Janus type water-splitting catalysts have attracted highest attention as a tool of choice for solar to fuel conversion. AISI Ni42 steel is upon harsh anodization converted into a bifunctional electrocatalyst. Oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are highly efficiently and steadfast catalyzed at pH 7, 13, 14, 14.6 (OER) and at pH 0, 1, 13, 14, 14.6 (HER), respectively. The current density taken from long-term OER measurements in pH 7 buffer solution upon the electro-activated steel at 491 mV overpotential (\(\eta\)) is around four times higher (4 mA cm\(^{-2}\)) in comparison with recently developed OER electrocatalysts. The very strong voltage–current behavior of the catalyst shown in OER polarization experiments at both pH 7 and at pH 13 are even superior to those known for IrO\(_2\)-RuO\(_2\). No degradation of the catalyst is detected even when conditions close to standard industrial operations are applied to the catalyst. A stable Ni-, Fe-oxide based passivating layer sufficiently protects the bare metal for further oxidation. Quantitative charge to oxygen (OER) and charge to hydrogen (HER) conversion are confirmed. High-resolution XPS spectra show that most likely \(\gamma\)-NiO(OH) and FeO(OH) are the catalytic active OER and NiO is the catalytic active HER species.

**1. Introduction**

The limited availability of primary forms of energy including nonrenewable fossil based energy sources such as oil and gas is increasingly forcing engineers and scientists to develop techniques to extract electric energy from renewable energy sources.\[^{1-6}\] Electrochemically initiated water splitting allows the conversion of electricity into fuel hydrogen plus oxygen, with which a fuel cell can be operated.\[^{7-12}\] Thus, photo synthesis, i.e., the conversion of light energy into “chemical energy,” can be artificially realized via the combination of, e.g., light-driven solar cells plus a water electrolysis cell.\[^{13}\] It is well known that the effectiveness of this attractive solar to fuel conversion route is severely restricted by the high overpotentials caused by commonly used electrode materials on the anode side.\[^{14,15}\] This is particularly true when the electrochemical cleavage of more or less untreated water is performed, when the splitting procedure is carried out at neutral pH value.\[^{14}\] Ideally electrode materials that have proved to be highly attractive toward electrochemically driven splitting of water in alkaline regime should also show superior OER characteristics in neutral regimes ensured by potentials that are stable over long operating times and do not differ much from the reversible H\(_2\)O/O\(_2\) potential (1.228 V vs RHE at 298.15 K). Particularly OER electrocatalysts that function under neutral conditions are promising in as much as they could form part of a concept for seawater splitting using renewable energy sources. In addition to multiple pH suitability of OER sources.\[^{1-6}\]
electrocatalysts, such state-of-the-art electrocatalysts will definitely derive further benefits from their multifunctionality, i.e., should be an ideal tool to catalyze both OER plus HER.

To date the development of cheap, earth abundant electrocatalysts exhibiting appropriate characteristics regarding catalytic activity and stability while initiating HER plus OER over a broad pH range is still considered to be very challenging.

Noble metals such as Pt, Ir, Ru, Au or noble metal containing compounds such as IrO$_2$-RuO$_2$, IrNiO$_x$, Ru$_2$O$_5$NiO are famous for their comparatively low overpotential when used as an OER electrocatalyst in both alkaline and neutral regimes.[16–20] The often claimed high costs of iridium and ruthenium can, at present, not be considered as a serious obstacle taken into consideration the fact that commercially available IrO$_2$-RuO$_2$ based catalysts made of micrometer thick, PVD sputtered IrO$_2$-RuO$_2$ layers deposited on titanium support material are rarely more expensive than 6 $/100$ cm$^2$. However it is hard to deny that for widespread use in catalysis the noble metals, iridium as well as ruthenium need to be replaced because of their scarcity in Earth’s crust. The electrocatalytic OER properties of Copper oxide based films were recently improved significantly by Sun and co-workers.[21] For decades Nickel metal as well as Ni containing compounds are known for their sophisticated properties in terms of electrocatalysis.[22] The high OER performance of known Ni containing alloys and oxides is to the best of our knowledge at least up to some extent restricted to alkaline media, i.e., at higher pH regions.[23–25] Thus, Chatenet and co-workers reported on very good electrocatalytic OER properties of AISI 316 steel under alkaline conditions.[26] Different metals and steel types are since decades in the focus of interest for electrochemical applications.[27–29] Chlorine oxidized AISI 304 steel (Cr-Ni stainless steel) was found to be a mediocre OER electrocatalyst requiring 500 mV overpotential to ensure 0.65 mA cm$^{-2}$ current density in pH 7 corrected 0.1 M K$_2$HPO$_4$/KH$_2$PO$_4$ solution.[23] Generally, the determined overpotentials for OER on recently developed materials in pH 7 media are relatively close to 500 mA$\cdot$V$^{-1}$ at 1 mA cm$^{-2}$ current density.[30] An overpotential of 610 mV for the onset of OER at pH 6.9 was reported for ZrS$_x$ nanosheets.[31] Wu et al.[30] reported a 480 mV overpotential at stable current density of 1 mA cm$^{-2}$ for iron based thin films. Ramirez et al. evaluated MnO$_x$, Mn$_2$O$_5$, and Mn$_2$O$_4$ electrodeposited films for OER in alkaline and neutral media and under optimal synthesis condition the films exhibited sufficient water splitting at pH 7 (470 mV overpotential at 1 mA cm$^{-2}$ current density).[32] Very recently, we reported on surface oxidized mild steel S 235 as a prospective electrode material for the anodic splitting of water under neutral conditions and determined for the OER in 0.1 M phosphate (pH 7) buffer solution $\eta$ = 462 mV at 1 mA cm$^{-2}$ current density.[33] We suggested manganese- and iron-oxide species as the potential catalytic active species on the periphery of the chlorinated steel.[33] Electrodeposited FeO(OH)[34,35] besides cobalt-phospho compound,[36,37] are among the known nonnoble compounds for which slightly better OER activity (down to 410 mV overpotential at 1 mA cm$^{-2}$) and acceptable stability during water splitting at neutral pH have been demonstrated.[35] However, even these state-of-the-art electrocatalysts exhibit at pH 7 an OER performance far below that of the PSII tetrameric Mn clusters which is able to sufficient split water under neutral conditions at overpotentials around 160 mV.[38–41] Thus, under alkaline conditions, nonnoble metal-based OER electrocatalysts efficiently split water at overpotentials in the range of 200 mV[42–46] and show in addition high catalytic stability. In contrast, the evolution of nonnoble metal-based OER electrocatalysts exhibiting similar steady-state performance in neutral medium is not nearly as far. In addition, multiple pH characteristics of earth abundant materials, i.e., the suitability to catalyze OER over a wide pH range on benchmark level which would pave the way for the widespread use, have to be the best of our knowledge not been shown so far. Electrocatalytically initiated hydrogen evolution is considered to be less demanding than the oxygen evolution reaction. High catalytic activity for HER with overpotentials far below 200 mA at 10 mA cm$^{-2}$ current density under alkaline or acidic conditions was proven for a large number of materials.[47–53] However, very rarely groups succeeded in designing an electrocatalyst that shows both, substantial OER + HER activity.[51,54] Electrocatalysts that are suitable to support OER as well as HER in the same media can be utilized for the bipolar electrolyzers of water electrolysis.[55] Conductive plates which are placed in an electrolyte between two “outer” electrodes connected to the positive and the negative pole of a power source will carry opposite charges on their periphery transforming the electrodes to the so-called bipolar electrodes. A bipolar cell configuration substantially simplifies the design of a water-splitting device as both, OER and HER, are catalyzed upon each of these bipolar electrodes and only both “outer” electrodes but not the central electrodes require a direct power feed.

We herewith show that a surface modification of AISI Ni42 steel converts it to a highly efficient OER electrocatalyst working under neutral and alkaline conditions (pH 7, 13, 14, and 14.6). In addition, HER was initiated at pH 0, 1, 13, 14, and 14.6 upon those steel samples at sufficient low overpotentials leading to a remarkably stable HER current.

2. Results and Discussion

2.1. OER Properties in Neutral Medium

Figure 1 represents a comparison of the electrochemical OER properties of AISI Ni42 which had been anodized prior to electrocatalysis in 7.2 $\times$ NaOH at 2000 mA cm$^{-2}$ for 300 min, henceforth referred to as sample Ni42-300, with untreated AISI Ni42, designated as sample Ni42 in pH 7 phosphate buffer solution. The significant enhancement of the current to voltage ratio determined in polarization experiments in neutral medium of Ni42 alloy upon electro-activation can be taken from both, the non-steady-state (cyclic voltammetry; Figure 1a–c) and the steady-state (chronopotentiometry) measurements (Figure 1d). The current density of the OER initiated in pH 7 medium upon sample Ni42-300 within the voltage range 1–1.9 V versus RHE reaches its maximum of ~12 mA cm$^{-2}$ at a potential of 1.9 V versus RHE (Figure 1a) whereas untreated Ni-42 ensured at 1.9 V versus RHE less than 2 mA cm$^{-2}$ (Figure 1b). The cyclic voltammogram of Ni42 (Figure 1b) showed no signs of Ni existing on the surface of the alloy. Remarkably, neither was the characteristic Ni(II)-Ni(III) oxidation wave obtained nor any
peak in the cathodic part of the CV could be assigned to typical Ni(III)-Ni(II) transition. In contrast, a significant cathodic peak at a potential of \( \approx 1.30 \) V versus RHE exists in the CV of sample Ni42-300 (Figure 1a) that can be clearly assigned to the Ni(III)-Ni(II) reduction. From OER on pure Ni electrodes is known that there exists a direct proportionality between the amount of active material based on the Ni(II)/Ni(III) redox system and the charge capacity, \( Q \), calculated by integrating the cathodic voltammetric sweep between the uppermost limit and \( \approx 1 \) V versus RHE. \[56,57\] Such an analysis performed on the CV given in Figure 1a between \( \approx 1.55 \) V and 1.04 V versus RHE delivers \( Q = 11.55 \) mC cm\(^{-2}\) (Ni42-300); 668 mV (Ni42).

This impressively implies a high amount of electrocatalytic active material. On the contrary, the CV of untreated ASIS Ni42 showed no cathodic voltammetric sweep suggesting a capacity of 0 (Figure 1b). We recently reported on electro-activated AISI304 steel as a potential OER electrocatalyst in alkaline regimes, i.e., in 0.1 M KOH, and found under optimized surface modification conditions for the integrated \( Q \) of the corresponding CV curve a value of 27.57 mC cm\(^{-2}\) at 20 mV s\(^{-1}\) sweep rate.\[45\] However Ni based compounds have rarely been considered as an anode for water splitting in neutral medium, and to the best of our knowledge the charge capacity \( Q \) as a scale for the amount of catalytic active mass referring to the Ni(II)-Ni(III) redox system has not been determined in pH 7 medium.

Chronopotentiometry data demonstrate the very high stability of sample Ni42-300 during electrocatalysis under working conditions (0.1 M KH\(_2\)PO\(_4\)/K\(_2\)HPO\(_4\) pH 7 solution; 4 mA cm\(^{-2}\) current density) see Figure 1d, gray curve and in addition underpin the high OER performance of sample Ni42-300 derived from non-steady-state measurements (Figure 1a). The potential required to ensure 4 mA cm\(^{-2}\) OER current density in pH 7 phosphate buffer did not vary substantially in the course of 40 000 s and amounted to 1.719 V versus RHE. This corresponds to 491 mV of overpotential for the OER (Figure 1d, black curve) in 0.1 M KH\(_2\)PO\(_4\)/K\(_2\)HPO\(_4\). A similar outcome was achieved from a 450 ks chronopotentiometry plot (\( \eta = 502 \) mV at 4 mA cm\(^{-2}\); Figure S1 black curve, Supporting Information). These data represent an outstanding OER activity under neutral condition and represent a significant enhancement when compared with the OER characteristics of sample Ni42 (Figure 1d, gray curve). On untreated Ni42 steel the required overpotential for OER to guarantee 4 mA cm\(^{-2}\) current density in 0.1 M KH\(_2\)PO\(_4\)/K\(_2\)HPO\(_4\) was positively shifted by \( \approx 180 \) mV when compared to sample Ni42-300 (\( \eta = 668 \) mV; Figure 1d, gray curve plus black curve). This impressively confirms the
increase of OER performance of Ni42 steel at pH 7 upon this type of surface oxidation. To date the highest electrocatalytic activity for OER on steel surfaces under neutral conditions was reported for surface activated mild steel S235 exhibiting \( \eta = 462 \text{ mV at 1 mA cm}^{-2} \) in pH 7 buffered solution.\[^{[33]}\] In general, most of the established OER electrocatalysts show at similar overpotentials of around 500 mV an OER current density that is \( \approx 4 \) times lower (1 mA cm\(^{-2}\)).\[^{[31,30,34–37]}\] In polarization measurements, Co\(_3\)O\(_4\) nanowire arrays\[^{[38]}\] developed by He et al. showed an unusual strong voltage–current behavior at pH 7.2. However, no steady-state measurements performed at pH 7.2 were shown and Faraday efficiency was not determined, which makes it at least difficult to conclusively assess the overpotential for the OER at a predetermined current density. Very recently the OER performance of graphene-Co\(_3\)O\(_4\) nanocomposites have been investigated under neutral conditions and also exhibited similarly low overpotentials for the OER derived from cyclic voltammograms (498 mV at 10 mA cm\(^{-2}\)).\[^{[59]}\] Unfortunately no long-term voltage–current behavior was shown and the release of oxygen was not quantified.\[^{[59]}\]

The release of gas bubbles visible to the eye on the surface of sample Ni42-300 was observed throughout the chronopotentiometry measurements. Our electro-activation procedure creates on the AISI Ni42 steel a passivating oxide layer which sufficiently protects the metal matrix below the layer against further oxidation. Cross sectional analysis (vertical plane imaging) of samples was performed by dual beam FIB–SEM (focused ion beam) technique in order to estimate the thickness of the oxide layer (Figure S2, Supporting Information). The thickness was around 4.7 \( \mu \text{m} \). To confirm the assumption that the current determined upon electrochemical measurements is due to oxygen evolution we determined the Faradaic Efficiency by direct fluorescence-based sensing of the evolved oxygen (Figure 2a) during chronopotentiometry at constant current density of 2 mA cm\(^{-2}\) in 0.1 pH 7 phosphate solution (Figure 2b). The course curve of the dissolved oxygen (Figure 2a) as a function of time (dotted curve) shows a good agreement with the theoretically possible increase of dissolved oxygen on the basis of a 100% charge to oxygen conversion (100% Faradaic efficiency; Figure 2a, gray line). The Faradaic efficiency of the OER upon sample Ni42-300 (in 0.1 M KH\(_2\)PO\(_4\)/K\(_3\)PO\(_4\) at 2 mA cm\(^{-2}\) and at 470 mV overpotential for the OER) was found to be 99.4% after 4000 s running time (Figure 2a), proving the overall brilliant electrocatalytic oxygen evolution properties (see Experimental section for details). The Faradaic Efficiency regarding OER of mild steel S235 at the same current density was significantly lower and amounted to only 67% after 3000 s of chronopotentiometry in 0.1 M KOH.\[^{[33]}\] The Faradaic efficiency of a variety of OER electrocatalysts under neutral conditions has been investigated by several groups and in most cases exhibited significantly lower values than in the current study. Manganese oxides based OER electrocatalysts as a model system for the oxygen evolving complex of photosystem II were frequently studied and based on head space measurements the Faradaic efficiency amounted to 78% after 90 min of OER in pH controlled Na\(_2\)SO\(_4\).\[^{[60]}\] The charge to oxygen conversion rates of recently developed full-water-splitting electrocatalysts determined in alkaline solution ranged between 95.8 and 100%.\[^{[109,110,112]}\] A comparison of the OER properties of Ni42-300 at pH 7 with the corresponding characteristics of noble metal containing catalysts is a sine qua for an in-depth evaluation of the electrocatalytic characteristics of our material. We chose commercially available IrO\(_2\)-RuO\(_2\) sputtered on titanium as reference sample (sample IrO\(_2\)-RuO\(_2\)) for OER activity and stability at pH 7 and pH 13. A direct comparison of the OER performance of sample Ni42-300 and IrO\(_2\)-RuO\(_2\) can be derived from Figure 3 and reveals the non-steady-state (3a) as well as the steady-state (3b) voltage–current behaviors regarding OER based polarization experiments. In the cyclic voltammograms shown in Figure 3a, it can be seen that astonishingly only at very low overpotentials (<200 mV) does IrO\(_2\)-RuO\(_2\) (Figure 3a, gray curve) show slightly higher current densities in comparison with the electro-oxidized Ni42 (Figure 3a, black curve). Over the entire range of overpotentials, typically important regarding OER in neutral regime (200 mV > \( \eta \) < 700 mV) sample Ni42-300 exhibited superior electrocatalytic OER activity when compared to IrO\(_2\)-RuO\(_2\) (Figure 3a). Especially at elevated potentials (\( E \geq 1.7 \) V vs RHE) sample IrO\(_2\)-RuO\(_2\) loses performance significantly (Figure 3a, gray curve). In comparison with the outcome of our earlier studies\[^{[23,33,45]}\] with respect to the overall electrocatalytic OER specifications of surface treated steel under neutral conditions, our current results present a significant improvement. Whereas surface activated AISI 304 steel showed at pH 13 superior electrocatalytic OER properties when compared to IrO\(_2\)-RuO\(_2\),\[^{[45]}\] our group failed until recently to significantly improve the OER properties of
steal upon surface oxidation to a level that makes it at least nearly competitive to IrO$_2$-RuO$_2$ regarding water-splitting properties under neutral conditions.\cite{23,33}

Tafel plots (Figure 3b) reflect the findings based on non-steady-state electrochemical measurements made. Whereas in the lower overpotential region (<500 mV) IrO$_2$-RuO$_2$ (Figure 3b, gray triangles) exhibited substantial higher upon OER initiated current density at a defined potential when compared to sample Ni42-300 (Figure 3b, black squares), this changes at an overpotential of ≈550 mV. Sample Ni42-300 reached (at pH 7) a current density of 10 mA cm$^{-2}$ at 1.85 V versus RHE (Figure 3b, black squares) whereas a 50 mV higher potential was required for IrO$_2$-RuO$_2$ to show the same current density (Figure 3b, gray triangles). Therefore, Tafel lines that can be assigned to both samples move (toward higher potentials) apart from each other in the higher overpotential region (<500 mV) and move (toward higher potentials) in this region. Therefore, Tafel lines that can be assigned to both samples move (toward higher potentials) apart from each other in the higher overpotential region (<500 mV) and move (toward higher potentials) apart from each other in the higher overpotential region (>500 mV), respectively (Figure 3b). Interestingly, the Tafel line belonging to sample Ni42-300 was substantially steeper in the lower overpotential (slope 198.16 mV dec$^{-1}$) region than the one assigned to IrO$_2$-RuO$_2$ (slope 345.1 mV dec$^{-1}$). A substantial horizontal shift (=160 mV) of the Tafel line of sample Ni42-300 (black squares) compared to the corresponding Tafel line of untreated steel Ni42 (gray circles) toward lower potentials (Figure 3b) proves the meaningful enhancement of the OER relevant electrocatalytic properties under neutral conditions upon the applied surface oxidation. This horizontal shift between Tafel lines assigned to the Ni42 sample and the Ni42-300 sample can be explained by a change in the chemical nature of the surface during surface oxidation. An increase in the active area caused by the surface oxidation, which could be one possible reason for higher currents at specific potentials, would lead to a vertical shift of the CV curves toward higher current densities. However we checked the surface area of sample Ni42 and sample Ni42-300 by performing multiple point nitrogen gas adsorption BET measurements (Figure S3a,b, Supporting Information) as well as AFM investigations (Figure S4, Supporting Information). As expected there are no substantial differences regarding surface area (Ni42: 0.354 m$^2$ g$^{-1}$; Ni42-300: 0.37 m$^2$ g$^{-1}$), or the adsorption/desorption plots of both samples (Figure S3a,b, Supporting Information), and sample Ni42-300 (roughness 29.538 nm) proved to be even smoother than sample Ni42 (71.521 nm) (Figure S3, Supporting Information).

Single Tafel slopes could be obtained throughout the potential region (IrO$_2$-RuO$_2$: 345.10 mV dec$^{-1}$; Ni42: 150.88 mV dec$^{-1}$; Ni42-300: 198.16 mV dec$^{-1}$). Tafel slopes of OER electrocatalysts determined in pH 7 solutions have rarely been published, but very recently graphene-Co$_3$O$_4$ nanocomposites and ZrS$_3$ nanosheets were reported as prospective OER electrocatalysts for water splitting under neutral and alkaline conditions. For these materials, Tafel slopes of 98 and 102 mV dec$^{-1}$ in 0.1 M phosphate buffer solution,\cite{31,89} respectively, were determined. We investigated oxidized standard carbon manganese steel S235 as a potential OER electrocatalyst in pH 7 regime and found at lower potentials a Tafel slope of 172.4 mV dec$^{-1}$, which is comparable to the slopes reported here and those slopes reported in the literature.\cite{30,31,13}

2.1.1 Origin of the Layer Formation—The Catalytic Active Species

We recently showed that the Ni enrichment in the outer sphere of AISI 304 steel during the electro-activation (300 min, 1.77 A cm$^{-2}$, 7.2 M NaOH) very likely occurs due to a dissolution mechanism rather than upon an electro migration process.\cite{45} However electromigration, as a potential driving force for the layer formation, could not be excluded with absolute certainty, and may at least reinforce the observed changes of the composition of the surface of AISI 304 steel during anodization.\cite{45} This role of electromigration applies substantially more for the data we present in the current study. Whereas AISI 304 steel revealed a considerable mass loss (=7.1 mg) via electro-activation,\cite{45} the average mass loss detected after electro-oxidation of Ni42 steel amounted to 0.092 mg (Table S1, Supporting Information), which is over 70 times less than in
the case of activated AISI 304 steel.\textsuperscript{[45]} Due to the relatively high amount of electrolyte (200 mL), the concentration of Fe, Ni, and Mn was below the detection limit of our ICP OES device, and in addition did not leave sufficient material for an analysis via Atomic Absorption Spectroscopy as performed in our recent study.\textsuperscript{[45]} Neither Ni nor Fe ions could be detected upon an analysis “by hand” (Supporting information) of the electrolyte used for electro-activation. XPS experiments (results shown in the main text; Figure 4) were carried out with our samples after polarization experiments: cyclic voltammetry plus chronopotentiometry measurements carried out for \(t < 4000\) s. Additional results from XPS studies are shown in the Supporting Information (Figure S4): The spectra shown were recorded after 40 000 s of OER upon sample Ni42-300 at 4 mA cm\(^{-2}\) in pH 7 solution (200OER) and after 40 000 s of HER at 10 mA cm\(^{-2}\) in pH 13 solution (200HER), respectively. A further extension of the polarization tests up to duration of 450 000 s did not influence the XPS findings summarized in Figure S4 in the Supporting Information. The composition of the electrode periphery derived from the cationic distribution on the surface of sample Ni42-300 (80.8% Ni, 18.55% Fe, 0.57% C) confirmed our expectation that an Ni containing compound is the predominant cationic species of the surface oxidized Ni42 alloy (Table S2, Supporting Information). In direct comparison with untreated alloy (sample Ni42), the Ni content was substantially increased from 26.6 to 80.8 at% whereas the iron content was found to be substantially decreased (Table S2, Supporting Information). Due to the lack of mass loss (Table S1, Supporting Information) during electro-activation, and the absence of hints that would support the hypothesis that dissolution at least of some ingredients of the steel takes place (no coloration of the electrolyte, no Ni, Fe ions in the electrolyte, no layer deposited on the counter electrode) we conclude that electromigration of Ni to the surface is the most likely origin for the Ni enrichment and Fe depletion in the outer sphere of the activated steel obtained during anodization. Electromigration, which means a mass transport caused by a momentum transfer \(e^{-} \rightarrow M^{+}\) at high current densities,\textsuperscript{[63]} is supposed to be responsible for the growth of thin layers and was obtained by Medway et al. for a film growth on Ni metal during electrochemical cycling.\textsuperscript{[62]}

In one of our previous reports dedicated to electrocatalytically supported oxygen formation upon oxidized steel surfaces, we determined, on the basis of XPS studies, \(\gamma\)-NiO(OH) as the potentially catalytic active species, or at least the dominating source for catalytic active species on the periphery of the treated steel for OER in alkaline medium (0.1 M KOH).\textsuperscript{[45]} Bediako et al. investigated OER at pH 9.2 upon Ni containing films that have been generated via electrodeposition starting from Ni\textsuperscript{II} containing borate solutions.\textsuperscript{[63]} Detailed, XANES and EXAFS based structure-activity correlations indicated that it is very likely that \(\gamma\)-NiO(OH) is the catalytic active OER species in this Ni containing film under more neutral conditions (pH 9.2). These data challenged the long-held notion that the beta phase of NiO(OH) is a more efficient catalyst. Therefore, based on our findings for OER at pH 13\textsuperscript{[45]} and the findings of other groups for OER at pH 9.2, we expected to also detect \(\gamma\)-NiO(OH) as the catalytic active OER species on the surface of sample Ni42-300 during water splitting in 0.1 M phosphate buffer solution (pH 7).

Figure 4a,b displays high-resolution Ni 2p and Fe 2p spectra of Ar etched, as well as untreated Ni42 and Ni42-300 samples. The 2p\(3/2\), as well as some reference compounds\textsuperscript{[64–66,69,70]} are indicated by gray, respectively black vertical bars. The Ni 2p spectrum of the untreated sample Ni42 (Figure 4a) contains both metallic and oxidized Ni. The Ar etched Ni42 showed predominantly unoxidized Ni, whereas the Ar etched Ni42-300 exhibited metallic (Ni) fractions plus oxidized species that we determined as \(\gamma\)-NiO(OH). Ar ion etching obviously reduced +3 oxidized Ni because Ni\textsuperscript{0} is missed in the surface of untreated Ni42-300 similar to data reported by Leinen et al.\textsuperscript{[63]} The significantly enhanced signal-to-noise ratio and higher resolved satellite structure of the spectrum for the nonetched sample Ni42-300 (compared to that of untreated sample Ni42) are due to the higher Ni concentration on the surface of the sample and can clearly be seen in Figure 4a. The presence of metallic Ni and Ni(II), species such as NiO or Ni(OH)\textsubscript{2}, on the surface of

**Figure 4.** High-resolution XPS spectra of samples Ni42 and Ni42-300 untreated as well as Ar etched. a) Ni 2p 3/2 and Ni 2p 1/2 core level spectra. Fitting results for Ni42 (Ar etched): Ni 2p 3/2, position 852.735 eV; Ni 2p 1/2, position 870.035 eV; Ni 2p 1/2, position 854.099 eV; Ni 2p 1/2, position 871.399 eV; Ni 2p 3/2, position 855.988 eV; Ni 2p 1/2, position 873.288 eV. Fitting results for Ni42-300 (Ar etched): Ni 2p 3/2, position 852.949 eV; Ni 2p 1/2, position 870.249 eV; Ni 2p 1/2, position 855.535 eV; Ni 2p 1/2, position 872.835 eV; Ni 2p 1/2, position 862.034 eV; Ni 2p 1/2, position 879.413 eV. b) Fe 2p 3/2 and Fe 2p 1/2 core level spectra. Fitting results for Ni42 (Ar etched): Fe 2p 3/2, position 706.997 eV; Fe 2p 3/2, position 709.67 eV; Fe 2p 1/2, position 720.097 eV; Fe 2p 1/2, position 722.77 eV. Fitting results for Ni42-300 (Ar etched): Fe 2p 3/2, position 710.813 eV; Fe 2p 1/2, position 723.913 eV. Binding energies of reference compounds\textsuperscript{[64–67,69]} are indicated by vertical lines as visual aid.
sample Ni42-300 can be rather excluded. To our experience, very harsh oxidative conditions of the anodization procedure (300 min, 2 A cm\(^{-2}\) current density) completely convert Ni\(^0\) in Ni-based steels into Ni(III) species.\(^{[45]}\) \(\gamma\)-NiO(OH) was found to be the dominating Ni species on the surface of anodized Ni42 steel and this confirms our expectation that Ni species are responsible for the electrocatalytic activity regarding oxygen formation upon the surface in aqueous media. This agrees very well with a recent operando X-ray absorption spectroscopy study in which (Ni, Fe)OOH catalysts were characterized during OER operating conditions.\(^{[46]}\) From the Fe 2p spectra (Figure 4b), we find a small metallic fraction for all samples. The iron of sample Ni42 (untreated) may be oxidized to Fe\(_2\)O\(_3\) (Fe\(^{3+}\)) at the surface and is likely to be caused by long exposure to air during storage. Due to Ar ion etching, Fe\(^{3+}\) on the surface of sample Ni42 was reduced to Fe\(^{2+}\) and Fe\(^0\) as can be determined from the Fe 2p spectrum of Ni42 recorded after the etching procedure (Figure 4b). There is no significant difference between the outcome of the Fe 2p-XPS analysis of sample Ni42-300, nonetched and Ar etched Ni42-300 (Figure 4b). The presence of Fe\(^{3+}\) can be excluded given the binding energies of the Fe\(_{2p_{3/2}}\) core level spectra. With respect to the Fe 2p\(_{3/2}\) binding energies of sample Ni42-300 the FeOOH species of iron dominates on the surfaces compared to the peak positions found for the reference compounds\(^{[86,88]}\), indicated by vertical bars in Figure 4b. The results of the XPS studies carried out after non-steady-state or short time OER chronopotentiometry experiments (Figure 4a,b) are in agreement with the findings obtained after 40 000 s of OER at 4 mA cm\(^{-2}\) in pH 7 medium (see Figure S5a,b, Supporting Information; black curves), i.e., the electrocatalytic active species remained the same.

The roles that Fe species (cationic distribution of Ni42-300:80.8% Ni, 18.55% Fe) may play in enhancing the oxygen evolution from water upon Ni-based electrocatalysts is to date not fully understood. In our recent study dedicated to activated AISI 304 steel, we were able to prove a strong dependence of the electrocatalytic OER properties at pH 13 on the Ni:Fe relation, and found optimal OER performance in case of a cationic distribution of 67% Ni and 33% Fe.\(^{[49]}\) Several groups including Corrigan et al.\(^{[73]}\) and Trotochaud et al.\(^{[85]}\) already discussed the effects of Fe incorporation on Ni/Fe oxyhydroxide thin films. In addition to full experimental approaches, computational based results have also been exploited.\(^{[72]}\) Generally, in case of thick layers a substantial portion of the applied potential during OER polarization experiments will drop across the catalyst film to drive the transport of electrons through it when the layer is not sufficiently conductive. As stated in these reports Fe embedded in NiO(OH) films will reduce the resistivity and thus for thick films (>1 µm) Fe impurities is a prerequisite for low overpotentials determined in electrochemically initiated OER. On the basis of these findings we assume that in our case an “incorporation” of 18.5% Fe into the Ni-oxide based layer (Table S2, Supporting Information) is required to ensure a low conductivity of the relatively thick layer (≈4.7 µm, see Figure S2, Supporting Information) and will lead to the low overpotentials obtained by us. An activity enhancement of the catalytically active Ni ions in our samples upon partial-charge transfer between them and Fe ions resulting in the formation of Ni\(^{3+}\)/\(^{4+}\) with increased oxidizing power as shown by various groups for the binary Ni-Fe-oxides\(^{[33]}\) could also play a role. For instance, a charge transfer was confirmed between ultrathin NiO(OH) layers and gold substrate by Yeon and Bell.\(^{[78]}\) The electron withdrawing effect of highly oxidized Fe (Fe\(^{3+}\)) should be similar to noble metals and is likely to be the origin of an increase in OER activity of NiO(OH) doped with Fe\(^{3+}\) as obtained by Trotochaud et al. who used NiO(OH) films 40–60 nm in thickness.\(^{[85]}\) As can be taken from Figure 4b Fe in oxidation state +3 indeed dominates also on the surface of sample Ni42-300.

In addition, it is long been a discussion about the transition between for instance \(\gamma\)-NiO(OH) and \(\beta\)-NiO(OH) due to unintentional or intentional Fe incorporation and its effect on the electrocatalytic OER efficiency.\(^{[74,75]}\) Redox phase transitions between Fe(II)/Ni(III)/Ni(IV) oxyhydroxides in Fe-Ni OER electrocatalysts at oxidative potentials have been obtained very recently upon exploiting ambient-pressure X-ray photoelectron spectroscopy (APXPS).\(^{[76]}\)

### 2.2. OER Properties in Alkaline Medium

Given the composition of the surface of our oxidized steel Ni42 (Table S2, Supporting Information), and based on our studies on OER under alkaline conditions upon modified Ni-Fe alloys,\(^{[45]}\) we expected strong electrocatalytic OER performance of sample Ni42-300 also under alkaline conditions. We evaluated the OER properties of sample Ni42-300 in 0.1 m KOH and 1 m KOH on the basis of non-steady-state (Figure 5a,b) and steady-state (Figure 5c–e) electrochemical characteristics. The significant improvement of the OER behavior upon surface modifications of Ni42 steel can be seen in the cyclic voltammetry studies (Figure 5a,b) in which sample Ni42-300 (Figure 5b, black curve) exhibited a much higher current density to voltage ratio than sample Ni42 over the entire voltage range (Figure 5a). The current density in 0.1 m KOH at 1.7 V versus RHE amounted to around 31 mA cm\(^{-2}\) (Figure 5b, black curve) for sample Ni42-300 while for untreated Ni42 the current density was about half (16 mA cm\(^{-2}\)) at the same potential. The CV curve of untreated Ni42 recorded at pH 13 (Figure 5a) is similar to the one recorded at pH 7 (Figure 1b), again neither the characteristic Ni(II)-Ni(III) oxidation wave was obtained, nor any peak in the cathodic part of the CV could be assigned to typical Ni(III)-Ni(II) transition. In contrast, the CV curve of sample Ni42-300 showed at a potential of \(\approx 1.4\) V versus RHE, the expected Ni(II)-Ni(III) oxidation wave (Figure 5b, black curve), and in the cathodic part at a potential of 1.3 V versus RHE also showed the corresponding Ni(III)-Ni(II) reduction wave (Figure 5b, black curve). An overpotential of 254 mV was detected from 2000 s of chronopotentiometry using sample Ni42-300 at 10 mA cm\(^{-2}\) current density (Figure 5c, black curve) in 0.1 m KOH. This presents an OER performance similar to the one determined for OER at pH 13 on AISI 304 steel, electrodeoxidized in a comparable way (269.2 mV overpotential at 10 mA cm\(^{-2}\))\(^{[49]}\) and is significant superior to the OER properties of both, chlorinated AISI 304 steel (260 mV at 1.5 mA cm\(^{-2}\))\(^{[29]}\) or chlorinated S323 steel (347 mV overpotential at 2.0 mA cm\(^{-2}\))\(^{[11]}\) at pH 13. At this pH value sample Ni42-300 exhibited stronger voltage current ratios within OER polarization experiments than IrO\(_2\)/RuO\(_2\) \((\eta = 351\) mV at \(j = 10\) mA cm\(^{-2}\)) (Figure 5c,
The OER performance of Ni42-300 at pH 13 is on a similar level to that of nonnoble metal based state-of-the-art catalysts recently developed by other groups including Co₃O₄ nanoparticles,[77,78] Co₂P nanoparticles,[79] NiCo₂O₄–graphene hybrids,[80] Ni₃S₂ nano arrays supported by Ni metal,[81] CuFe(MoO₄)₃,[82] Pr₀.5Ba₀.5CoO₃,[83] NiCo₂O₄ aerogels,[84] Ni₃Fe₂(OH)₄,[85] and Ni₃Fe₂O₅ nanoparticles supported on glassy carbon,[44] all of which are significantly more expensive and complex to produce. The OER performance of our catalyst Ni42-300 did not suffer upon extension of the operating time up to 450 ks (Figure S1, Supporting Information, blue curve); η amounted to 251 mV through 450 ks of OER in pH 13 regime at 10 mA cm⁻². As expected, substantial stronger voltage–current behavior in polarization tests was achieved when OER was performed in higher concentrated KOH instead of 0.1 M KOH (pH 13). This can be seen in the graphical representation Figure 5d that comprises a CV (black curve) and a chronopotentiometric plot derived from pH 14 measurements (gray curve).

**Figure 5.** Steady-state and non-steady-state OER properties of samples Ni42, Ni42-300, and IrO₂–RuO₂ at pH 13 and 14. Electrode area of all samples: 2 cm². Cyclic voltammetric plots are based on 20 mV s⁻¹ scan rate and 2 mV step size. a) Cyclic voltammogram of sample Ni42 recorded in 0.1 M KOH. b) Cyclic voltammograms of samples Ni42 (black curve) and IrO₂–RuO₂ (gray curve) in 0.1 M KOH. c) Chronopotentiometry measurements performed with samples Ni42-300 (black curve) and IrO₂–RuO₂ (gray curve) in 0.1 M KOH at 10 mA cm⁻² current density. Average overpotential for the OER through 2000 s scan: 351 mV (IrO₂–RuO₂), 254 mV (Ni42-300). d) Cyclic voltammogram of sample Ni42-300 recorded in 1 M KOH (black curve) and 2000 s chronopotentiometric plot of sample Ni42-300 determined in 1 M KOH at 10 mA cm⁻² (gray curve); average overpotential for the OER through 2000 s plot: 215 mV. e) Tafel plots of samples Ni42-300 and IrO₂–RuO₂ based on 200 s chronopotentiometry scans in 0.1 M KOH at current densities of 0.66, 1.33, 2, 2.67, 4, 5.33, 6.67, 8, 10, 13.33, 16.67, and 20 mA cm⁻².
KOH at the same potential (Figure 5b, black curve). The corresponding 2000 s chronopotentiometric scan exhibited averaged \( \eta = 215 \text{ mV} \) at 10 mA cm\(^{-2}\) (Figure 5d, gray curve). To check the performance and stability of the catalyst under more realistic industrial conditions OER was performed in 7 M KOH at 70 °C (Figure S6 and S7, Supporting Information). The potential required to ensure 10 mA cm\(^{-2}\) current density was found to be even reduced throughout the 450 000 s of chronopotentiometry (\( \eta = 196 \text{ mV} \); Figure S6, Supporting Information). Under repeated cycling of the potential the degradation of electrocatalysts is usually found to be increased. However a stronger current-voltage behavior can be derived from the CV recorded after 1000 cycles when compared to the one determined at the beginning of the experiment (Figure S7, Supporting Information), thus confirming our expectation that the OER performance of sample Ni42-300 will become even better during usage in OER experiments. After 1000 cycles a current density of 130 mA cm\(^{-2}\) was reached at 1.5 V versus RHE (purple colored dashed curve in Figure S7, Supporting Information) whereas the first scan showed 115 mA cm\(^{-2}\) at 1.5 V versus RHE (black curve in Figure S7, Supporting Information). This increase of the OER activity of an electrocatalyst upon strong usage is initially unexpected. However the group of Chatenet made similar obtainments for 316 steel based electrodes in lithium-air batteries.\(^{[86]}\) The Tafel line created on the basis of chronopotentiometry measurements performed with sample Ni42-300 (Figure 5e, black squares) was significantly negatively shifted compared to the one derived from sample IrO\(_x\)-RuO\(_2\) in 0.1 M KOH (Figure 5e, gray triangles), underpinning the overall superior OER performance of surface-oxidized Ni42 alloy. The difference in overpotential required for a defined current density between both samples increases substantially with increasing current density. The corresponding Tafel lines move apart from each other toward the higher potential regions (Figure 5e). The Tafel line of sample Ni42-300 exhibited a slope of 71.6 mV dec\(^{-1}\) whereas the slope of the Tafel line of IrO\(_2\)-RuO\(_2\) amounted to 101.1 mV dec\(^{-1}\) (Figure 5e). Doyle and Lyons found for OER on passive oxide covered iron electrodes Tafel slopes of 40 mV dec\(^{-1}\)\(^{[88]}\) at lower potentials.

As can be taken from previous reports, Tafel lines of the surfaces of activated steel samples showed in the lower potential region slopes of 49 mV dec\(^{-1}\) (AISI 304)\(^{[45]}\) and 58.5 mV dec\(^{-1}\) (S235)\(^{[31]}\) whereas untreated steel showed significant higher slopes of 66 mV dec\(^{-1}\) (AISI 304)\(^{[45]}\) and 102 mV dec\(^{-1}\) (S235)\(^{[31]}\) with one exception: 30 mV dec\(^{-1}\) (AISI 316 in 1 M KOH).\(^{[87]}\) In addition, the value for the Tafel slope of sample Ni42-300 in 0.1 M KOH (71.6 mV dec\(^{-1}\)) is similar to recently reported Tafel slopes of NiFe alloy,\(^{[88]}\) iron electrodes,\(^{[89]}\) carbon supported NiO nanoparticles,\(^{[44]}\) and for “fresh” Ni metal surfaces.\(^{[89]}\) Recently developed bi-functional electrocatalysts exhibited slopes between 52 and 89 mV dec\(^{-1}\) for the OER at pH 14.\(^{[79,110-112]}\)

IrO\(_2\)-RuO\(_2\) showed at pH 13 Dual Tafel behavior (within the investigated potential region) with lower slopes at lower overpotential regions (101.1 mV dec\(^{-1}\)) and higher slopes at higher overpotential regions (Figure 5 e). It should be mentioned that all non-steady state electrochemical measurements were carried out without any correction of the voltage drop. Regarding the steady state electrochemical measurements we corrected Ohmic voltage drop within the chronopotentiometry measurements manually by subtracting the Ohmic voltage drop from the measured potential on the basis of electrolyte resistances reported in the literature (Table S3).\(^{[114]}\) Thus, it can be excluded that the Dual Tafel behavior mentioned is due to an artifact caused by the electrolyte resistance. The value determined for sample Ni42-300 (71.6 mV dec\(^{-1}\) \( \approx 2.1 \times RT/F \)) agrees well with the value that was found to be characteristic of an O\(_2\) evolution mechanism involving a reversible one-electron transfer \((2.3 \times RT/F)\).\(^{[90]}\) In summary, supported by the electrochemical measurements, our surface-oxidized Ni-42 steel proved to be an OER electrocatalyst, that is, highly active in neutral as well as in alkaline conditions (pH 7, 13, 14, and 14.6).

2.3. OER Properties in Acidic Medium

Ni based alloys are famous for their excellent OER properties in alkaline regimes.\(^{[91]}\) Generally very few metal oxides can survive under oxidative potentials in acidic regimes\(^{[92]}\) and metal oxide based catalysts have very rarely been checked for catalytic activity under both, alkaline and acidic conditions. Again, Rutile type IrO\(_2\) and RuO\(_2\) seem to be the material of choice when good water-splitting properties are desired at low (\(<7\) ) and high (\(>7\) ) pH values.\(^{[92-96]}\) In terms of the overall OER activity and stability under acidic catalysis conditions, IrO\(_2\) is considered as the best compromise.\(^{[96]}\) In order to evaluate the anodic water-splitting properties in acidic regimes, we performed cyclic voltammetry studies on sample Ni42-300 in 0.05 M H\(_2\)SO\(_4\) from which an overpotential of \(\approx 360 \text{ mV} \) at 1 mA cm\(^{-2}\) current density can be revealed (Figure S8, Supporting Information). An overpotential of \(\approx 200 \text{ mV} \) for the OER on mesoporous templated IrO\(_2\) surfaces in 0.5 M H\(_2\)SO\(_4\) was reported by Strasser co-workers.\(^{[98]}\) However we did not detect reasonable steady-state behavior for the OER at pH 1 initiated on the surface of sample Ni42-300. The sample was found to be unstable in pH 1 medium at positive potentials for longer time and exhibited even at very low potentials (\(\approx 0.2 \text{ V} \) versus RHE) significant current densities. This finding agrees well with previous studies where McCrory et al. evaluated Ni-oxide, Co-oxide and mixed oxides consisting of different nonnoble transition metals as well as IrO\(_2\) as prospective OER catalysts in 1 M H\(_2\)SO\(_4\). Every system tested apart from IrOx was unstable under oxidative conditions in acidic solutions.\(^{[92]}\) The pronounced solubility of metal oxides that were formed on the surface of Ni42 metal during the electro-activation process is, in our view, a reasonable potential explanation for the poor stability of sample Ni42-300 under oxidative conditions in diluted sulfuric acid.

2.4. HER Properties in Acidic/Alkaline Medium

OER is considered as the more challenging water-splitting electrode reaction and it is considered worth to be a focus of optimization efforts.\(^{[97-99]}\) In part certainly also motivated by the fact that hydrogen, with a price of 8 € kg\(^{-1}\), is the more valuable water-splitting product, improving HER also has a high research status. The electrochemically initiated hydrogen evolution on metal surface is well established. More than
one hundred years ago, Tafel et al. investigated the electrode kinetics,[100,101] with more detailed reaction mechanisms suggested in follow-up studies, and hydrogen evolution activities quantified by Trasatti[102,103] and Miles,[104] respectively.

It should be noted that for all HER measurements presented in this work, cathodic currents were applied, i.e., even if not explicitly stated, all values of current densities carry a negative sign. Even untreated Ni42 exhibited measurable HER activity (5.7 mA cm\(^{-2}\) at \(-400\) mV versus RHE in 0.05 M H\(_2\)SO\(_4\); Figure 6a, gray curve). Nevertheless, the voltage–current characteristics in the voltage range one typically has to sweep over for HER (\(-450\) to 0 mV vs RHE) were improved substantially upon our chosen surface modification (11 mA cm\(^{-2}\) at 400 mV versus RHE in 0.05 M H\(_2\)SO\(_4\); Figure 6a, black curve). The performance difference between the electrochemical HER properties of surface modified and nonmodified Ni42 examined on the basis of non-steady-state electrochemical measurements was even more pronounced at pH 13 (Figure 6b). Sample Ni42 was found to be relatively inactive toward electrocatalytically initiated HER in alkaline media as seen in the weak current to voltage behavior in the corresponding cyclic voltammogram (Figure 6b, gray curve). While moving from positive toward negative potentials the increment of the current density was found to be moderate. At the limit of our measuring interval of \(-0.4\) V versus RHE the current density amounted to less than 2 mA cm\(^{-2}\) (Figure 6b, gray curve). In stark contrast, the CV curve of sample Ni42-300 was found to be much steeper, showing a significant increase of the current density toward higher overpotentials (Figure 6b, black curve) and almost 15 mA cm\(^{-2}\) current density was reached at \(-0.4\) V versus RHE (Figure 6b, black curve). To ensure sufficient comparability with earlier published results, the electrochemical behavior was also examined in more concentrated electrolytes. Significantly higher current densities were achieved for the HER of sample Ni42-300 when CVs were recorded in tenfold higher concentrated solutions (0.5 M H\(_2\)SO\(_4\), 1 M KOH; Figure 6c). HER initiated in 0.5 M H\(_2\)SO\(_4\) on sample Ni42-300 resulted at \(-0.4\) V versus RHE in 60 mA cm\(^{-2}\) current density and required for 10 mA cm\(^{-2}\) current density at \(\eta = 220\) mV (Figure 6c, gray curve). The sample was found to be less active for HER in 1 M KOH leading to \(\approx 30\) mA cm\(^{-2}\) current density at \(\eta = 400\) mV and 10 mA cm\(^{-2}\) current density at \(\eta = 325\) mV, respectively (Figure 6c, black curve).

Chronopotentiometry and Tafel plots for HER in H\(_2\)SO\(_4\) (0.05 and 0.5 M) and in KOH (0.1 plus 1 M) allowed to evaluate the stability of sample Ni42-300, while electrocatalytically initiated H\(_2\) formation under acidic (pH 1 and 0) and alkaline conditions (pH 13 and 14) and are shown in Figure 7a–c and Figure 9a,b. A reliable assessment of the HER efficiency can only be extracted from the outcome of these steady-state measurements. Sample Ni42-300 proved to be a stable HER electrocatalyst for tens of hours of chronopotentiometry at 1 or 10 mA cm\(^{-2}\) at pH 1 and also at pH 13 (Figure 7c), at pH 0 and 14, respectively (data not shown). Even after more than 100 h operating time the HER performance in the pH 1 regime was similar to that at the start level (Figure S9, Supporting Information). Repeated cycling of the potential of Ni42-300 between \(+25\) and \(-200\) mV versus RHE in pH 1 medium increased the HER performance of Ni42-300 showing the very good stability of the sample toward HER in acidic regime (Figure S10, Supporting Information).
active toward HER in acidic solutions, too, but Ni and Ni-Mo alloys, generally all known remaining earth-abundant solid catalysts, exhibited rather poor catalytic stability upon hydrogen for-
formation under acidic conditions. Based on the data obtained from the non-steady-state measurements (Figure 6a–c), we expected to determine (under steady-state conditions in the lower overpotential region) a somewhat better HER performance, i.e., lower overpotentials for the HER in acidic solution. Indeed, sample Ni42-300 exhibited $\eta = 240.1 \text{ mV at } 1 \text{ mA cm}^{-2}$ at pH 13 (Figure 7a, black curve) whereas at pH 1 the overpoten-
tial was substantially lower ($\eta = 128.6 \text{ mV at } 1 \text{ mA cm}^{-2}$ current density Figure 7b; black curve). At 10 mA cm$^{-2}$ current density, the overpotential for the HER amounted to 283.6 mV (pH 13) and 316.5 mV (pH 1), respectively (Figure 7a, gray curves). The values for the HER overpotential of sample Ni42-300 derived from long-term (50 000 s) chronopotentiometric measurements carried out at 10 mA cm$^{-2}$ in 0.1 M KOH ($\eta = 333 \text{ mV at pH 13}$; Figure 7c, black curve) and 0.05 M H$_2$SO$_4$ ($\eta = 321 \text{ mV at pH 1}$; Figure 7c, gray curve) did not significantly differ from those values derived from 1000 s chro-
notentiometry plots (Figure 7a, gray curves). These elec-
trochemical HER experiments demonstrate the very good stability of sample Ni42-300 under HER catalysis conditions, i.e., under reductive potentials in alkaline and acidic regimes.

We therefore expected a quantitative charge to hydrogen for-
mation, and this was confirmed by determining the Faradaic efficiency for the HER upon Ni42-300 at pH 13 because the efficiency amounted to 101.8% as seen in Figure 8. Typically, the charge to hydrogen conversion rate of up to date bifunctional electrocatalysts amounts to $\approx$100% in alkaline solutions with one exception: Co$_2$P nanowires exhibited an HER faradaic efficiency of $\approx$80% in 1 M KOH.

Log $j$ versus $\eta$ plots derived from catalyzed HER performed at pH 1 and 13 (Figure 9a) and at pH 0 and 14 (Figure 9b) revealed single Tafel behavior within a reasonable voltage range (400–0 mV versus RHE). Tafel slopes dropped in less diluted electrolytes differed not much from the ones recorded in more dilutes electrolytes (Figure 9b, gray hexagons; 0.5 M H$_2$SO$_4$: 117.9 mV dec$^{-1}$; Figure 9b, black squares, 1 M KOH: 117.47 mV dec$^{-1}$). In diluted media, Tafel slopes of sample Ni42-300 amounted to 80.47 mV dec$^{-1}$ (0.05 M H$_2$SO$_4$ and 124.44 mV dec$^{-1}$ (0.1 M KOH), respectively (Figure 9a, gray hexagons and black squares). Tafel slopes for the HER in acidic regime have been determined by various groups. First investi-
gated by Trasatti and co-workers, Tafel slopes exhibited at reasonable $\eta$ values (84 and 141 mV dec$^{-1}$) as such close to the one of Ni42-300 shown for the HER at pH 14 (117.47 mV dec$^{-1}$).

Given the strong current-to-voltage ratio in more concentrated acidic or alkaline solutions extracted from cyclic voltammmograms

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**Figure 7.** Steady-state HER properties of sample Ni42-300 at pH 1 and 13. Electrode area: 2 cm$^2$. Cathodic currents were applied, i.e., even if not explicitly stated, all values of HER current densities carry a negative sign.

- **a)** Chronopotentiometry measurements performed in 0.1 M KOH at 1 mA cm$^{-2}$ (black curve), at 10 mA cm$^{-2}$ (gray curve), respectively. Average overpotential for the HER through 1000 s scan: 240.1 mV (1 mA cm$^{-2}$), 283.6 mV (10 mA cm$^{-2}$), respectively.
- **b)** Chronopotentiometry measurements performed in 0.05 M H$_2$SO$_4$ at 1 mA cm$^{-2}$ (black curve) and at 10 mA cm$^{-2}$ (gray curve) respectively. Average overpotential for the HER through 1000 s scan: 128.6 mV (1 mA cm$^{-2}$), 316.5 mV (10 mA cm$^{-2}$), respectively.
- **c)** Long-term chronopotentiometric measurement of sample Ni42-300 performed at 10 mA cm$^{-2}$ current density in 0.05 M H$_2$SO$_4$ (gray curve), in 0.1 M KOH (black curve), respectively. Average overpotential for the HER through 50 000 s: 321 mV (0.05 M H$_2$SO$_4$), 333 mV (0.1 M KOH), respectively.

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result is by far not self-evident. Ni-Mo alloys, famous for their low overpotentials for HER in alkaline media at industrially relevant current densities, were indeed found to be highly
(Figure 6c), we expected to determine from steady-state data significant lower overpotentials for the HER at pH 0 and pH 14 when compared to the values derived from chronopotentiometry performed for 4000 s at 10 mA cm$^{-2}$ current density. Electrode area of sample Ni42-300 was 2 cm$^2$; Amount of the electrolyte: 1.7 L. a) Correlation of oxygen evolution upon sample Ni42-300 in 0.1 M KOH (dotted curve) with the charge passed through the electrode system; gray line corresponds to 100% Faradaic efficiency with a line equation: $y = 4.9863 \times 10^{-3} x$ with $y =$ amount of hydrogen (cm$^3$); $x =$ time (s). End value of oxygen amount ($t = 4000$ s): 20.3 mL (nominal value (100%): 19.945 mL). Faradaic efficiency of the OER after 4000 s runtime: 101.8%. b) Corresponding chronopotentiometry plot. Current density: 10 mA cm$^{-2}$; average overpotential for the HER through the 4000 s plot: 428 mV.

HER upon sample Ni42-300 in 1 M KOH (pH 14), respectively (Figure 9b, black squares). In addition, the suitability of Ni42-300 as hydrogen evolving electrode in industrial electrolyzers was proven under harsh conditions (7 M KOH, 70 °C) (Figure S11 and S12, Supporting Information) exhibiting very good stability. Upon 450 ks of chronopotentiometry at 10 mA cm$^{-2}$ current density the overpotential decreased from 330 to 230 mV (Figure S11, Supporting Information). A slightly better performance of sample Ni42-300 during heavy usage is also reflected in comparison of the cyclic voltammograms gained after one and after a thousand cycles (Figure S12, Supporting Information). Other groups found that incorporation of nonmetals like sulfur, nitrogen, carbon into Ni based alloys appeared to be an encouraging strategy to increase the efficiency and the stability of materials toward HER in acidic solutions. For instance, Schaa and co-workers reported on the outstanding electrocatalytic activity (100 mV overpotential at 10 mA cm$^{-2}$ current density) and stability of nanostructured Ni$_2$P toward HER in 0.5 M H$_2$SO$_4$. However, a catalyst capable of catalyzing both HER and OER in different or even the same media with appropriate performance is still difficult to find. Martindale and Reisner reported on bi-functional iron only electrodes for full water splitting at pH 13 at a bias of $\approx 2V$. Significant lower cell voltages of 1.65, 1.68, and 1.63 V were required for overall water splitting upon CoSe film, NiCo$_2$S$_4$ nanowires, and NiSe films in 1 M KOH as shown by T. Liu et al., D. Liu et al., and Tang et al., respectively. However, the scarcity of selenium can certainly be considered as an obstacle for practical usage. Very recently, Stern et al. and Antonietti and co-workers published data on Ni$_2$P nanoparticles (NPs) respectively Ni$_5$P$_4$ NPs as Janus catalyst in alkaline regime. Besides the already mentioned HER properties under acidic conditions relatively high OER activity (290 mV overpotential) and high HER activity (200 mV overpotential) combined with sufficient stability under catalysis conditions could be attested to Ni$_2$P NPs and Ni$_5$P$_4$ NPs as Janus catalyst in alkaline regime. However, Schaak and co-workers achieved a contradicting result and reported on quickly degraded Ni$_2$P to Ni when used as an HER electrocatalyst in 1 M KOH. A comparable HER/OER activity and very good stability under catalysis conditions in 1 M KOH was reported for Ni$_5$P$_4$ NPs (HER: $\eta = 150$ mV at 10 mA cm$^{-2}$; OER: $\eta = 117.9$ mV dec$^{-1}$).
η = 330 mV at 10 mA cm$^{-2}$.$^{[34]}$ Table S4 (Supporting Information) gives an idea of the overall electrocatalytic OER and HER properties of recently developed bifunctional electrocatalysts.

Although the OER performance of Ni$_3$P as well as Ni$_5$P$_4$ NPs in 1 M KOH is not on benchmark level the combination of outstanding HER and adequate OER properties makes both compounds to attractive catalysts. However, especially in direct comparison with these very recently published data, our catalyst constitutes in our opinion a highly promising alternative given the unrivaled low production costs, the very reasonableHER catalyst constitutes in our opinion a highly promising alternative given the unrivaled low production costs, the very reasonable.

2.4.1. The Catalytic Active Species while HER upon Ni42-300

Figure S5 (Supporting Information) represents the outcome of our XPS study performed with the sample Ni42-300 after long-term OER (200OER) and HER (200HER) chronopotentiometry. Whereas the curve form of the Fe 2p core level spectrum of 200OER and 200 HER does not significantly differ (Figure S5b, Supporting Information), the corresponding Ni 2p core level spectra show indeed slight differences (Figure S5a, Supporting Information). The Ni 2p core level spectrum of 200HER was found to be shifted toward lower binding energy and Ni(II) species like NiO instead of γ-NiOOH is likely the predominant catalytic active species during HER upon the surface of Ni42-300 (Figure S5a, gray curve, Supporting Information). A further increase of the HER operating time up to 450 000 s did not influence the XPS results.

3. Conclusion

Improving the conversion of water into its cleavage products H$_2$ and O$_2$ photo- or electrocatalytically realized using renewable energy sources is a key challenge to overcome the limited availability of fossil fuels for future applications. This conversion route is especially promising if a catalyst is suitable to catalyze both, OER and HER, and ideally with both electrodes exhibiting half reactions in one single electrolyte. An identical catalyst for OER and HER catalytically initiated in the same medium, which is classically termed full-water-splitting catalyst, would pave the way for the implementation of an electrolyzer module with bipolar cell configuration thus substantially simplifying the design of a water-splitting device. The studies reported here evaluate the suitability of AISI Ni42 steel, surface oxidized upon an electrochemical approach, as a water-splitting OER and HER electrocatalyst in alkaline, neutral, and acidic solutions. We found that anodization under harsh conditions (2000 mA cm$^{-2}$ current density; duration: 300 min, 7.2 M KOH) converted relatively less active untreated Ni42 steel into an outstanding OER and reasonable HER electrocatalyst. The layer, firmly attached to the alloy matrix, formed during this kind of activation basically consists of γ-NiO(OH), Fe$_2$O$_3$ besides FeO(OH). The most significant results of the work described can be highlighted as follows:

1. Ni42 steel, electro-activated for 300 min under harsh conditions (sample Ni42-300) exhibited unusual high catalytic activity combined with very good long-term (for the entire 450 000 s tested) stability when used as an OER electrocatalyst in pH 7 phosphate buffer solution given an average overpotential of 491 mV at 4 mA cm$^{-2}$ in pH 7 corrected 0.1 M KH$_2$PO$_4$/K$_2$HPO$_4$ through 40 000 s chronopotentiometry plot. The Ni-Fe-oxide layer, around 5 µm in thickness, generated on the alloy during electro-oxidation sufficiently protected the matrix against further (inner) oxidation highlight by an outstanding Faradaic efficiency of sample Ni42-300 of 99.4% (4000 s of chronopotentiometry at 2 mA cm$^{-2}$) that makes the OER properties even superior to those of IrO$_2$-RuO$_2$.

2. Sample Ni42-300 also proved to be highly active and stable (up to the 450 000 s maximum tested) toward OER electrocatalysis under alkaline conditions (under steady-state and non-steady-state conditions) at pH 13 (0.1 M KOH) and pH 14 (1 M KOH), and exhibited significantly better electrocatalytic efficiency than IrO$_2$-RuO$_2$. The catalytic OER key figures of Ni42-300 were η = 251 mV at 10 mA cm$^{-2}$ in 0.1 M KOH and η = 215 mV at 10 mA cm$^{-2}$ in 1 M KOH. In addition, the catalyst exhibited very good activity and outstanding stability (η = 196 mV at 10 mA cm$^{-2}$ through 450 000s chronopotentiometry plot) for OER performed at 70 °C in 7 M KOH.

3. Sample Ni42-300 was found to be well suitable as an HER electrocatalyst with regard to activity and stability in aqueous solutions over a wide pH range spanning from pH 0 to 14.6. In diluted acidic and alkaline media (0.05 M H$_2$SO$_4$ and 0.1 M KOH), the overpotential for HER amounted to around 268.4 mV (pH 1) and 333 mV (pH 13) to guarantee a stable current density of 10 mA cm$^{-2}$. Long-term chronopotentiometry measurements carried out at 10 mA cm$^{-2}$ current density for 450 000 s of HER (pH 1) and for 50 000 s of HER (pH 13), respectively, exhibited sufficient stability under catalysis conditions as shown by the nonexistent increment of the potential through the 450 000 s plot (pH 1) and 50 000 s plot (pH 13), respectively. The current-to-voltage ratio within the cyclic voltammetric and chronopotentiometric studies was much stronger when those were carried out in 1 M KOH and 0.5 M H$_2$SO$_4$ instead of 0.1 M KOH and 0.05 M H$_2$SO$_4$, respectively (η = 299 mV at 10 mA cm$^{-2}$ at pH 14, η = 189 mV at 10 mA cm$^{-2}$ at pH 0). No signs of degradation of the catalyst were obtained when HER polarization tests carried out in 7 M KOH at 70 °C for long operating times up to the maximum 450 000 s tested.

In summary, surface-oxidized Ni42 alloy combines good HER performance and stability at pH 14.6 (η = 275 mV at 10 mA cm$^{-2}$), pH 14 (η = 299 mV at 10 mA cm$^{-2}$), pH 13 (η = 333 mV at 10 mA cm$^{-2}$), pH 1 (η = 268.4 mV at 10 mA cm$^{-2}$), and pH 0 (η = 189 mV at 10 mA cm$^{-2}$) with outstanding OER activity and stability at pH 7 (η = 491 mV at 4 mA cm$^{-2}$), pH 13 (η = 251 mV at 10 mA cm$^{-2}$), pH 14 (η = 215 mV at 10 mA cm$^{-2}$), and at pH 14.6 (η = 196 mV at 10 mA cm$^{-2}$). Especially when compared with very recently achieved Janus type characteristics of Ni$_3$P$_4$[113] and Ni$_2$P$_4$[54] our catalyst therefore constitutes a highly promising alternative full-water-splitting catalyst. The unrivaled cost efficiency of a water-splitting device consisting of modified...
4. Experimental Section

Preparation of the Ni42-300 Samples—Electro-Oxidation of Stainless Steel at Constant Potential: Samples with a total geometry of $45 \times 10 \times 1.5$ mm were constructed from 1.5 mm thick AISI Ni42 steel. Pretreatment: prior to each surface modification, the surface of the metal was cleaned intensively with ethanol and polished with grit 600 SiC sanding paper. Afterward, the surface was rinsed intensively with deionized water and dried under air for 100 min. The weight was determined using a precise balance (Sartorius 1712, 0.01 mg accuracy) prior to electro-activation. For the electro-oxidation, a two-electrode setup was used consisting of the steel sample as WE, and a platinum wire electrode ($4 \times 5$ cm) used as CE. The WE (anode) was immersed exactly 2.1 cm deep (around 4.5 cm$^2$ geometric area), and the CE (cathode) was completely immersed into the electrolyte.

The electrolyte was prepared as follows: In a 330 mL glass beaker, 57.6 g (1.44 mol) of NaOH (VWR, Darmstadt, Germany) was dissolved under stirring and under cooling in 195 g deionized water. The solution was allowed to cool down to 23°C before usage. The anodization was performed under stirring (450 r min$^{-1}$) using a magnetic stirrer and a stirring bar (21 mm in length, 6 mm in diameter). The distance between WE and CE was adjusted to 6 mm. A power source (Electra Automatic, Viessern, Germany) EA-PSI 8360-15T which allows to deliver a constant voltage even at strongly changing current loads was used for the electrochemical oxidation. The procedure was carried out in current controlled mode. The current was set to 8.7 A according to deliver a constant voltage even at strongly changing current loads was and a stirring bar (21 mm in length, 6 mm in diameter). The distance between WE and CE was adjusted to 6 mm. A power source (Electra Automatic, Viessern, Germany) EA-PSI 8360-15T which allows to deliver a constant voltage even at strongly changing current loads was used for the electrochemical oxidation. The procedure was carried out in current controlled mode. The current was set to 8.7 A according to 2000 mA cm$^{-2}$ current density. The voltage varied during the electro-activation. At the beginning of the experiment, it amounted to around 6.7 V but was reduced within the duration of 300 min to around 4.5 V. These data proved to be reliably reproducible for all 10 replicates. If however for some reasons the decrease of the voltage is more abrupt, i.e., the voltage drops down to 4.5 V earlier, the activation procedure should be stopped when a voltage of 4.5 V is reached. The temperature of the electrolyte increased within the first 30 min and reached a value of 323 K. After every hour $\approx 2.5$ mL of fresh 6 M NaOH was added to the electrolysis vessel in order to compensate the loss occurred due to evaporation. After 300 min of electro-activation, the CE and the WE samples were taken out of electrolyte and rinsed intensively with tap water for 15 min and afterward with deionized water for a further 10 min. The used NaOH electrolyte was transferred quantitatively into a plastic bottle and was stored for further analysis. The counter electrode was immersed into 30 mL of 2 M HCl for 12 h. The acidic solution was stored for further analysis via ICP OES. Prior to the electrochemical characterization the samples were dried under air at ambient temperature and the weight was determined upon a precise balance as described above. The sample preparation was repeated 10 times, i.e., in total 11 samples of Ni42–300 were prepared this way.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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H.S. had the idea to perform the experiments the manuscript is based on. He planned and performed the electrochemical measurements and all sample preparations. H.S. wrote the manuscript as well as the Supporting Information. D.M.C., P.Z., K.K., and J.W. planned, performed, and evaluated the XPS measurements. K.-M.-B. and J.S. planned and performed the BET measurements. J.D.H. helped in the evaluation of some experiments. H.S., S.S., U.K., M.S., S.D., and L.W. performed and evaluated the AFM as well as the FIB/SEM experiments. All authors have read the manuscript.

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