFe LDH nanotubes on carbon nanotubes resulted in catalyst with higher activity than NiFe LDH mixed with carbon black or with the carbon nanotubes.\[96\] This improvement was investigated by performing x-ray absorption at the carbon k-edge which showed evidence for strong interaction between the NiFe LDH and the carbon nanotubes. Finally, Bates et al. discussed charge transfer resistance in the case of Raney-Ni support by electrochemical impedance spectroscopy analysis and found conductivity comparable with standard Ir black catalyst.\[80\]

### 4.2.4. Size and Crystallinity

The influence of crystallinity on the activity has not been extensively studied. Trotochaud et al. showed that the activity does not change in a detectable amount between a poorly crystallized NiFe (oxy)hydroxide film and the same film after the long-range order has been improved by aging.\[45\] On the other hand, Xu et al. compared NiFe nanofibers after hydrothermal aging at different temperatures and found a clear trend where the low crystallinity samples were the most active.\[35\] However, we notice that in this comparison it was not possible to distinguish between crystallinity effects and size effects since both...
improves with aging temperature, as shown by the authors. The important of size effect is also discussed by Song et al.\cite{57} Song et al. compared NiFe LDH nanoplates with the same material after exfoliation and found that the latter performed better both in terms of overpotential and Tafel slope.\cite{57} The authors proposed that the origin of this improvement might be attributed to the increase in the number of active sites at the edge of the nanosheets due to their concomitant fragmentation and smaller size occurring during exfoliation and to enhanced electronic conductivity.

4.2.5 Nature of Intercalated Anions

The influence of the intercalated anion on the OER activity has been investigated by Xu et al.\cite{55} Comparing NiFe LDH intercalated with NO$_3^-$ and CO$_3^{2-}$ the author found a superior activity for the NO$_3^-$ intercalated compounds. The intercalated NO$_3^-$ anion increases the interlayer distance respect to CO$_3^{2-}$ and it is easier to exchange by OH$^-$, that is the main reactant for OER in alkaline. Reduced charge transfer resistance was also found for the NO$_3^-$. Therefore the authors attributed the enhanced activity to these effects. An investigation of the intersheets population of anions in the active state of the catalyst under OER and during potential cycling will be important for further understanding of the anions effect. Recently, Hunter et al. analyzed the effect of interlayer anions in NiFe LDH in detail and in strict carbonate-free conditions obtaining new insights.\cite{110} The authors synthesized NiFe-based materials with a wide variety of intercalated anions (NO$_3^-$, BF$_4^-$, Cl$^-$, ClO$_4^-$, CO$_3^{2-}$, C$_2$O$_4^{2-}$, F$^-$, I$^-$, PO$_4^{3-}$, SO$_4^{2-}$) either by anion exchange of nitrate intercalated NiFe LDH or directly by PLAL. The authors confirmed the high affinity of NiFe LDH for the carbonate anion and found that carbonate substituted all the other anions after immersion in 1.0 m KOH solution in ambient air. Therefore the activity was tested in CO$_2$-free atmosphere (glove box) and carbonate free solution (saturated by barium hydroxide to precipitate carbonate as BaCO$_3$). In these conditions the authors found no correlation of the OER activity with basal spacing (layer-to-layer distance) but with the pK$_a$ of the conjugate acid of the interlayer anions. The authors proposed that his trend suggests a base-assisted deprotonation step with important implication in the OER mechanism.

4.2.6 Incorporation of a Third Metal

Incorporation of a third metal has also been proposed as a strategy to improve the activity of NiFe LDH by affecting the conductivity and the structure of the binary catalyst. For example, ternary NiFeMn LDH\cite{111} and NiFeCo\cite{80} mixed metal oxide film exhibited enhanced OER activity than reference NiFe LDH catalysts, supporting the idea that this approach is effective in tuning the catalyst activity towards higher value. Interestingly, ternary AlFeNi amorphous oxides were found to exhibit very low Tafel slopes (typically lower than 20 mV dec$^{-1}$).\cite{112} This result suggests that Al, despite its oxide being inert for OER, has a beneficial role when incorporated in amorphous NiFe-based catalysts. Other recent screening studies\cite{113} investigating the introduction of foreign metals in NiFe-based catalysts have been reviewed by Gong et al.\cite{26} These studies also reported high OER activity for ternary AlFeNi oxide catalysts.
4.3. Stability of NiFe LDH Catalysts During OER

The long term stability of a catalyst is amongst the paramount requirements for practical water splitting device. Assessing catalyst stability during long term operation conditions (tens of hours, days and years), variable load conditions simulating switch on/off processes and at high current densities > 500 mA cm\(^{-2}\) in the case of industrial electrolyzer conditions demands substantial efforts. Some protocols have been proposed to monitor the catalysts stability in milder conditions and shorter operating time frames. A useful protocol for screening stability among several catalysts consists in running the anodes at a current density of 10 mA cm\(^{-2}\) for 2 hours while recording the potential changes.[36] This method is particularly valid in substituting unstable catalysts, however of course is not meant to substitute long term stability tests. A more rigorous testing protocol for evaluate short term stability has been proposed combining the monitoring of mass losses to the previously mentioned protocol.[114] The methods proposed for checking corrosion are electrochemical quartz crystal microbalance (EQCM) and inductively coupled plasma mass spectroscopy (ICP-MS) applied to the electrolyte. NiFe LDH particles and oxyhydroxides films generally show good stability in short term tests in alkaline conditions. The long term stability has also been addressed and in particular Ni foam is often reported as the best substrate for these conditions.[115] Particularly long term conditions were investigated by Gong et al. with NiFe LDH nanoplates on Ni foam (>5 mg cm\(^{-2}\) loading). The stability test was performed in 1 \(\text{M KOH}\) at the constant current density of 20 mA cm\(^{-2}\) and oxygen evolution was observed for more than 4 days.[66] From the reported graph we can estimate a decrease of \(\approx\) 30 mV from the minimum potential to the final measured potential. Other works also report good stability for operating conditions of 10 hours or longer at current densities > 10 mA cm\(^{-2}\).[57,64,70,83,101,102,115,116]

Bubbles evolve at the electrodes at these high current densities and are often blocking active sites resulting in “bubble overpotentials” and apparent deactivation. Lu et al. reported that this problem is mitigated when macroporous Ni foam substrates are used instead of flat GC electrodes.[83] In the latter case removal of bubbles completely “reactivated” the catalyst. A reactivation of the catalyst was also observed by Luo et al.[117] The authors investigated the stability of NiFe LDH on Ni foam in 1 \(\text{M KOH}\) in a two electrode configuration using two electrodes of the same kind for cathode and anode. A small degradation in the current density was observed after 10 hours of operation at the applied potential of 1.8 V. The current density was however recovered after a resting period of 8 hours, as shown by the authors in the next two tests of 10 hours each.

5. Advanced In Situ Characterization

5.1. Electrical Conductivity

Electrical conductivity is different among metal hydroxides and oxyhydroxides and might influence substantially the reported activity and the comparison amongst different catalysts.[94] In situ electrical conductivity experiments were performed by Trotzchau et al. using interdigitated microelectrodes and cathodically electrodeposited NiFe (oxy)hydroxide.[65] The catalyst is deposited on top of two working electrodes forming a bridge between them. The experiment shows that the “effective” conductivity is low for the reduced Ni and reduced NiFe containing films, independent of the Fe content. In all cases the conductivity increases when the potential passes the Ni\(^{2+}/\text{Ni}^{3+}\) oxidation potential (Figure 7a). This change in conductivity could be associated to a transition from semiconductor to half-metal, that was suggested by Li et al.[118] and it is concomitant with a change in color of the film.[12,76] Finally, it was found that the incorporation of Fe increases the conductivity of the oxidized NiFe-based film respect to Fe free NiOOH, even though this increase is not enough to explain the activity enhancement.

5.2. X-ray Absorption Spectroscopy (XAS)

In situ and in operando X-ray near edge absorption (XANES) and complementary X-ray absorption fine structure (XAFS) are employed to reveal the nature of the active sites, metal oxidation states and local coordination structure of the catalyst during oxygen evolution reaction. Friebl et al. investigated in operando Ni and Fe K-edge XANES and XAFS of electrodeposited Ni-Fe catalysts on Au film over a wide range of Fe\% in 0.1 \(\text{M KOH}\).[96] Complementary XAFS was performed also for 25% Fe containing NiFe film (Ni:Fe = 3:1) obtained by sputter deposition that was later oxidized by electrochemical conditioning in 0.1 \(\text{M KOH}\). XAS shows a clear shift of the pre-edge peak and the main absorption edge in Ni K-edge when the potential is increased from 1.12 V above 1.52 V (Figure 7b). The shift further reaches a saturation value for higher potential (up to a measured potential of 1.92 V). The potential at which this shift occurs corresponds well with the Ni(II)/Ni(III) redox potential.

In the same potential range no significant shift is observed for the pre-edge and edge in the Fe K-edge. Complementary XAFS analysis of both Ni and Fe K-edge of the oxidized/sputter-deposited sample confirm potential induced contraction of Ni-O and Fe-O distances as well as of the nearest metal-metal distances (Table 2). The correlation of bond length contractions in the Ni and Fe K-edge EXAFS and the further appearance of similar multiple scattering features in both EXAFS spectra confirm that Fe is substituting Ni and it is not interstitial. EXAFS of the electrodeposited samples that have different Ni:Fe ratio, show that the Ni-O bond length at rest (1.12 V) and during OER (1.62 V) is not dependent on the Fe content. Conversely, the Fe-O bond length during OER depends on Fe content. This could be due to formation of a secondary FeOOH phase and overlapping of the signal from the Fe species in the two phases. For high ratio of Ni:Fe (low Fe content, <25%), where the FeOOH is negligible, the study shows that Fe-O bond distance in NiFe LDH during OER is smaller than in \(\gamma\)-NiOOH at the same potential and that this is almost identical to Ni-O, confirming the substitution of Fe in the NiOOH lattice.

In conclusion, the XANES and EXAFS observation of the Ni K-edge are associated with increased oxidation state of Ni and structural change from a \(\alpha\)-Ni(OH)\(_2\)-like to a \(\gamma\)-NiOOH-like phase. The average oxidation state of Ni and Fe under OER condition was found to be +3.6 and +3 respectively, so the authors...
exclude the formation of Fe$^{4+}$ species. In a following study Bates et al. also analyzed the in operando XAS of Ni K-edge of Ni-Fe mixed metal oxide (Ni:Fe ratio = 9:1) in 0.1 m KOH. The NiFe catalyst was supported on carbon and obtained by electrochemical conditioning of metal NiFe catalyst formed by chemical reduction of metal nitride precursors.$^{[80]}$ They also observed shift of the Ni K-edge when the potential reached 1.5 V vs RHE, which stabilizes at higher potentials of 1.55 and 1.6 V. Both Ni K-edge and Ni-O and Ni-M bond distances match well with data of Friebel et al.$^{[46]}$ A slightly different XANES spectra was measured by Wang et al. who studied in operando XAS of Ni and Fe K-edge of NiFe hydroxide catalyst Ni:Fe ratio = 9:1) electrodeposited on carbon paper in 1 m NaOH.$^{[119]}$ They observed a larger shift of the Fe K-edge of 2.8 eV when the potential is increased to $\sim$1.72 V vs RHE (reported 650 mV vs SCE) compared to the small shift of 1.3 eV observed by Friebel et al. at similar potentials and considered by the latter authors negligible.$^{[46]}$ The authors attributed the measured shift to oxidation of Fe from the +3 value observed for the as-prepared catalyst to values close to +4 under OER conditions at the reported potentials. The result was compared with previous finding by Balasubramanian et al., which reported a shift of 2.3 eV and also suggest predominance of Fe(IV) in the oxidized NiFe oxhydroxide state.$^{[120]}$ However, the potential range for OER condition was not examined. In contrast to different degree of oxidation of Fe species found in the literature, the analysis of the Ni K-edge confirmed the previously observed shift of the edge with increasing potential. In particular the authors observed that the oxidation state of +3 is reached at $\sim$1.45 V vs RHE and that by increasing potential the average oxidation gradually changed till reaching $\sim$+3.6 at potential of 1.72 V vs RHE. Ex situ L-edge measurements were carried out in support to the in operando K-edge for both Ni and Fe. In the ex situ Fe L-edge no shifts were observed. This difference

Table 2. Comparison between bond distances of as prepared and under OER condition of NiFe hydroxide catalyst (Ni:Fe = 75:25) sputter deposited on Au film and electrochemically oxidized. Reproduced with permission.$^{[46]}$ Copyright 2015, American Chemical Society.

<table>
<thead>
<tr>
<th>Bond length (Å) @ E</th>
<th>Ni-O</th>
<th>Ni-Ni</th>
<th>Fe-O</th>
<th>Fe-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ E = 1.12 V (as prepared)</td>
<td>2.06 (±0.01)</td>
<td>3.10 (±0.01)</td>
<td>2.01 (±0.01)</td>
<td>3.10 (±0.01)</td>
</tr>
<tr>
<td>@ E = 1.62 V (OER)</td>
<td>1.89 (±0.02)</td>
<td>2.82 (±0.01)</td>
<td>1.90 (±0.02)</td>
<td>2.84 (±0.02)</td>
</tr>
</tbody>
</table>
respect to the in operando K-edge is explained as a reduction of the Fe(IV) back to Fe(III) after removal of the sample from the electrolyte for the ex situ measurements. The authors note how the oxidation state is sensitive to exposure to ambient environment and so in situ measurements are necessary. Despite the absence of energy shift, other features in the XANES spectra of the Fe L-edge are in agreement with the higher oxidation state of Fe during OER. Finally, the ex situ XANES spectra of the Ni L-edge confirmed the potential driven oxidation of Ni observed in the in operando Ni K-edge. In a recent study, Görlin et al. reported contrasting results respecting previous studies detecting high-valent Ni ions under OER conditions. The authors analyzed NiFeO x catalysts with different Fe content with quasi in situ X-ray absorption spectroscopy after being freeze-quenched under applied potential in 0.1 M KOH and OER conditions. In particular, they found that at Fe levels above 4%, the oxidation state of Ni atoms were stabilized in +2 under OER conditions, in contrast with higher oxidation observed with Fe-free NiOOH. The authors suggested in reconciliation with previous studies that the ratio between the rate of metal reduction occurring under OER and the rate of metal oxidation is governing the population of high-valent Ni centers and so affecting their detection.

5.3. Raman Spectroscopy

In situ Raman spectroscopy provides a powerful tool to investigate the structure and the potential dependent transformations of Ni(OH) 2 and NiFe (oxy)hydroxides. Notably, Lu et al. performed in situ Raman spectroscopy of NiFe LDH catalyst grown on Ni foam by urea based solvothermal synthesis. The experiment were conducted in 0.1 M KOH at 1.2 V vs RHE (resting state) and 1.6 V vs RHE (OER condition) and explored the 300–800 cm −1 Raman shift region, where Ni-O and Ni-OH stretching mode are observed in Ni(OH) 2 compounds. At 1.2 V only a broad band at 528 cm −1 was observed which disappeared under OER (1.6 V vs RHE) in concomitance with the appearance of two new bands at 476 and 556 cm −1 (Figure 7c). These bands are typical of β-NiOOH and γ-NiOOH phases and so the authors attributed their formation to the transition to a Ni(Fe)OOH-like phase. The authors compared the intensity ratio of the two bands (I 476/I 556) with the ratio of the bands observed at the same Raman shift values for Ni(OH) 2 under OER. The bands for the oxidized NiFe LDH appeared broader, weaker and having lower I 476/I 556 ratio respect to NiOOH. This was considered an indication of a more disorder local structure around Ni-O. This structural change induced by Fe is in agreement with the previous observation by Louie et al. that the intensity of the band at 555 cm −1 is growing with increasing Fe content in oxidized NiFe oxyhydroxide films that were prepared by electrodeposition on Au substrate. Similar effect was also reported by Klaus et al. for a Ni(OH) 2 film aged in unpurified 0.1 x KOH that was obtained by electrodeposition on a roughened Au electrode. The aging process leads to Fe incorporation, and under OER the samples shows two features at 476 and 555 cm −1 , that were broader and with a lower I 480/I 550 ratio than the same peaks observed in Ni(OH) 2 that was aged in purified electrolyte (where Fe incorporation is negligible). The authors also noticed a Au induced substrate interaction affecting the transformation of Ni(Fe)(OH) 2 to Ni(Fe)OOH. This transition begins 0.1–0.2 V below the electrochemical Ni(II)/Ni(III) oxidation observed in the linear potential scan and the potential at which this transformation start is consistent with the onset potential of Au oxidation.

5.4. Mössbauer Spectroscopy

Mössbauer spectroscopy has been used to elucidate the electronic structure, d-electron configuration of the metals in NiFe (oxy)hydroxides and discuss possible distortions of their ligand sphere. Recently, Chen et al. performed in operando Mössbauer spectroscopy on NiFe LDH catalyst (Ni:Fe = 3:1) prepared by homogeneous precipitation using urea on carbon paper in 0.1 M KOH. Their study develops on previous works that were done in ex situ conditions or not at potential high enough for substantial OER activity. The previous studies proposed the presence of Fe(IV) at potential higher than the Ni(II)/Ni(III,IV) redox transition. Consistently, Chen et al. observed a doublet in the Mössbauer spectra with isomer shift δ ≈0.34 mm s −1 and quadrupole splitting Δ ≈ 0.46 mm s −1 at open-circuit conditions, confirming the presence of high spin Fe 3+ species when the potential is not applied (Figure 7d). Upon increasing the potential to OER conditions 1.62 and 1.76 V, the authors observed the appearance of a shoulder in the Mössbauer spectra interpreted as oxidation of Fe 3+ to Fe 4+. However, the disappeared when the potential was kept at open-circuit potential for enough time, indicating that the oxidation of Fe(III) to Fe(IV) was somewhat reversible. These species were not detected in Ni-free FeOOH under OER conditions. Therefore the authors conclude that the formation of the Fe(IV) is due to stabilization of the NiOOH host lattice. The authors also speculated that these detected Fe(IV) species are located at an internal position in the layer and fully surrounded by Ni, since Fe(IV) species at the edges, corners or defects are not expected to be detected in the measurement conditions. On the other hand, these latter undetected Fe(IV) species, if present, are proposed by the authors as possible active sites.

5.5. Ambient-Pressure XPS

Surface characterization in liquid electrolyte solution and under operating conditions is of foremost importance for electrocatalysts and extremely challenging. Recently, Ali-Löytty et al. performed ambient pressure x-ray photoelectron spectroscopy (APXPS) on a 7 nm thick film of NiFe oxyhydroxide that was electrodeposited on Au electrode. The authors used tender X-rays (at photon energy of 4020 eV) and the “dip and pull” method, that allowed to measure in operando conditions with a ≈18–30 nm thin film of 0.1 x KOH electrolyte on the electrode and water pressure of 18 Torr in the chamber. The sample was measured as prepared (at 9 Torr water exposure, without electrode immersion in the electrolyte) and at fixed
potential (with the thin film electrolyte), after electrochemical conditioning by potential cycling. The authors analyzed the Ni 2p3/2 and the Fe 2p3/2 spectra and detected metallic Ni⁰ and Fe⁰ species in the as prepared sample and their irreversible oxidation after conditioning. These species were codeposited during the preparation of the NiFe oxyhydroxide catalyst by cathodic electrodeposition. The authors also observed an increase in the relative intensity of the M-O compared to M-OH peak in the O 1s XP spectra when they increased the potential from 0 to 0.3 V vs Ag/AgCl (≈1.264 V vs RHE), a potential range where surface Au oxide forms but the transition from Ni(OH)₂ to NiOOH should not occur. The authors could not find further evidences of occurrence of Au oxidation and so proposed another explanation for the change in the O 1s spectrum. They suggested that this change is associated to a partial deprotonation of Ni(OH)₂ occurring at lower potential than the oxidation of the Ni(II) to Ni(III). This process forms a negative [Ni(OH)ₓ₋ₓO₂] xe⁻ layer that is stabilized by the electrostatic interaction with the gold surface. Therefore in this mechanism the transition from Ni(OH)₂ to NiOOH mediated by a gold surface is seen as a reaction that does not occur with a concerted proton-electron transfer (CPTE), but the proton transfer precedes the electron transfer.¹²⁴ This explanation is in agreement with the observation by Klaus et al. of a NiOOH feature appearing at a potential ≈0.1–0.2 V lower than the Ni(II) to Ni(III) oxidation in the in situ Raman measurements of an Fe incorporated Ni(OH)₂ film on Au electrode.¹⁵¹ Unfortunately, as Ali-Löytty et al. noticed, it was not possible to support this explanation by assignment of Ni oxidation state from the analysis of the Ni 2p₃/₂ since the sensitivity was not enough to distinguish between Ni(II)(OH)₂ and γ-Ni(III/IV)OOH.

5.6. In Situ Differential Electrochemical Mass Spectroscopy

In situ differential electrochemical mass spectroscopy (DEMS) has been used to estimate OER Faradaic efficiencies of NiFe (oxy)hydroxides and to identify volatile species generated in electrolytes with different pH or containing different ions.¹¹⁵,¹¹¹,¹¹² For example, Görlein et al. investigated changes in Faradaic efficiencies for OER with NiFeOx/C tested in 0.1 m KOH after cycling the catalyst in 0.1 m phosphate buffer (pH 7) or 0.1 m borate buffer (pH 9.2).¹¹⁵ In both cases, the Faradic efficiencies after cycling at lower pH were similar respect to the measurements before the cycling protocol. However, the Faradic efficiency was significantly lower during the cycling at pH 7 due to carbon corrosion, as confirmed by monitoring the CO₂ signal. In a further study, the authors used in situ DEMS-based Faradaic charge analysis to investigate the oxidation change of Ni in NiFe oxyhydroxides with different Fe content by distinguishing between the charge associated with oxygen evolution and with Ni oxidation, respectively.¹¹²

6. Proposed Mechanisms for OER

The mechanism for OER on oxide surfaces is still under debate and investigation. Several reaction mechanisms have been proposed in the literature for the OER on oxides¹⁰⁸,¹²⁵–¹²⁸ in acid and alkaline electrolyte solution and reviewed recently by Hong et al. and Fabbrì et al.¹²⁷ Important differences among the mechanisms include the reaction intermediates, the number of metal sites directly involved in the reaction per generated oxygen molecule (only one or multiple sites) and the nature of the proton-electron steps involved, that can consist in a decoupled or concerted proton-electron transfer (CPET).

Selloni and Li conducted a theoretical study on the OER mechanism for higher index surfaces of γ-NiOOH and β-NiOOH, considering both pure and Fe doped phases.¹¹¹ The higher Miller-index surfaces are expected to be more active, in analogy to what have been predicted for CoOOH.¹¹³ The model for the structures was based on previous theoretical and experimental works for pure NiOOH (see section 2.1) and monoclinic surface cells were used to model the surfaces.¹³⁵,³⁷,⁴³ By using spin-polarized density functional theory the authors found that Fe replacing surface Ni sites results in lower OER overpotential than the one calculated for the respective pure NiOOH phase in both cases. In particular they found that Fe doped β-NiOOH(01-15) has a lower overpotential than the Fe doped γ-NiOOH(101) and the OER mechanism on the two surfaces is slightly different (Figure 8a,b). The mechanisms were investigated by a recursive method based on addition of water and stepwise simultaneous removing of a proton and an electron resulting in four CPET steps. In both mechanisms, an O-O bond forms between an O atom and a surface lattice three-fold coordinated oxygen. On the other hand, the rate determining step was found to be the first deprotonation for Fe doped β-NiOOH(01-15) and the second deprotonation for Fe doped γ-NiOOH(101).

A different mechanism has been proposed by Bell and co-workers based on four CPET, the intermediates O*, OH*, OOH* and one active metal site per oxygen (Figure 8c).⁴⁶ The mechanism was derived from the comparison between XAS, OER activity measurements and density functional theory calculations with Hubbard U framework (DFT-U). The calculations were performed for pure and Fe doped γ-NiOOH and for pure and Ni doped γ-FeOOH. Due to insufficient experimental data for the structure of γ-NiOOH, this phase was simulated by β-NiOOH γ* = 0.5 with Ni oxidation state of +3.5, so a half-deprotonated β-NiOOH. The authors refer to the work by Van der Ven et al. for the choice of the structure.³⁵ The (01-12) surface has been chosen as example for high index surface of the Fe doped γ-NiOOH. These surfaces have μ₃ (“metal on top”) and μ₂ (“metal-metal bridge”) sites and are considered to be more active than the natural (0001) facet (where μ₁ sites are dominant). The theoretical overpotential is obtained from comparison of the calculated Gibbs free energy differences of the reaction intermediates at each step. Pure γ-NiOOH is shown to adsorb all the OER intermediates too weakly, while pure γ-FeOOH too strongly. The lower overpotential was found for Fe sites that are surrounded by Ni next-nearest neighbors in either γ-NiOOH or γ-FeOOH. This site shows near optimal binding energies for the OER intermediates and the formation of OOH* was found to be the rate limiting step (RLS). The oxidation of O* to OOH* has also been predicted to be the rate-determining step for NiFe LDH by DFT calculations reported in a recent work by Duan and co-workers.⁴⁵ Interestingly, the calculations by Bell and co-workers also show that subsurface Fe in γ-NiOOH increases the overpotential...
at a Ni surface site by further weakening the O* intermediate binding energy on Ni site, whose formation in this case is the RLS. Therefore the surrounding Ni next-nearest neighbors increase the activity of Fe sites, that becomes the most active and are consequently considered the active sites, while (subsurface) Fe actually decrease the activity of the Ni sites. Recent TOF calculation on a per-Fe site basis by Klaus et al. supports the prediction that Fe in the NiOOH host is the OER active sites.[31]

Figure 8. OER mechanisms proposed for NiFe (oxy)hydroxides (a–c) and activation steps proposed for Ni(OH)\textsubscript{2} (d,e). (a,b) OER pathway proposed by Selloni and Li for Fe: β-NiOOH(01-15) (a) and Fe doped γ-NiOOH(101) (b). Nickel (blue), iron (gray), oxygen (red) and hydrogen (white) atoms are shown and the O–O bond is marked by a black ellipse. Molecular oxygen is liberated after the last step. Reproduced with permission.[118] Copyright 2014, American Chemical Society. c) OER mechanism proposed by Bell and co-workers for Fe-doped γ-NiOOH(01-12). Nickel (green), iron (yellow), oxygen (red) and hydrogen (white) atoms are shown. Reproduced with permission.\textsuperscript{[46]} Copyright 2015, American Chemical Society. d) Two-electron two-proton PCET activation process leading to highly active oxyl radicals proposed by Nocera and co-workers for Ni(OH)\textsubscript{2} electrodeposited in borate buffer. Reproduced with permission.\textsuperscript{[126]} Copyright 2013, American Chemical Society. e) Chemical deprotonation step proposed by Koper and co-workers for Ni(OH)\textsubscript{2} toward negatively charged and highly active surface species. Reproduced with permission.\textsuperscript{[125]} Copyright 2016, Royal Society of Chemistry.

Calle-Vallejo and co-workers also performed DFT calculations aimed at understanding the effect of transition-metal doping on the activity of Ni-based double hydroxides in alkaline conditions.\textsuperscript{[60]} The authors considered a modified rocksalt NiO structure where the (001) surface was partially protonated (one hydrogen per two oxygen atoms) and doped with the second metal (50% surface Ni substitution) in order to model the surface as NiMOOH. This choice was based on the consideration
that the limited information available for the active surface structure under OER conditions make several choices (i.e., Fe doped γ-NiOOH) arbitrarily equivalent at the present understanding of the structure provided that they take into account a partially deprotonated surface and octahedral metal centers. A similar mechanism to the one considered by Bell and co-workers with OH*, OOH* and O* intermediates was chosen in the calculations of the overpotentials for OER. The calculations shown that the effect of Fe on the Ni sites is to slightly increase its overpotential, while the effect of the NiO host lattice on Fe sites results in near optimal binding energies and consequently in a low overpotential for the OER on this site. Therefore, besides the different structure, the DFT calculations of Calle-Vallejo and co-workers are in agreement with the results of the DFT calculations by Bell and co-workers regarding the identification of Fe surrounded by Ni as the active sites for NiFe oxyhydroxide.[46] The authors also noticed that coverage effects are important in the calculations and that due to the different RLS on Ni sites, where formation of O* (from OH*) is RLS, and on Fe sites, where formation of OOH* (from O*) is RLS, the sites should be covered respectively by OH* and O* under OER conditions.

These studies investigated the nature of the active sites of mixed NiFe (oxy)hydroxides based on considerations about the affinity of a surface site towards adsorbed OER intermediates and their relative stabilities derived from DFT predictions and in comparison with experimental results.

It is worth to compare the mechanisms that we just described for NiFe (oxy)hydroxides with the ones proposed for "pure" phase Ni (oxy)hydroxides (or unintentionally incorporating Fe impurities). The following mechanisms are based on the interpretation of the results from in operando spectroscopy or kinetics investigations, where a parallel investigation by DFT calculations has not been reported yet.

Nocera and co-workers proposed a OER mechanism based on a detailed kinetics study using an anodized Ni(OH)2 film that was electrodeposited on FTO in borate electrolyte.[126] They proposed that the turnover-limiting-step (TLS) has a chemical nature and most likely does not involve deprotonation of the catalyst. This TLS, where O-O bond forms, is anticipated by proton coupled electron transfer steps producing highly active oxyl radicals (Figure 8d). The importance of deprotonation of Ni oxyhydroxide for the OER mechanism highlighted by Nocera and co-workers was later further investigated by Smith and co-workers and Koper and co-workers.[12,125] The former authors analyzed the surface enhanced Raman spectra (SERS) of an electrodeposited Fe containing Ni(OH)2 on Au electrode in 0.1 M KOH in the region ca. 900–1150 cm−1.[12] The authors observed broad peaks after the transition α/γ that resulted to be pH dependent and attributed them to the formation of "active oxygen" that may exist as peroxide or superoxide, species, in agreement with a previous work by Merril et al.[116] These species is proposed to origin from deprotonation of NiOOH into Ni(II)OO−, that is negatively charged. Smith and co-workers suggested that this species can act as precursor for the OER and so as the active site for this reaction. Recently, Koper and co-workers further elaborated this mechanism based on measurements on electrodeposited Ni(OH)2 in rigid Fe-free electrolyte.[125] They also confirmed for their catalyst the formation and pH dependence of similar broad peaks in the SERS in the region ca. 800–1150 cm−1. The OER mechanism proposed by Koper and co-workers involves proton-electron decoupled transfer. One of the four concerted proton–electron transfer steps described in the "classical" OER mechanism[127] is decoupled into two steps: a deprotonation step leading to negatively charged surface species and a following electron transfer step. The deprotonation step has a chemical nature and may occur if the pH of the electrolyte is higher than the pKa of the proton attached to the NiO(OH) (Figure 8e). Two possible deprotonation pathways are considered where, in both associated mechanisms, O2 forms in the last step, via decomposition of adsorbed OOO⁻.

7. Summary and Outlook

NiFe-based (oxy)hydroxides and layered double hydroxides have proven to be among the most active OER electrocatalysts in alkaline electrolyte solutions, competing and in many cases surpassing state of the art oxides. In the as-prepared state, the structure is quite well understood, especially for the more crystalline catalysts. However, there are undeniable evidences of structural transformations induced by anodic electrical potential and likely also by the oxygen evolution reaction. Therefore the relevant structure under OER operating conditions is different than the as-prepared one and must be determined using in operando methods combined with theoretical predictions and modeling. In this review, we have discussed the recent advance in the determination of the atomic and electronic structure of these excellent catalysts in their OER active state and the efforts towards the understanding of the OER mechanism at the molecular level. We believe that these studies set the basis for the rational development of even more active and stable electrocatalysts for this important reaction. Future works should address the fundamental aspects that are still controversial and provide new strategy that will lead to catalysts that evolve oxygen at high rates at lower overpotentials and are stable in the time scale of years. Among the fundamental questions that still remain open, the clear determination of the catalytically active sites allowing more accurate estimation of intrinsic activity is probably one of the most important. This task is strongly connected with the clarification of the role of Fe and Ni atoms in the OER mechanism, which in turn requires an undisputable experimental verification. Other challenges include the elucidation of the dependence of the Fe and Ni oxidation state on the OER at different Fe contents, the inclusion of surface charged species in a priori theoretical models, a detailed analysis of the electrical conductivity and a deeper understanding of the active structure providing refined models for DFT calculations. Finally, the establishment of long term stability tests in combination with a detailed analysis of the deactivation mechanisms is required for the application to industrial electrolyzer systems or photoelectrochemical devices. For the latter application, in particular the understanding of the solid-solid interface between the semiconductor and NiFe LDH electrocatalysts needs to be further investigated, including a deeper study of charge injection/transfer dynamics and interfacial resistance.
Acknowledgements

We acknowledge financial support by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) and the German Federal Ministry of Economy and Energy (Bundesministerium für Wirtschaft und Energie, BMWi) under the grant reference number 03SF0433A “MEOKATS”. Financial support by the German Research Foundation (DFG) through grant reference number STR 596/8-1 is greatly acknowledged. P.S. acknowledges partial support by German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under Grant #03SF0523 - “CO2EKAT”. We thank also Mikaela Görlin for the fruitful discussions in these years on NiFe oxides and hydroxides.

Received: March 22, 2016
Revised: April 28, 2016
Published online: July 4, 2016
