

In-Liquid Plasma Modified Nickel Foam: NiOOH/NiFeOOH Active Site Multiplication for Electrocatalytic Alcohol, Aldehyde, and Water Oxidation

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Abstract

The oxygen evolution reaction (OER) and the value-added selective oxidation of renewable organic substrates are the most promising reactions to supply electrons and protons for the synthesis of sustainable fuels. To meet industrial requirements, new methods for a simple, fast, environmentally friendly, and cheap synthesis of robust, self-supported, high surface area electrodes are required. Herein, we report on a novel in-liquid plasma electrolysis approach for the growth of hierarchical nanostructures on nickel foam. Under retention of the morphology, iron could be incorporated into this high surface area electrode. For the oxidation of 5-hydroxymethylfurfural and benzyl alcohol, the iron free plasma treated electrode is more suitable reaching current densities up to 800 mA/cm² with Faradaic efficiencies above 95%. For the OER, the iron incorporated nickel foam electrode reached the industrially relevant current density of 500 mA/cm² at 1.473±0.013 V_{RHE} (60 °C) and showed no activity decrease over 140 h. The different effects of the iron doping is rationalised using MeOH doping and *in situ* Raman spectroscopy. Furthermore, we could separate changes in intrinsic activity per active site and number of active sites for the OER as well as reveal diffusion limitations of the organic oxidation reactions which we explain with respect to the surface morphology. We anticipate that the plasma modified high surface area nickel foam could potentially be applied for various electrocatalytic processes.

Broader context

The formation of fuels (e.g., hydrogen, hydrocarbons...) from green electricity is a suitable approach to compensate the fluctuations of sustainable energies, as fuels can be transported by pipelines,

stored in salt caverns or tanks and no resource and cost intensive batteries must be constructed. Fuel formation requires electrons and protons that are supplied by the oxygen evolution reaction (OER). To drive the OER or any other electrocatalytic process efficiently, high surface area electrodes are required. Herein, we use an oxygen plasma to directly modify the surface of nickel foam and obtain a hierarchically nanostructured electrode that robustly and efficiently drives the OER and the value-added organic oxidation of organics that is required for e.g., sustainable future polymers from sugars. The plasma process requires only 10 min, no toxic chemicals, and little energy, as the high temperatures (up to 10,000 K) only occur locally at the electrode surface. The plasma treated nickel foam is a promising substrate for various (electro)catalytic reactions, due to its high number of surface exposed sites, the possibility to modify it chemically after the plasma process while keeping the high surface area, its chemical and mechanical robustness as well as being quick, cheap and environmentally friendly.

Introduction

The oxygen evolution reaction (OER) is critical for a sustainable energy economy, as it supplies protons and electrons for the most prominent fuel formation processes, the hydrogen evolution reaction (HER) and CO₂ reduction.¹⁻⁵ Partly, the OER can be replaced by economically more viable processes, where the electrons are supplied by value-added oxidations of organic molecules (hybrid water electrolysis).^{3,4,6} For all processes, to be economically viable, the applied electrodes must operate at large current densities and elevated temperatures without degradation over long operating times.^{7,8} In this regard, powder catalysts fixed with binders are not suitable, as they neither meet the required mechanical and chemical stability nor are cost effective in their manufacturing.⁸ A more suitable alternative is the direct modification of metallic electrode substrate surfaces.⁹⁻¹¹ In this context, the most promising electrode substrate is conducting and cheap nickel foam (NF) which provides a porosity in the micrometer range (10-1000 μm).¹² The surface area and active sites of NF could be drastically enhanced by the formation of hierarchical nanostructures on its surface. Such a NF could potentially be applied for various electrocatalytic reactions without the need of any further catalyst to fulfill the industrial requirements. However, the inert nature and high melting point of NF makes it challenging to modify and usually high externally applied temperatures and pressures are required (hydrothermal methods) or long reaction times of hours or days (immersion based methods).^{9,13,14}

To meet this challenge, we applied a novel, in-liquid (gas/liquid dual phase), thermal, glow discharge, anodic plasma electrolysis (PE) approach that consumes little energy and takes only minutes. For this PE approach, a simple two-electrode setup is sufficient to achieve the surface modification within minutes. Furthermore, it does not require environmentally harmful chemicals or energy intensive

external heating.¹⁵ Recently, gas-phase plasma based methods have been reported for the synthesis or modification of electrocatalysts.^{16–18} In contrast to our approach, these methods are almost exclusively based on nonequilibrium ionized gases with low gas bulk temperatures (room temperature or below).^{17,18} None of these plasma methods were applied directly to the electrode substrate, most likely because such non-thermal gas plasmas are not suitable for the surface nanostructuring of metals. During the herein used PE, local, instantaneous temperatures of up to 10,000 K were estimated and the pressure inside discharge channels could reach about 10^2 - 10^3 MPa while potentials of several hundred volts are applied.¹⁹ We hypothesized that such conditions are ideal to form a chemically stable and nanostructured anode for electrocatalytic oxidation reactions, since a phase formed in such an environment, should easily endure the electrocatalytic conditions ($V < 2.0$) and thus overcome the persistent stability problem of OER catalysts.^{20,21}

The herein reported PE approach creates a hierarchical, flower-like nanostructure on commercial NF. The modified NF is applied for the value added selective oxidation of two organic substrates reaching record high current densities of up to 800 mA/cm². Additionally, the PE modified NF shows a strongly increased OER activity compared to NF due to more accessible nickel sites. Without changing the morphology or surface area of the modified NF, we succeed in including iron showing that the plasma treated NF can be chemically altered to be suitable for different catalytic reactions while profiting from its increased surface area. The iron modification leads to an increase of the intrinsic OER activity without significantly changing the accessible redox active sites. Combining PE treatment and iron incorporation results in an OER activity enhancement of three orders of magnitude compared to NF at the same potential, and OER investigations at industrial relevant temperatures and current densities reveal a high long term stability. However, for the organic oxidation reaction, the iron-free sample is more active. Consistent with previous reports and herein supported by *in situ* Raman spectroscopy and MeOH probing, we propose an explanation for this phenomenon connecting the reaction intermediates of both processes with each other. Furthermore, we find that the OER activity is proportional to the number of redox active sites, while, in contrast, the organic substrate oxidation is diffusion-limited and its turnover scales with the double layer capacitance (C_{dl}) at high current densities.

Results

Plasma treatment. Using the setup shown in Fig. 1a, we investigated the anodic high potential (0-630 V) electrical characteristics of NF in 0.01 M KOH. From the current-potential plot (Fig. 1b), three regions can be classified: (i) the conventional, (ii) the transition, and (iii) the plasma region. After the conventional OER region, the current drops due to the high resistance of the dense gas bubble formation at the electrodes. Eventually, at a potential of 575 V, a uniform plasma-discharge is

observed in the O₂ gas bubble region of the anode (see Fig. 1b). Scanning electron microscopy (SEM) images reveal that a voltage of 630 V applied for 10 min is most suitable for the formation of a homogeneously nanostructured surface (Fig. S1 and S2). For the applied parameters (630 V, 0.6 A, 10 min) and assuming an electricity price of 0.15 US\$ per kWh, a low energy consumption of 63 Wh and a small electricity cost below 0.02 US\$ per cm² electrode is obtained.

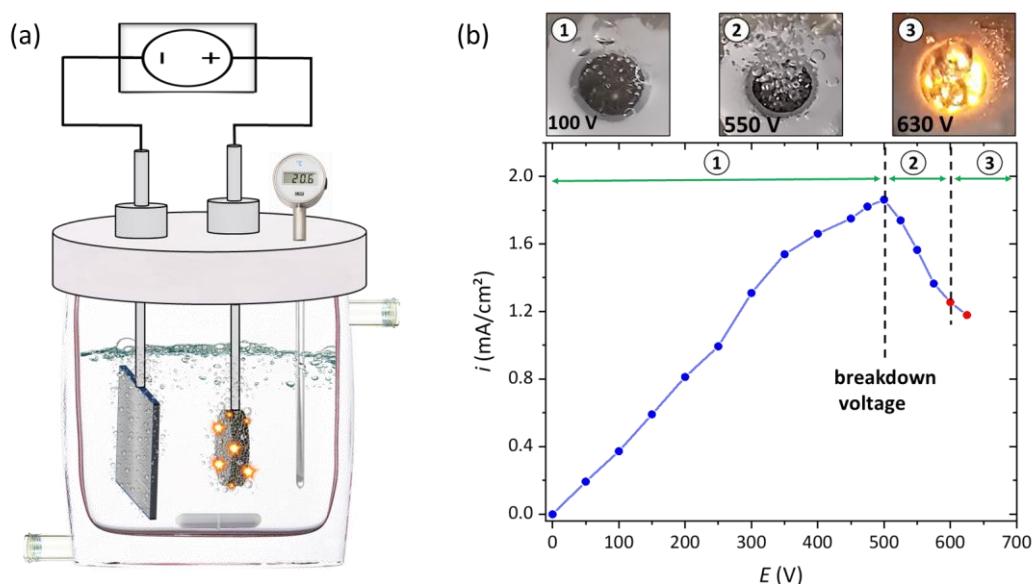


Fig. 1. The oxygen plasma treatment process. (a) The experimental setup of the in-liquid plasma treatment, a two electrode setup with a high voltage power supply filled with 0.01 M KOH. (b) The high potential electrical characteristics of NF in setup containing three regions: (i) the conventional OER, (ii) the transition, and (iii) the plasma region. The images at the top show the NF in the three different potential regions with the characteristic glowing of the plasma in the region (iii).

Morphology, redox activity, and surface area. SEM shows that untreated NF has a flat surface, and, in the cross section, no surface oxide layer can be seen (Fig. 2a-c and S3-S6). After plasma treatment (NF-Plasma), a hierarchical nanostructure is visible consisting of 0.1-1 μm large spherical objects that stack on each other, partly agglomerate, and form a thick, homogeneous layer covering the entire NF surface (Fig. 2d-i and S7-S10). Larger magnifications reveal that these spheres consist of smaller nano petals that are only a few nanometer thick and give the spheres a flower-like appearance. Cross section images reveal an around 200-500 nm thick, porous surface layer (Fig. 2i, 2m, and S8). SEM energy dispersive X-ray (EDX) mappings demonstrate a homogenous distribution of Ni and O and the respective EDX spectrum contains a clear oxygen peak compared to the one of untreated NF (Fig. 2j-l, S4 and S9). An EDX mapping of the cross section shows that the porous surface layer contains Ni and O (Fig. 2m-o and S10, see Fig. S6 for untreated NF). For NF and NF-Plasma, cyclic voltammetry (CV) in 1 M KOH revealed reversible redox features that can be assigned to the oxidation of Ni^{II} (Fig. S11a).²²⁻
²⁴ Integration of the reduction peak yields an increase of the nickel redox activity by around 40 times

through the plasma treatment (Fig. S11b,c) and the double layer capacitance (C_{dl}) increased around six times (Fig. S11e and S12).

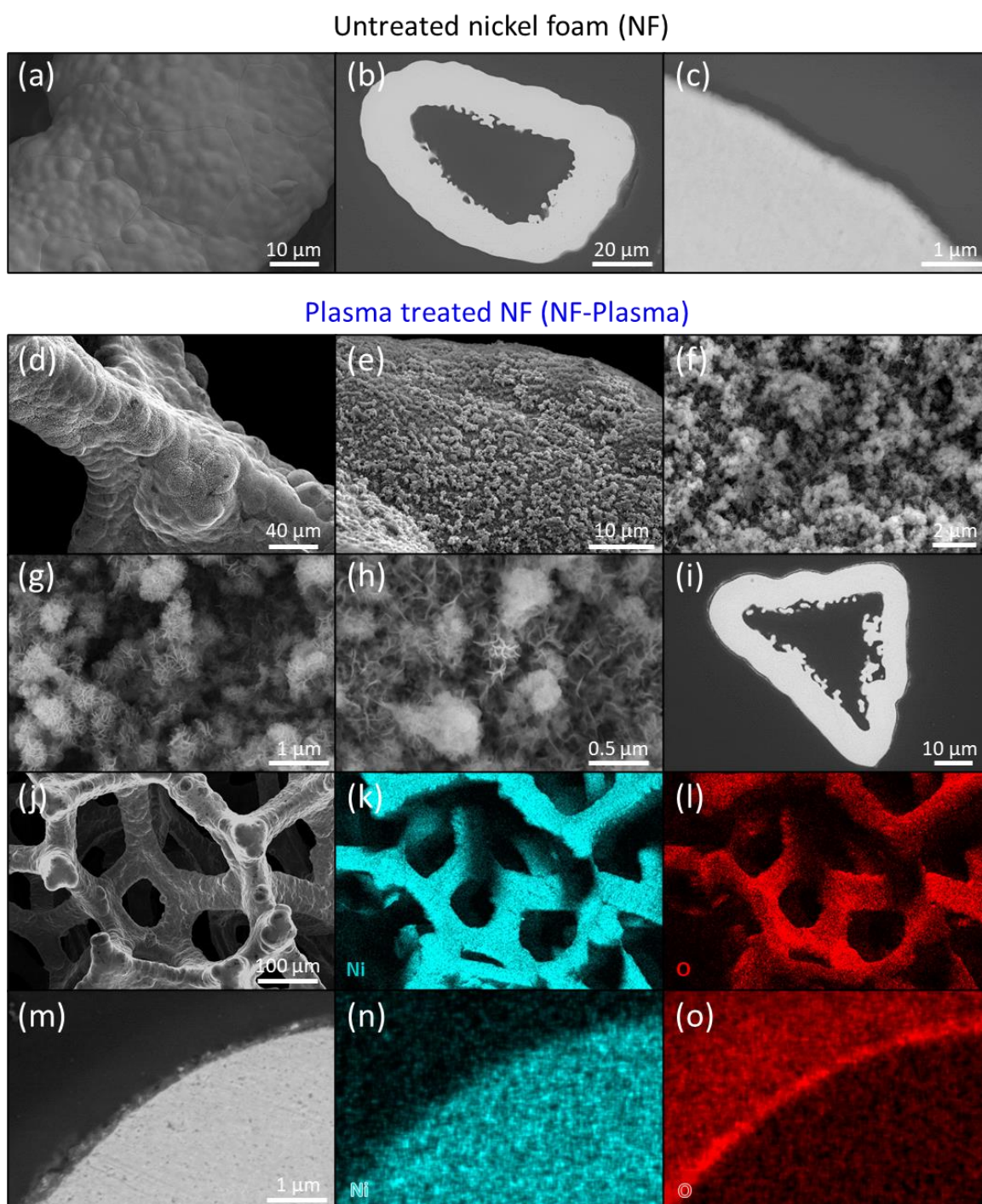


Fig. 2. SEM investigations showing the plasma electrolysis induced morphology changes. SEM images with a top view (a) and cross section view (b, c) of untreated, commercially available nickel foam (NF). No hierarchical nanostructure or surface modification can be seen (see Fig. S3-S6 for more SEM images and elemental mappings). (d-h) SEM images of NF after the plasma treatment from a top view showing the presence of hierarchical nanostructures (see Fig. S7 for more images). (i) SEM image of the cross section of plasma treated NF showing a thin, porous surface layer (see Fig. S8 for more images). (j-l) SEM/EDX elemental mapping of the plasma treated NF with a top view (see Fig. S9 for EDX spectrum), showing a homogeneous distribution of nickel and oxygen. (m-o) SEM/EDX elemental mapping of the cross section of plasma treated NF (see Fig. S10 for EDX

spectrum) revealing an oxide surface layer. The cross section images were taken of samples that were embedded into epoxy resin and grounded down to obtain cross-sections.

Iron incorporation. Iron doping was achieved by cycling NF-Plasma in $\text{Fe}(\text{NO}_3)_3$ saturated 1 M KOH (Fig. S12a). Ten CV cycles were chosen as the OER activity merely changed after the tenth cycle. This treatment increases the redox peak potential while the current maximum height remained almost the same (see Fig. S11c and S12a) which is typical for iron incorporation at easily accessible edge or defect sites of nickel oxyhydroxides.²⁵ It is reported that such an incorporation leads to dramatically improved OER activity but only marginally affects the majority of the nickel redox species that reside surrounded by six nickel atoms within a layer and most likely do not participate in catalysis.²⁵ SEM images taken after the iron incorporation into a NF-Plasma sample show that the morphology was unaltered (Fig. S13). Furthermore, SEM/EDX analysis reveals the presence of iron and potassium and shows a homogeneous distribution of Ni, Fe, K, and O (Fig. S14). Also, the C_{dl} remains almost unchanged by the iron incorporation (Fig. S12b).

PXRD and XPS. The powder X-ray diffractogram (pXRD) contains only reflexes of metallic nickel. Thus, the newly formed $\text{Ni}(\text{Fe})\text{O}_x\text{H}_y$ phases are all amorphous (Fig. S15). For all three samples, the X-ray photoelectron spectra (XPS) in the Ni 2p region are consistent with the presence of a Ni^{2+} surface species (Fig. 3a).^{26,27} Only for the NF-Plasma-Fe sample, a clear Fe 2p doublet with a binding energy typical for Fe^{3+} is present (Fig. 3b).²⁷ The O 1s spectrum of NF can be deconvoluted into a hydroxide peak and a much less intense peak for adsorbed water (Fig. 3c).^{28,29} The O 1s spectra of NF-Plasma and NF-Plasma-Fe also contain these two peaks in a similar intensity but additionally have a shoulder at lower binding energy which is consistent with metal oxide (O^{2-}) species. The elemental surface composition determined from the XPS measurements reveals that 26 at% of iron compared to nickel were incorporated through the CV (Fig. 3c). In principle, as a potential of 630 V was applied during the plasma treatment, nickel phases with higher oxidation states are expected but only Ni^{2+} was observed by XPS. The nickel at the surface most likely reacted with air forming Ni^{2+} after the plasma treatment. XPS depth profiling detects shows a decline of the Ni^{II} species until only Ni^0 from the NF can be found (Fig. 3e). detects nickel in higher oxidation states (mainly NiOOH) below the surface Ni^{2+} and ultimately the main species is Ni^0 from the metallic NF beneath the surface oxide layer

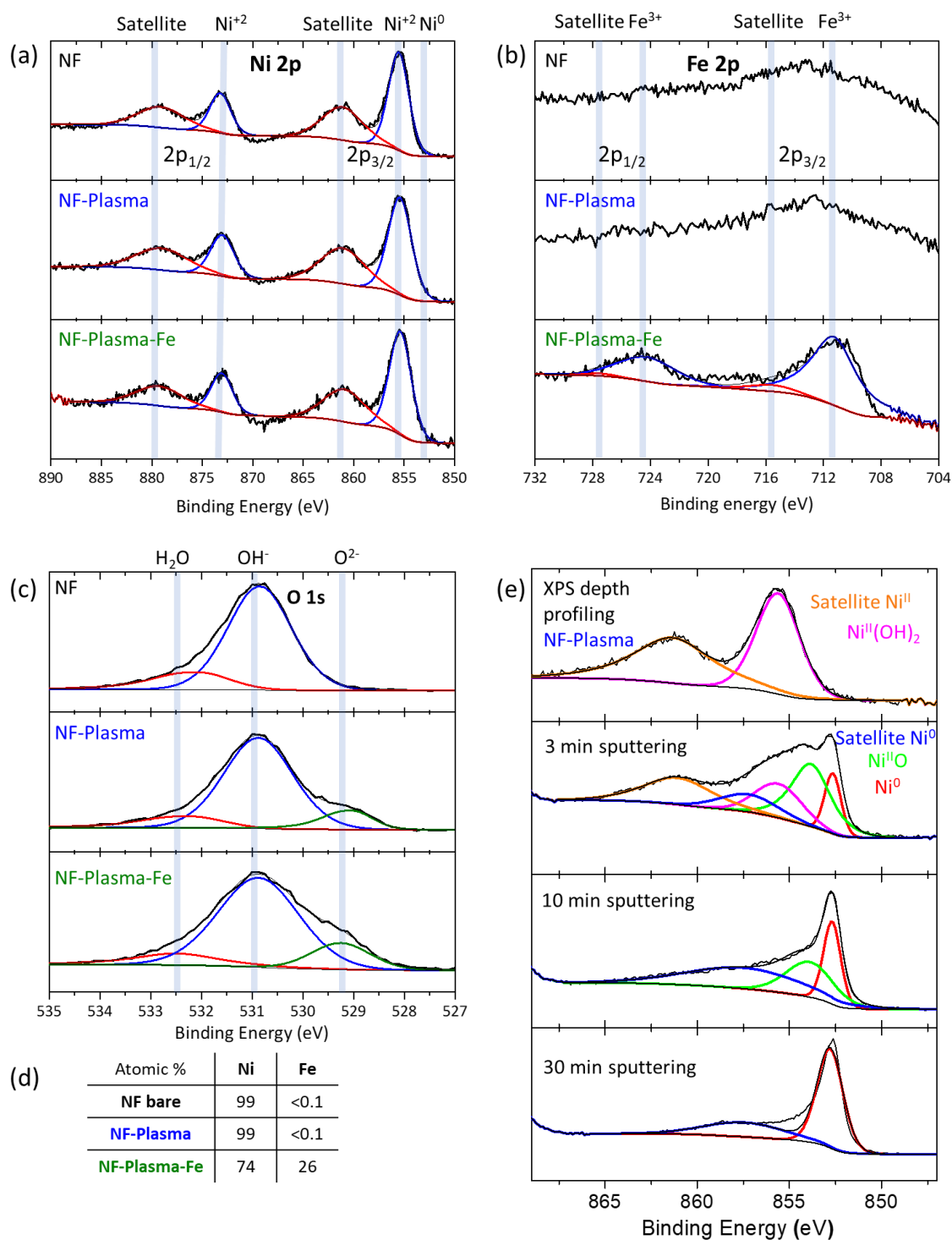


Fig. 3. The core-level XPS analysis of NF, NF-Plasma, and NF-Plasma-Fe. The Ni 2p spectra (a) of all films show two dominant 2p_{3/2} and 2p_{1/2} peaks with accompanying satellites that are typical for Ni^{II}(OH)₂.^{26,27} The presence of Fe can only be found for NF-Plasma-Fe and the observed doublets in the Fe 2p spectra (b) correspond to a Fe^{III} species.²⁷ The O 1s spectra (c) of NF-Plasma and NF-Plasma-Fe displayed similar peaks responsible for metal oxide, hydroxides, and adsorbed water while NF mostly displayed surface hydroxide species.^{28,29} The XPS quantification of Ni and Fe content of NF-Plasma-Fe on the surface is given in (d). The Ni 2p XPS depth profiling of NF-Plasma (e) at three different sputtering times where the amount of hydroxide and oxide peaks diminished continuously with subsequent increase of Ni⁰ species.^{26,27}

OER activity and stability. The electrocatalytic OER properties in 1 M KOH of four samples were measured and compared (NF, NF-Fe, NF-Plasma, and NF-Plasma-Fe; see Fig. 4a for an overview). The reverse scan of the CV measurements reveals the activity trend $\text{NF} < \text{NF-Plasma} = \text{NF-Fe} < \text{NF-Plasma-Fe}$ with NF-Plasma-Fe yielding the current densities 10, 100, and 500 mA/cm² at 207±4 mV, 248±5 mV, and 304±11 mV overpotential, respectively (Fig. 4b). This OER activity trend is confirmed by the diameter of the Nyquist plots obtained by electrochemical impedance spectroscopy (Fig. S16). To provide a meaningful comparison, we investigated several previously published iron-nickel catalysts as well as iridium and ruthenium oxides under the same conditions (Fig. 4c, Fig. S17).^{11,30} The NF-Plasma-Fe electrode shows the lowest overpotential of all studied systems. Besides activity, a critical parameter is the long-term stability at industrially relevant current densities. Thus, we performed a chronopotentiometry (CP) stability test at 200 mA/cm² for 140 h showing a stable overpotential of 275±5 mV (Fig. 4d). Further improvements can be achieved by operating at elevated temperatures like in industrial systems. The potential required to reach 500 mA/cm² is reduced by 60 mV to 1.473±0.013 V_{RHE} when the temperature is increased to 60 °C (Fig. 4e). A stability test at 60 °C and 400 mA/cm² also shows no decline in activity (Fig. 4e inset).

Tafel analysis and OER activity normalisation. Steady state Tafel measurements reveal small Tafel slopes of 32 and 34 mV/dec for the iron incorporated samples and Tafel slopes of 43 and 46 mV/dec for the samples without intentional iron incorporation (Fig. 4f). For rigorous iron free nickel oxyhydroxides, Tafel slopes of around 70-110 mV/dec are typical.^{31,32} The inclusion of iron then continuously decreases this slope to around 30 mV/dec.³² Commercially available NF foam is never completely iron free and the NF used by us contains 0.008 wt% (80 ppm) iron while the 1 M KOH contained <0.05 ppm Fe. Thus, the Tafel slopes observed by us are in accordance with nickel oxyhydroxide with iron traces (NF and NF-Plasma) and with nickel-iron oxyhydroxides close to an optimum nickel-iron ratio for the OER (NF-Fe and NF-Plasma-Fe).^{31,32} Most importantly, the similar Tafel slope values indicate that the plasma treatment does not alter the reaction mechanism or the nature of the active site. Nevertheless, one clear effect of the plasma treatment on the Tafel plot can be seen: the plasma treated samples possess a linear behavior until current densities of 500 mA/cm² while the non-treated samples show deviation from linearity starting at 10-30 mA/cm². The earlier deviation from linearity indicates that additional effects to the molecular kinetics inhibit the OER for these samples which could be mass transport limitations (hydroxide or oxygen diffusion, oxygen bubble detachment) or a too high surface intermediate coverage caused by the smaller surface area and number of active sites. As redox active sites fulfill various prerequisites for the OER (anodically wired, access to electrolyte (proton transfer), ability to change the oxidation state)³³ and considering that similar Tafel slopes indicate similar reaction mechanisms/active sites, we normalized the steady

state OER data by the number of nickel redox active sites obtained by integration of the redox peak (Fig. 4g).²¹ With this normalization, the two iron incorporated electrodes have a similar activity as well as the two non-incorporated ones.

Post OER analysis. XPS and SEM investigation of the NF-Plasma-Fe samples after 24 h at 200 mA/cm² showed no change in the chemical nature or morphology of the sample, which is reasonable considering that the as prepared phases were formed under much harsher alkaline anodic conditions already (Fig. S18 and S19).

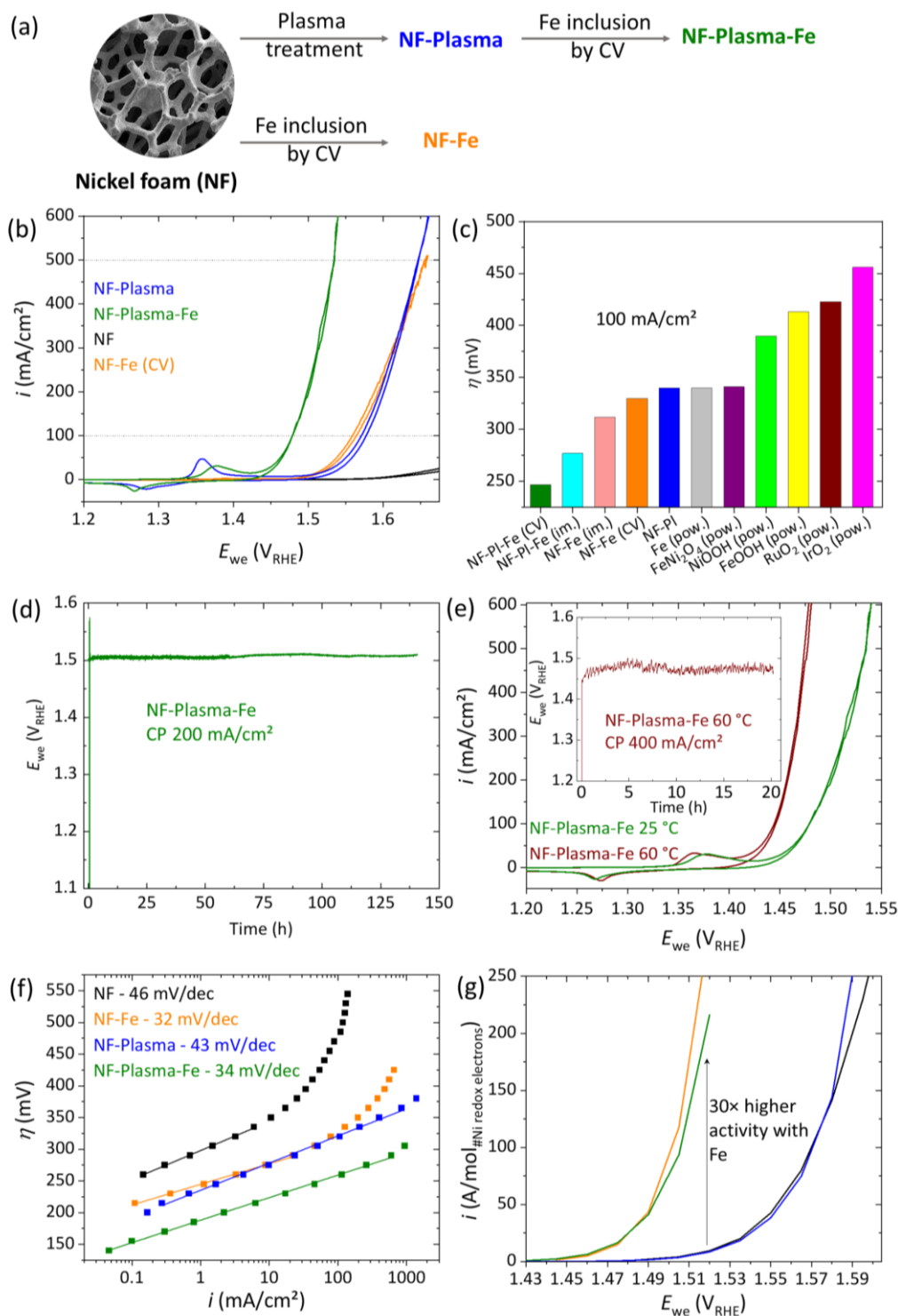


Fig. 4. Electrochemical characterisation. All measurements are with iR compensation (see ESI). (a) Overview of the samples that were electrocatalytically investigated. (b) Cyclic voltammograms at a scan rate of 5 mV/s. (c) Comparison of the overpotentials at 100 mA/cm² with various other Ni-, Fe-, NiFe-, and noble metal-based catalysts (see S17 for details).³⁰ The loading of the powder samples was (0.8 mg/cm²). Immersion means that the iron incorporation was performed by simple immersion in a 20 mM aqueous Fe(NO₃)₃ solution for 4 h, as reported previously.¹¹ (d) CP stability test at 25 °C. (e) CV and CP stability test at 60 °C. (f) Tafel slopes from steady state CA measurements. (g) Normalization by the amount of redox active sites from the reduction peaks of Fig. S11 and S12a.

Methanol probing and *in situ* Raman spectroscopy. Recently, Liu et al. suggested MeOH as a probing molecule for electrophilic oxygen species ($^*[\text{O}_e]$) on a catalyst surface (see Supplementary Information for a discussion on the nature of this species).³⁴ In this regard, for NF-Plasma and NF-Plasma-Fe, we recorded CVs with and without MeOH in 1 M KOH (Fig. 5a and b). For both catalysts, in the presence of MeOH, high current densities are observed between the nickel redox feature and the OER onset of the MeOH free CVs probing $^*[\text{O}_e]$. In this range, MeOH oxidation occurs and no bubbles form at the anode, as previously reported.³⁵ The addition of iron has three effects: (i) it decreases the current density of selective MeOH oxidation (the current density at 1.40 V_{RHE} is around three times higher for NF-Plasma), (ii) it shifts the redox peak anodically, and (iii) it shifts the OER onset cathodically. Thus, NF-Plasma-Fe oxidizes MeOH slower and the potential range and maximum potential where MeOH oxidation without OER interference occurs is narrower making NF-Plasma the better alcohol oxidation catalyst.

In and *ex situ* Raman data was recorded under various potential and conditions of NF-Plasma (Fig. 5c) and NF-Plasma-Fe (Fig. 5d). Consistent with the XPS results, the Raman spectrum of as prepared NF-Plasma exhibits the typical $\text{Ni}^{\text{II}}\text{-O}$ vibration of dehydrated or disordered nickel hydroxide along with small features that could be related to a nickel oxide.^{36–39} When applying an increased anodic potential, the $\text{Ni}^{\text{II}}\text{-O}$ vibration vanishes, and two other bands related to the bending $\delta(\text{Ni}^{\text{III}}\text{-O})$ (482 cm^{-1}) and stretching $\nu(\text{Ni}^{\text{III}}\text{-O})$ (564 cm^{-1}) vibrations typical for NiOOH appear. Furthermore, at 1.53 V_{RHE} , a peak previously assigned to an $[\text{O-O}]$ vibration is present at 1072 cm^{-1} .^{36,40} For NF-Plasma-Fe, the same vibrational modes can be observed, in line with the presence of a $\text{Ni}(\text{Fe})\text{OOH}$ phase. Comparing the various Raman spectra, differences in the intensity ratios of the bands observed at 482 and 564 cm^{-1} are detectable. In this regard, decreasing I_{482}/I_{564} ratios have been correlated to higher iron contents.³² Furthermore, such a decrease can also be caused by Ni-OH deprotonation and by higher nickel oxidation states which both can be induced by anodic potentials.⁴¹ These trends are further confirmed herein: iron incorporated samples show lower I_{482}/I_{564} ratios, and, for NF-Plasma and NF-Plasma-Fe, the I_{482}/I_{564} ratio is smaller, for the *in situ* OER spectra at 1.53 V_{RHE} in comparison to the measurements accomplished *ex situ* after OER. The spectra recorded during MeOH oxidation exhibit the same features as those monitored during OER, including the $[\text{O-O}]$ vibration, but reveal an additional band at 1026 cm^{-1} characteristic for MeOH. For NF-Plasma during MeOH oxidation, the $\nu(\text{Ni}^{\text{III}}\text{-O})$ vibration is red-shifted and the I_{482}/I_{564} ratio is comparable to the one observed in the spectrum acquired without MeOH at a more cathodic potential (1.23 V_{RHE}) than the nickel redox feature indicating a lowered nickel oxidation state. Comparing the spectra after OER (1 h under air and at room temperature) to the ones after stirring in 0.1 M MeOH for 5 min, it is obvious that, after OER, the spectral features of NF-Plasma and NF-Plasma-Fe resemble those of $\text{Ni}^{\text{III}}(\text{Fe})\text{OOH}$ species, while after

MeOH stirring, they are similar to the $\text{Ni}^{\text{II}}\text{O}_x\text{H}_y$ phase (see NF-Plasma as prepared).³⁶⁻³⁹ As already reported, this shows that MeOH can reduce NiOOH to $\text{Ni}(\text{OH})_2$ (potential independent mechanism).^{42,43}

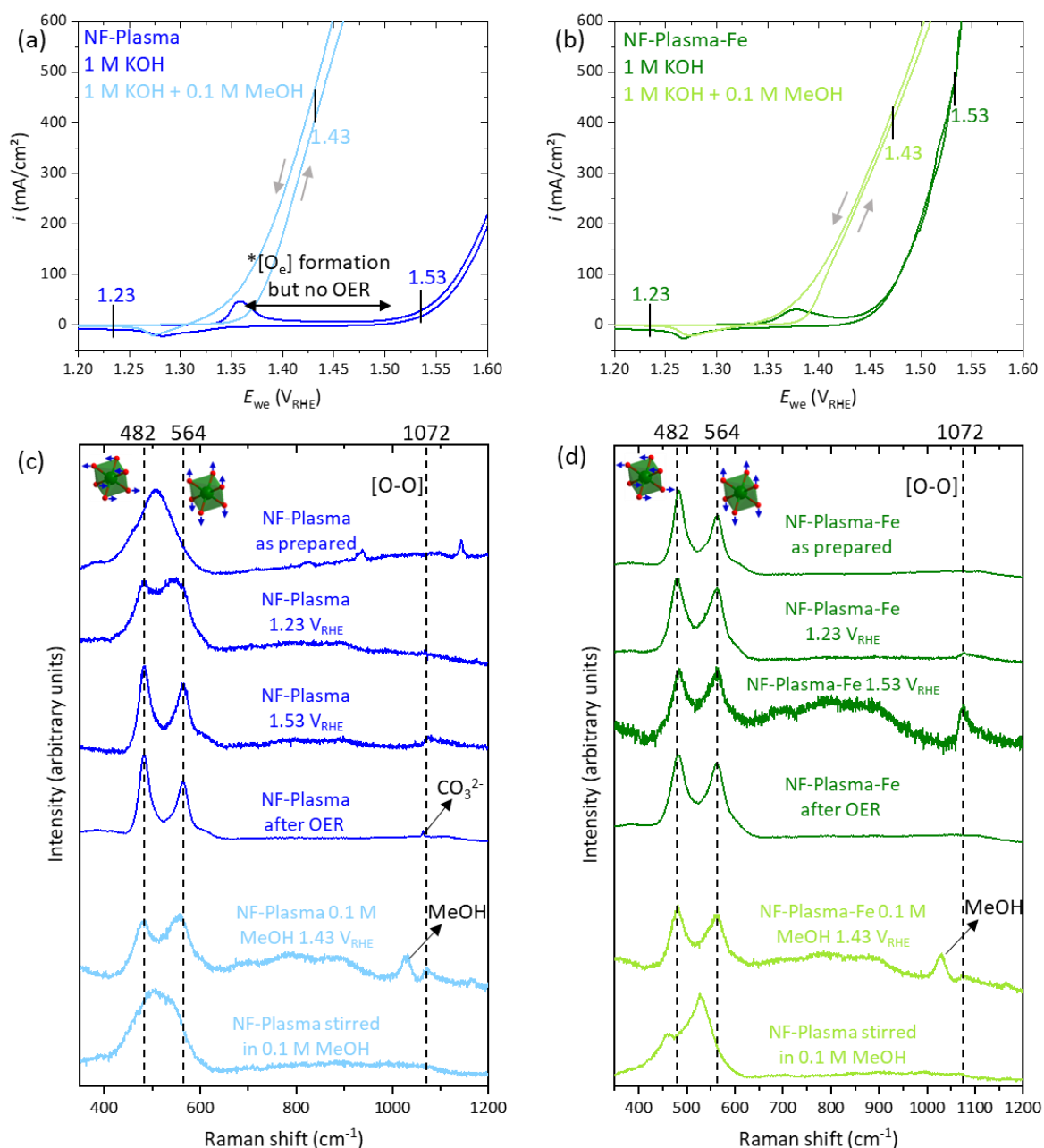


Fig. 5. MeOH probing and *in situ* Raman spectroscopy. CVs (5 mV/s, stirring) in 1 M KOH with and without MeOH of NF-Plasma (a) and NF-Plasma-Fe (b). The grey arrows mark the scan direction. The addition of MeOH leads to much higher current densities assigned to the oxidation of MeOH through an electrophilic oxygen intermediate ($^*\text{[O}_e\text{]}$). *In situ* Raman spectra taken at various potentials shown in (a) and (b) of NF-Plasma (c) and NF-Plasma-Fe (d). The horizontal dashed lines mark the three most prominent vibrations and their assignment to vibrations of the $[\text{NiO}_6]$ octahedra of $\text{Ni}(\text{Fe})\text{OOH}$ (Ni/Fe in green and O in red) and a previously reported [O-O] vibration.^{36,40}

Value-added selective oxidation of organic substrates. Inspired by the high current densities and large potential range for the selective oxidation of MeOH, we investigated the value-added oxidation of benzyl alcohol (BA) and 5-hydroxymethylfurfural (HMF) to benzoic acid and 2,5-furandicarboxylic acid (FDCA), respectively (see Fig. 6c and 6f for reaction equations). Benzoic acid is a widely applied chemical with an annual production of more than 640 kt and so far relies on the resource- and energy-intensive toluene oxidation process.^{44,45} HMF is a biomass derived substrate and FDCA can be used as a precursor for polymers.^{30,46} Thus, electrocatalytic HMF oxidation is a route to sustainable polymers. First, in 1 M KOH without stirring, LSVs were recorded with NF-Plasma or NF (reference) as working electrode and with or without 0.1 M HMF (Fig. S20) or BA (Fig. S21). Like for MeOH, the LSVs reveal a potential range where HMF/BA oxidation occurs before the OER onset. Furthermore, for industrial applications, the transformation rate is crucial. We find that the HMF/BA oxidation rate depends on stirring, substrate concentration, and potential under steady-state high current density conditions (Fig. 6). Based on these investigations, we performed bulk CA electrolysis experiments with the intention of full conversion of both substrates at a potential just below the OER onset (1.49 V_{RHE}). The achieved current densities are larger than previously reported ones reaching 800 and 600 mA/cm² for 0.1 M HMF and BA, respectively.^{30,47–49} Over time, the current decreases due to reduced substrate concentration. After exactly the required amount of charge for full conversion was passed (578.91 C for HMF and 385.94 C for BA), ¹H-NMR reveals >95% transformation for HMF (<5% non-electrochemical decomposition product was detected as reported previously in 1 M KOH, Fig. S22),⁴⁸ and 96% isolated yield for BA could be obtained (Fig. S23). Thus, for both reactions, Faradaic efficiencies of above 95% were achieved. NF also shows some oxidation activity but with a six times lower current density and a ¹H-NMR taken after the same time as for NF-Plasma reveals various products and only partial substrate consumption (6c, 6f, S22, and S23).

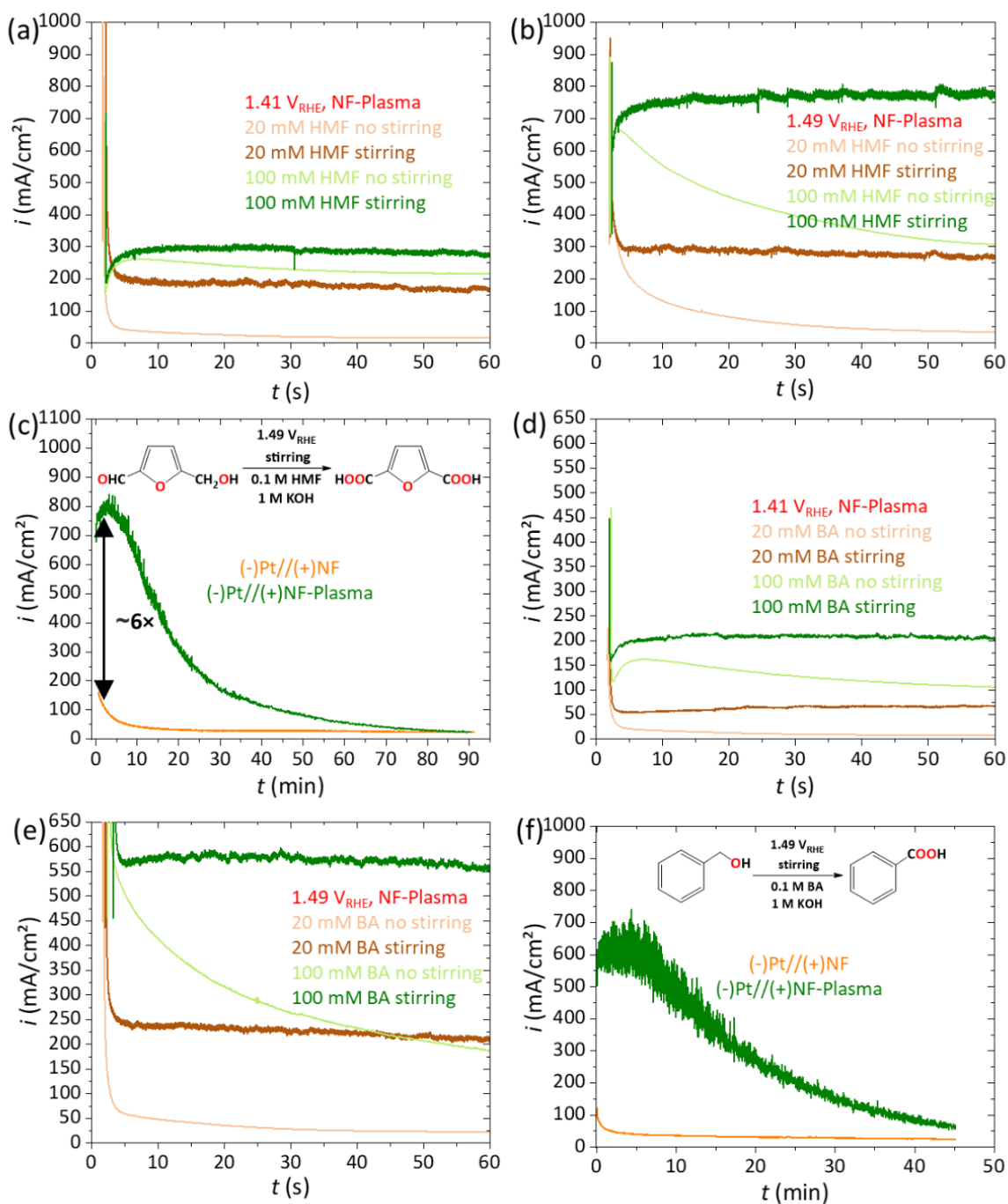


Fig. 6. Organic oxidation reactions. CA measurements of 1 M KOH solutions with NF-Plasma with either 5-hydroxymethylfurfural (HMF) or benzyl alcohol (BA) at different concentrations, with and without stirring, and at different potentials. The inset in (c) shows the reaction occurring in (a)-(c). The inset in (f) shows the reaction occurring in (d)-(f). The CA measurements shown in (c) and (f) were terminated after exactly the charge was passed required for full product formation. After that $^1\text{H-NMR}$ spectroscopy was performed (Fig. S22 and S23).

Discussion

We have successfully increased the surface area, number of redox active sites, and C_{dl} of NF by creating a hierarchically nanostructured surface with a flower-like appearance. Such a high surface area NF can be suitable for various electrocatalytic reactions. Furthermore, after the plasma treatment, we have incorporated iron without changing the morphology indicating that the plasma treated NF can potentially be chemically modified to be suitable for various catalytic processes. For the OER, the plasma treatment and iron incorporation lead to an activity enhancement of three orders of magnitude comparing current densities at the same potential. XPS, pXRD and *in situ* Raman data show that similar NiOOH or $Ni_xFe_{1-x}OOH$ are formed during OER for all samples. To explain the high activities and their differences, the two most important parameters to improve the turnover frequency of a catalytic system (electrode) must be separated and quantified (Fig. 7). The first one is to increase the number of active sites and the second one to enhance the intrinsic activity per active site. In this regard, we investigated four electrodes (Fig. 4a). The two electrodes without (NF and NF-Plasma) and the two with iron incorporation (NF-Fe and NF-Plasma-Fe) have a similar Tafel slope indicating the same reaction mechanism and same kind of active sites/phase. As redox active sites fulfill various prerequisites for the OER (anodically wired, access to electrolyte (proton transfer), ability to change the oxidation state)³³, we normalized the steady state OER data by the number of nickel redox active sites obtained by integration of the redox peak (e^-_{redox} , Fig. 4g).²¹ This normalisation results in similar currents for NF and NF-Plasma as well as NF-Fe and NF-Plasma-Fe. Thus, NF and NF-Plasma have the same kind of active sites/phase and the number of active sites is proportional to e^-_{redox} . The same is true for the pair NF-Fe and NF-Plasma-Fe. In general, the plasma treatment leads to a 40-time increased number of catalytic active sites. We note here that this proportional relation does not necessarily mean that all redox active nickel sites are catalytically active or have the same turnover frequency.^a As widely reported for NiO_xH_y phases,⁵⁰ iron incorporation leads to a changed Tafel slope and a 30-time increased activity per e^-_{redox} indicating a higher intrinsic catalytic activity per active site. Combining these two effects with an increase of the electrolyte temperature to 60 °C results in an increase of the OER activity by $30 \times 40 \times 6 = 7200$ times compared to untreated NF at the same potential at 25 °C and positions NF-Plasma-Fe among the most active, recently benchmarked OER catalysts (Fig. 7 and 4c).⁹

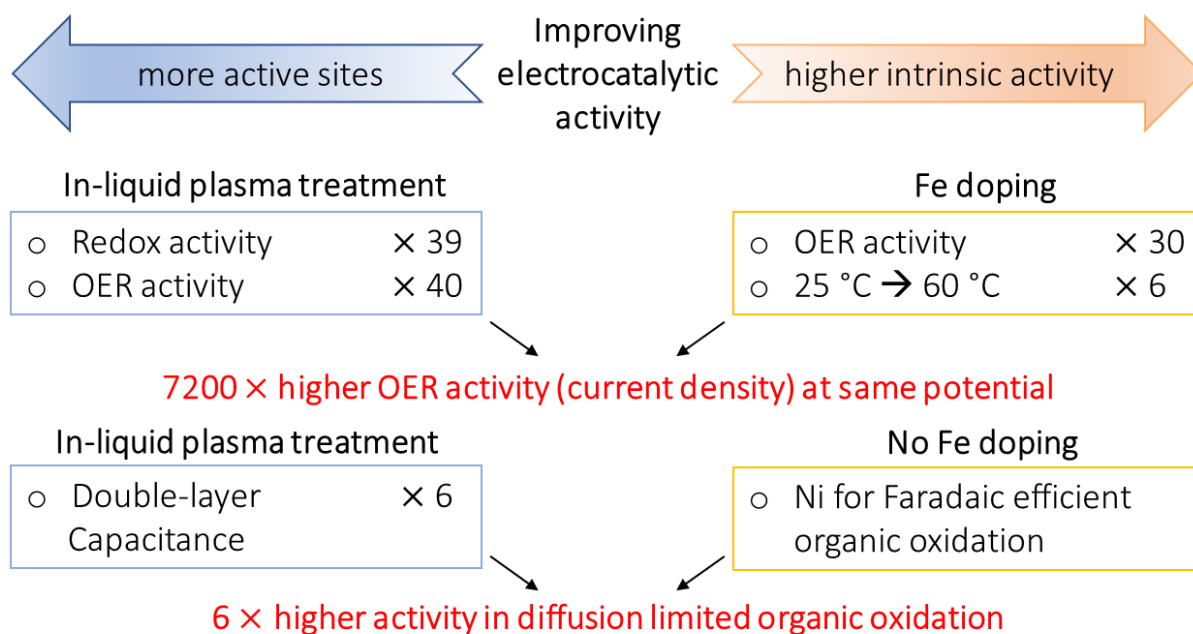


Fig. 7. Two ways to improve the activity of an electrocatalyst. Herein, the number of active sites was increased using an in-liquid plasma treatment, and the intrinsic activity was tuned by the addition of iron and by increasing the temperature. Compared to bare NF at RT, the OER activity was 7200 times larger at the same potential vs RHE. For the OER, the iron containing electrodes were 30 times more active than the one without; for the alcohol/aldehyde oxidation, it was the other way around and the iron free electrodes showed an around three times higher activity at the same potential.

For the oxidation of alcohols and aldehydes in 0.1 M KOH, two reaction mechanisms were proposed by Choi et al.^{4,43,51} One is potential independent meaning that the current density does not increase with increasing anodic potential after the onset. In this mechanism, the NiOOH reacts as a chemical oxidation reagent in the rate-determining step (rds) and the role of the applied potential is merely to regenerate NiOOH. The other one is potential dependent, which is favored at higher pH values (herein 1 M KOH is used) and involves the oxidation of [Ni^{III}-O^{II}]. In [Ni^{III}-O^{II}] oxidation, the [O^{II}] ligand cannot be considered redox innocent and various works have shown that an oxygen species with electrophilic character is formed.^{22,23,34,36,37,40,52} It has been suggested that the formation of electrophilic oxygen (*[O_e], see Supplementary Information for a discussion on the nature of this species) from water or hydroxide is the initial reaction step for the OER and the oxidation of alcohols.^{34,51,53-55} Thus, both reactions will compete for this intermediate. The oxidation potential of alcohols is much lower than the one of water,⁵⁶ and, in general, alcohol oxidation has been reported to proceed quickly after *[O_e] formation.^{34,57} However, for nickel based water oxidation, the consecutive reactions have been described to be the rds.^{34,55,58} So, a good alcohol oxidation catalyst should easily form *[O_e] and then have higher reaction barriers for the consecutive OER steps.⁵¹ This leads to a high selectivity towards alcohol oxidation. However, if the OER rds of a catalyst is the *[O_e] formation and the consecutive OER steps proceed quickly, it will immediately perform OER after *[O_e] formation.³⁴ *[O_e] formation was observed to occur simultaneously with the nickel oxidation peak at 1.36 V_{RHE} (Fig. 5a, 5b, S20, and

S21),^{34,36,54} which involves around 1.6 electrons per Ni^{II}.²²⁻²⁴ Herein, without organic substrate, no catalytic current is observed after the nickel oxidation peak until around 1.50 V_{RHE} (Fig. 5a), most likely because a consecutive OER step requires 1.50 eV. In this potential range (1.36-1.50 V_{RHE}), the pure nickel catalyst can perform the oxidation of an alcohol without the interference of the OER which has also been shown previously by rotating ring-disk electrode measurements.³⁴ The incorporation of iron into the electrode has three effects (Fig. 5a and b): (i) it decreases the current density of selective MeOH oxidation (the current density at 1.40 V_{RHE} is around three times higher for NF-Plasma than NF-Plasma-Fe), (ii) it increases the redox peak potential, and (iii) it reduces the OER onset potential. Thus, the * $[O_e]$ formation becomes more difficult while the following rds OER step becomes easier resulting in a higher OER activity that onsets directly after the redox peak.⁵¹ Therefore, a smaller range and lower maximum potential exist where selective MeOH oxidation could be performed on NF-Plasma-Fe compared to NF-Plasma. Taken together, for a pure nickel catalyst, the rds occurs after the initial adsorption and oxidation of OH⁻/H₂O (* $[O_e]$ formation), while the initial * $[O_e]$ formation is rate-determining for an iron-nickel catalyst. This conclusion also agrees with recent theoretical investigations.^{34,55} Therefore, NF-Plasma is the less active OER but better alcohol/aldehyde oxidation catalyst. As the NF-Plasma and NF-Plasma-Fe have the same morphology and surface area (Fig. 2d-h, S12b, and S13), the observed differences originate only from electronic and mechanistic effects.

After comparing iron containing and iron free samples, we arrive at the effects of the plasma treatment. NF-Plasma shows 40 times higher OER activity than NF; however, for the BA/HMF oxidation, under steady state conditions, NF-Plasma is only around six times more active. Thus, in contrast to the OER activity, the BA/HMF oxidation activity is not proportional to e^-_{redox} . However, herein and by others, it has been proposed that both reactions have similar kinds of active sites.³⁴ Therefore, another effect must be responsible for the reduced activity enhancement. In this regard, the HMF/BA oxidation steady state measurements clearly show an effect of substrate concentration and stirring revealing that the reaction is limited by substrate diffusion. For the OER, where hydroxide must be transported, no such effects have been observed, which is reasonable considering a hydroxide diffusion coefficient of 45 $\mu(\text{cm}^2/\text{s})$ and a concentration of 1 M compared to 9.2 and 8.5 $\mu(\text{cm}^2/\text{s})$ for HMF and BA, respectively, and a concentration of 0.1 M.⁵⁹⁻⁶¹ Furthermore, diffusion limitations are probably particularly relevant in this study due to the high current densities resulting from the large density of active sites or adsorbed * $[O_e]$ per geometrical surface area electrode. Diffusion limitations in the near electrode area affect how the surface area influences the catalytic turnover. In this regard, the HMF/BA activity scales well with the six times enhanced C_{dl} while the OER activity scales with the 40 times enhanced e^-_{redox} (Fig. S11). Fig. 8 shows how nanostructuring of surfaces affects the electrical double-layer (EDL) and the inner Helmholtz layer (IHL) area.⁶² The EDL of the anode contains more

solvated anions than cations while the distribution of the two species is even in the bulk electrolyte. During the C_{dl} measurement mainly hydroxide is migrating into the EDL which is several nm thick.⁶³ The IHL is comprised of specifically adsorbed species (e.g., hydroxide or OER reaction intermediates) and thus thinner than 0.3 nm. For the same material, e^-_{redox} should scale with the IHL area, as specific ad-/desorption of ions is required for the redox activity (e.g., $Ni(OH)_2 \rightarrow NiOOH + e^- + H^+$). The IHL area increases severely more than the EDL area, which is caused by the different thicknesses of these two layers. The larger thickness of the EDL results in a reduced sensitivity to nanostructures smaller than the EDL thickness (Figure 9b). Therefore, the green IHL area in Fig. 8b shows a much stronger increase from the nanostructuring than the gray EDL area. Coming back to the HMF/BA oxidation, in a stirred electrocatalytic reaction, the simplest model for diffusion is that on the surface of the electrode a diffusion layer exists followed by a bulk solution with constant concentration.⁶⁴ A larger surface results in a larger diffusion-layer to bulk-solution interface and thus faster mass transport. In our case, the EDL thickness during mainly hydroxide migration of the C_{dl} measurements scales well with the increased diffusion during electrocatalysis, probably because the diffusion layers of both processes have comparable thicknesses. The observation that the OER scales with e^-_{redox} (scales with the IHP area) and the diffusion-controlled reaction with the C_{dl} (scales with the EDL area) also implies that the optimal electrode morphology for both processes is different.

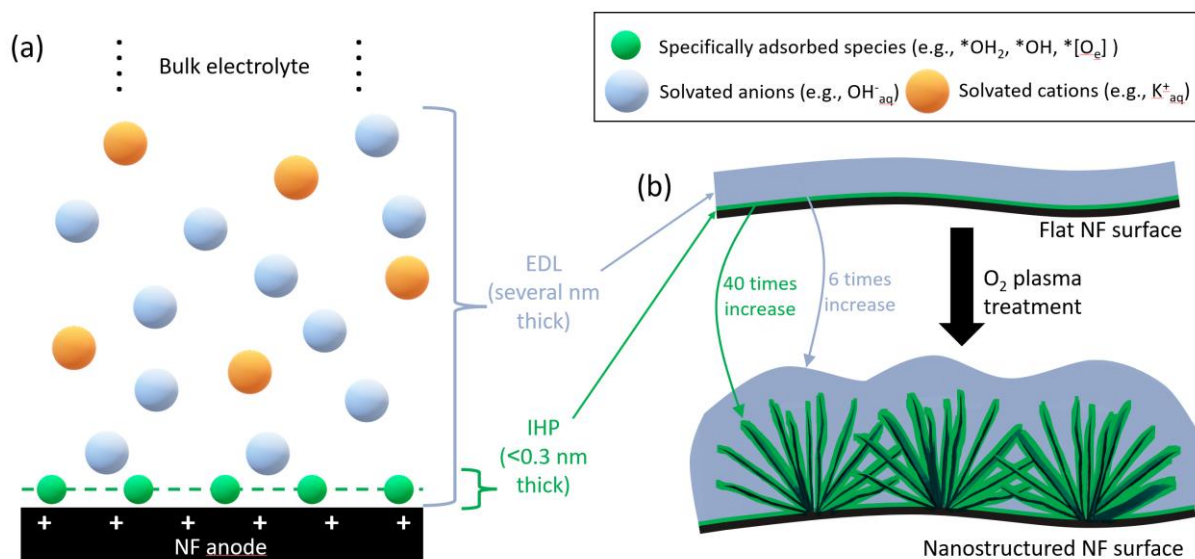


Fig. 8. Scheme on the effect of surface nanostructuring of an anode on the inner Helmholtz plane (IHP) and the electrical double-layer (EDL). (a) A scheme showing the IHP, which is comprised of specifically adsorbed species, and the EDL, which starts at the electrode surface until the bulk electrolyte. The EDL of an anode contains more anions than cations while both are evenly distributed in the bulk electrolyte. (b) Depiction of a flat and a through oxygen plasma treatment obtain nanostructured NF surface with three nano-flowers. The IHP area is proportional to the green area and the EDL to the grey area. Due to the much larger thickness of the EDL compared to the IHP, the IHP area increases by several times more than the EDL area through the nanostructuring. The thickness of the diffusion layer during electrocatalytic HMF/BA oxidation with stirring

seems to be comparable to the one of the EDL for hydroxide migration during the double-layer capacitance measurements.

Conclusion

Using a novel, glow discharge, thermal, in-liquid oxygen plasma electrolysis approach, the flat nickel foam surface was modified to a hierarchically nanostructured surface with a flower-like appearance and an increased surface area and number of active sites. This plasma electrolysis approach involves no expensive or toxic chemicals (only water and KOH), consumes little energy, takes only 10 min, requires only a simple two-electrode setup with a high-power supply and no external heating. We could incorporate iron into the plasma modified NF (NF-Plasma-Fe) under retention of its surface morphology and surface area by plain cycling. In this fashion, the high surface area electrode can be chemically modified to suit various catalytic processes. The obtained electrodes are self-supported, binder free, and stable under strongly anodic catalytic conditions and heavy gas formation due to the much harsher conditions during their synthesis. When applying NF-Plasma-Fe as electrodes for the OER, an industrially relevant current density of 500 mA/cm² could be achieved at 1.473±0.013 V_{RHE} (60 °C) and no activity decrease could be observed over 140 h at 200 mA/cm². Furthermore, using a NF-Plasma electrode, the electrocatalytic oxidation of 5-hydroxymethylfuran and benzyl alcohol with merely water as oxygen source could be accomplished selectively at current densities up to 800 mA/cm². Moreover, we found that the OER activity scales with the amount of redox active sites and that the organic oxidation reactions are limited by diffusion. This behaviour is explained with a model considering the diffusion coefficients, inner Helmholtz plain, the electrical double-layer, and the electrode morphology. In addition, we reveal that even though iron containing samples are more active for the OER, they are less suitable for the oxidation of alcohols and aldehydes.

Data availability

The data supporting the findings of this study are available in the paper and its Supplementary Information. Extra data are available from the corresponding authors on reasonable request.

Footnotes

‡ It has been proposed that this Ni^{II} oxidation involves 1-1.6 electrons per Ni site.²²⁻²⁴ Herein, we merely use this parameter to compare the plasma and not plasma treated samples relatively towards each other. We assume that the numbers of electrons transferred per nickel site are the same in the non plasma treated and the plasma treated samples. Therefore, for this relative comparison, it is not necessary to assume how many electrons are transferred per Ni sites.

Notes and References

- 1 O. J. Guerra, J. Zhang, J. Eichman, P. Denholm, J. Kurtz and B.-M. Hodge, *Energy Environ. Sci.*, 2020, **13**, 1909–1922.
- 2 Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, *Science*, 2017, **355**, eaad4998.
- 3 Y. Li, X. Wei, L. Chen and J. Shi, *Angew. Chemie Int. Ed.*, 2021, **60**, 19550–19571.
- 4 L. Du, Y. Sun and B. You, *Mater. Reports Energy*, 2021, **1**, 100004.
- 5 M. Chatti, J. L. Gardiner, M. Fournier, B. Johannessen, T. Williams, T. R. Gengenbach, N. Pai, C. Nguyen, D. R. MacFarlane, R. K. Hocking and A. N. Simonov, *Nat. Catal.*, 2019, **2**, 457–465.
- 6 Y. Lum, J. E. Huang, Z. Wang, M. Luo, D. H. Nam, W. R. Leow, B. Chen, J. Wicks, Y. C. Li, Y. Wang, C. T. Dinh, J. Li, T. T. Zhuang, F. Li, T. K. Sham, D. Sinton and E. H. Sargent, *Nat. Catal.*, 2020, **3**, 14–22.
- 7 O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson and S. Few, *Int. J. Hydrogen Energy*, 2017, **42**, 30470–30492.
- 8 H. Yang, M. Driess and P. W. Menezes, *Adv. Energy Mater.*, 2021, **11**, 2102074.
- 9 A. Peugeot, C. E. Creissen, D. Karapinar, H. N. Tran, M. Schreiber and M. Fontecave, *Joule*, 2021, **5**, 1281–1300.
- 10 F. Yang, K. Cheng, X. Xue, J. Yin, G. Wang and D. Cao, *Electrochim. Acta*, 2013, **107**, 194–199.
- 11 H. Yin, L. Jiang, P. Liu, M. Al-Mamun, Y. Wang, Y. L. Zhong, H. Yang, D. Wang, Z. Tang and H. Zhao, *Nano Res.*, 2018, **11**, 3959–3971.
- 12 N. K. Chaudhari, H. Jin, B. Kim and K. Lee, *Nanoscale*, 2017, **9**, 12231–12247.
- 13 H. Zhou, F. Yu, Q. Zhu, J. Sun, F. Qin, L. Yu, J. Bao, Y. Yu, S. Chen and Z. Ren, *Energy Environ. Sci.*, 2018, **11**, 2858–2864.
- 14 X. Xu, F. Song and X. Hu, *Nat. Commun.*, 2016, **7**, 1–7.
- 15 S. Sikdar, P. V Menezes, R. Maccione, T. Jacob and P. L. Menezes, *Nanomaterials*, 2021, **11**, 1375.
- 16 S. Dou, L. Tao, R. Wang, S. El Hankari, R. Chen and S. Wang, *Adv. Mater.*, 2018, **30**, 1705850.
- 17 H. Liang, F. Ming and H. N. Alshareef, *Adv. Energy Mater.*, 2018, **8**, 1801804.
- 18 D. Wang, Y. Zou, L. Tao, Y. Zhang, Z. Liu, S. Du, S. Zang and S. Wang, *Chinese Chem. Lett.*, 2019, **30**, 826–838.
- 19 M. D. Klapkiv, *Mater. Sci.*, 1996, **31**, 494–499.
- 20 D. Y. Chung, P. P. Lopes, P. Farinazzo Bergamo Dias Martins, H. He, T. Kawaguchi, P. Zapol, H. You, D. Tripkovic, D. Strmcnik, Y. Zhu, S. Seifert, S. Lee, V. R. Stamenkovic and N. M. Markovic, *Nat. Energy*, 2020, **5**, 222–230.
- 21 J. N. Hausmann, S. Mebs, K. Laun, I. Zebger, H. Dau, P. W. Menezes and M. Driess, *Energy Environ. Sci.*, 2020, **13**, 3607–3619.
- 22 D. A. Kuznetsov, B. Han, Y. Yu, R. R. Rao, J. Hwang, Y. Román-Leshkov and Y. Shao-Horn, *Joule*, 2018, **2**, 225–244.

- 23 M. Merrill, M. Worsley, A. Wittstock, J. Biener and M. Stadermann, *J. Electroanal. Chem.*, 2014, **717–718**, 177–188.
- 24 D. A. Corrigan and R. M. Bendert, *J. Electrochem. Soc.*, 1989, **136**, 723–728.
- 25 M. B. Stevens, C. D. M. Trang, L. J. Enman, J. Deng and S. W. Boettcher, *J. Am. Chem. Soc.*, 2017, **139**, 11361–11364.
- 26 A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart and N. S. McIntyre, *Surf. Sci.*, 2006, **600**, 1771–1779.
- 27 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- 28 G. C. Allen, M. T. Curtis, A. J. Hooper and P. M. Tucker, *J. Chem. Soc., Dalton Trans.*, 1974, **14**, 1525–1530.
- 29 H. W. Nesbitt, D. Legrand and G. M. Bancroft, *Phys. Chem. Miner.*, 2000, **27**, 357–366.
- 30 J. N. Hausmann, R. Beltrán-Suito, S. Mebs, V. Hlukhyy, T. F. Fässler, H. Dau, M. Driess and P. W. Menezes, *Adv. Mater.*, 2021, **33**, 2008823.
- 31 M. S. Burke, S. Zou, L. J. Enman, J. E. Kellon, C. A. Gabor, E. Pledger and S. W. Boettcher, *J. Phys. Chem. Lett.*, 2015, **6**, 3737–3742.
- 32 S. Lee, L. Bai and X. Hu, *Angew. Chemie Int. Ed.*, 2020, **59**, 8072–8077.
- 33 M. B. Stevens, L. J. Enman, A. S. Batchellor, M. R. Cosby, A. E. Vise, C. D. M. Trang and S. W. Boettcher, *Chem. Mater.*, 2017, **29**, 120–140.
- 34 H. B. Tao, Y. Xu, X. Huang, J. Chen, L. Pei, J. Zhang, J. G. Chen and B. Liu, *Joule*, 2019, **3**, 1498–1509.
- 35 A. M. Ullman, C. N. Brodsky, N. Li, S. L. Zheng and D. G. Nocera, *J. Am. Chem. Soc.*, 2016, **138**, 4229–4236.
- 36 O. Diaz-Morales, D. Ferrus-Suspedra and M. T. M. Koper, *Chem. Sci.*, 2016, **7**, 2639–2645.
- 37 C. Hu, Y. Hu, C. Fan, L. Yang, Y. Zhang, H. Li and W. Xie, *Angew. Chemie Int. Ed.*, 2021, **60**, 19774–19778.
- 38 J. R. Swierk, S. Klaus, L. Trotochaud, A. T. Bell and T. D. Tilley, *J. Phys. Chem. C*, 2015, **119**, 19022–19029.
- 39 G. George and S. Anandhan, *RSC Adv.*, 2014, **4**, 62009–62020.
- 40 S. Lee, K. Banjac, M. Lingenfelder and X. Hu, *Angew. Chemie Int. Ed.*, 2019, **58**, 10295–10299.
- 41 D. Chen, X. Xiong, B. Zhao, M. A. Mahmoud, M. A. El-Sayed and M. Liu, *Adv. Sci.*, 2016, **3**, 1500433.
- 42 M. Fleischmann, K. Korinek and D. Pletcher, *J. Chem. Soc. Perkin Trans. 2*, 1972, 1396.
- 43 M. T. Bender, Y. C. Lam, S. Hammes-Schiffer and K.-S. Choi, *J. Am. Chem. Soc.*, 2020, **142**, 21538–21547.
- 44 J. A. Matthews, in *Encyclopedia of Environmental Change*, SAGE Publications, Ltd., 2455 Teller Road, Thousand Oaks, California 91320, 2020.
- 45 T. Pfennig, J. M. Carraher, A. Chemburkar, R. L. Johnson, A. T. Anderson, J.-P. Tessonier, M.

- Neurock and B. H. Shanks, *Green Chem.*, 2017, **19**, 4879–4888.
- 46 N. Brun, P. Hessemann and D. Esposito, *Chem. Sci.*, 2017, **8**, 4724–4738.
- 47 H. Huang, C. Yu, X. Han, H. Huang, Q. Wei, W. Guo, Z. Wang and J. Qiu, *Energy Environ. Sci.*, 2020, **13**, 4990–4999.
- 48 D. H. Nam, B. J. Taitt and K. S. Choi, *ACS Catal.*, 2018, **8**, 1197–1206.
- 49 W.-J. Liu, L. Dang, Z. Xu, H.-Q. Yu, S. Jin and G. W. Huber, *ACS Catal.*, 2018, **8**, 5533–5541.
- 50 S. Anantharaj, S. Kundu and S. Noda, *Nano Energy*, 2021, **80**, 105514.
- 51 N. Heidary and N. Kornienko, *Chem. Sci.*, 2020, **11**, 1798–1806.
- 52 R. Gottschall, R. Schöllhorn, M. Muhler, N. Jansen, D. Walcher and P. Gütlich, *Inorg. Chem.*, 1998, **37**, 1513–1518.
- 53 H. Zhou, Z. Li, S. Xu, L. Lu, M. Xu, K. Ji, R. Ge, Y. Yan, L. Ma, X. Kong, L. Zheng and H. Duan, *Angew. Chemie Int. Ed.*, 2021, **60**, 8976–8982.
- 54 D. Drevon, M. Görlin, P. Chernev, L. Xi, H. Dau and K. M. Lange, *Sci. Rep.*, 2019, **9**, 1532.
- 55 H. Xiao, H. Shin and W. A. Goddard, *Proc. Natl. Acad. Sci.*, 2018, **115**, 5872–5877.
- 56 M. I. Abdullah, A. Hameed, N. Zhang, M. H. Islam, M. Ma and B. G. Pollet, *ACS Appl. Mater. Interfaces*, 2021, **13**, 30603–30613.
- 57 B. Mondal, N. Karjule, C. Singh, R. Shimoni, M. Volokh, I. Hod and M. Shalom, *Adv. Energy Mater.*, 2021, **11**, 2101858.
- 58 A. Govind Rajan, J. M. P. Martirez and E. A. Carter, *J. Am. Chem. Soc.*, 2020, **142**, 3600–3612.
- 59 S. H. Lee and J. C. Rasaiah, *J. Chem. Phys.*, 2011, **135**, 1–10.
- 60 F. Gharagheizi, *Ind. Eng. Chem. Res.*, 2012, **51**, 2797–2803.
- 61 K. Yui, N. Yamazaki and T. Funazukuri, *J. Chem. Eng. Data*, 2013, **58**, 183–186.
- 62 M. Dunwell, Y. Yan and B. Xu, *Curr. Opin. Chem. Eng.*, 2018, **20**, 151–158.
- 63 G. Li, L. Anderson, Y. Chen, M. Pan and P. Y. Abel Chuang, *Sustain. Energy Fuels*, 2018, **2**, 237–251.
- 64 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Ind, New York, 2nd ed., 2001.

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Author contributions

P.W.M. initiated the idea and developed it together with J.N.H.; J.N.H. performed the electrocatalysis experiments, analysed all data, and wrote the first draft; P.V.M. performed the plasma synthesis and the SEM experiments; M.D., T.J., and P.W.M. supervised the study; G.V. performed the organic oxidation experiments; K.L. and I.Z. performed the Raman experiments; T.D. performed the XPS measurements. All authors discussed the results and commented on the manuscript.

Competing interest

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at

In-Liquid Plasma Modified Nickel Foam: NiOOH/NiFeOOH Active Site Multiplication for Electrocatalytic Alcohol, Aldehyde, and Water Oxidation

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We report a novel in-liquid oxygen plasma approach for the growth of hierarchical nanostructures on nickel foam leading to surface area and active site enhancement. The obtained electrode was suitable for the oxidation of water and organic species

