Gold-Supported Cerium-Doped NiO_x Catalysts for Water Oxidation

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Abstract

The development of high-performance catalysts for the oxygen evolution reaction (OER) is paramount for cost-effective conversion of renewable electricity to fuels and chemicals. Here we report the significant enhancement of the OER activity of electrodeposited NiO_x films resulting from the combined effects of using cerium as a dopant and gold as a metal support. This NiCeO_x-Au catalyst delivers high OER activity in alkaline media, and is among the most active OER electrocatalysts reported to date. Based on experimental observations and theoretical modelling, we ascribe the activity to a combination of electronic, geometric and support effects, where highly active under-coordinated sites at the oxide support interface are modified by the local chemical binding environment and by doping the host Ni oxide with Ce. The NiCeO_x-Au catalyst is further demonstrated in a device context by pairing it with a nickel-molybdenum hydrogen evolution catalyst in a water electrolyser, which delivers 50 mA consistently at 1.5 V over 24 hours of continuous operation.

Water oxidation, also known as the oxygen evolution reaction (OER), is a critical reaction in many energy conversion technologies such as electrolyzers, regenerative fuel cells, metal-air batteries and photoelectrochemical cells¹⁻⁴. These energy conversion devices are promising technologies to address the intermittency issue⁵. However, commercialization of these devices is hampered by the challenge in developing high-performance yet cost-effective catalysts to overcome sluggish OER kinetics⁴⁻⁶. In acid media, the best-known OER catalysts are iridium and ruthenium-based oxides, but the scarcity of the metal constituents limit the ability to scale to the terawatt level needed⁷. In alkaline media, oxides of first-row transition metals display similarly high activity^{6, 8-14}. Nevertheless, there is significant room for improvement. Known strategies to improve activity include nanostructuring to increase surface area and alloying to improve intrinsic activity, with NiFeO_x being the most explored binary alloy, among others such as NiCoO_x, CoFeO_x, and NiCeO_x that have also been investigated^{8, 15-21}. Another alternative is through the use of an underlying metal support, as has been demonstrated for unary oxides based on nickel, cobalt and manganese²²⁻²⁴. This catalyst-substrate interaction has been suggested to modify the binding energy of the reaction intermediates via either electronic structure perturbation of the active sites or direct participation in the reaction²³⁻²⁵. Nevertheless, fundamental understanding of these effects is still lacking, especially for more complicated systems such as multi-metallic oxides deposited on metals.

Herein, we report the remarkable enhancement of the water oxidation activity of electrodeposited NiO_x films resulting from the combined effects of using a cerium dopant and a gold metal support. Optimization of the molar ratio of Ni to Ce in the deposition solution revealed that a 95:5 Ni:Ce solution ratio delivers the best performance. We also find that supporting NiCeO_x (95:5 Ni:Ce ratio) on a thin layer of gold (henceforth referred to as NiCeO_x-Au) results in a significant increase in the OER activity compared to NiCeO_x supported on bare glassy carbon (GC) (henceforth referred to as NiCeO_x-GC). The NiCeO_x-Au catalyst outperforms the 26 best water oxidation catalysts benchmarked in a recent study²⁶, which makes NiCeO_x-Au among the most active OER catalysts in base reported to date.

Synthesis and characterization of NiCeO_x-Au electrocatalyst

Various Ni_{1-x}Ce_xO_y-Au catalysts were synthesized by electrodepositing Ni- and Ce-nitrate precursors onto an Au-coated GC disk. This technique is similar to that used in the OER benchmarking study,²⁶ which allows for a direct comparison of the activity of Ni_{1-x}Ce_xO_y-Au and the benchmarked catalysts. During the deposition process, the nitrate ions are reduced to ammonium ions along with the generation of hydroxide ions, leading to an increase in the local pH near the electrode surface and induces the deposition of the metal ions^{18, 27}.

The best-performing NiCeO_x film was characterized by a suite of microscopy and spectroscopy methods. In-plane scanning electron microscopy (SEM) reveals the nanostructured morphology of the NiCeO_x film (Fig. 1a). This is in contrast to the relatively flat surface observed for the Au-coated substrate (Fig. 1a inset). Cross-sectional SEM (Fig. 1b) indicates that the NiCeO_x layer, synthesized via a 10 second deposition, is approximately 80 nm thick.

Survey X-ray photoelectron spectroscopy (XPS, Fig. 1c) coupled with Auger elemental mapping (Supplementary Fig. 1a) suggests that both Ni and Ce were deposited uniformly across the electrode. Of

note is that Fe, which has been shown to considerably affect the OER activity of Ni-based catalysts, is below the detection limits of XPS²⁸⁻³⁰. The absence of Fe was further corroborated by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The depth profile of NiCeO_x-Au (Fig. 1c) suggests that Au potentially diffuses into the NiCeO_x film. This, and the fact that electrodeposition can create a porous, electrolyte-permeable structure that exposes underlying active sites^{27, 31}, could allow for metal oxide-gold interfacial sites that drive the OER. High-resolution XPS spectra for the Ni 2p and Ce 3d regions of NiCeO_x-Au, NiO_x-Au, and CeO_x-Au were also recorded (Fig. 1d). Deconvolution of the Ni 2p and Ce 3d peaks reveals a 80:20 Ni:Ce surface atomic ratio, which differs from the 95:5 Ni:Ce molar ratio in the deposition solution. This suggests that Ce is either preferentially deposited or that it segregates to the surface. On the other hand, the Ni 2p_{3/2} peak at 855.4 eV is indicative of Ni(OH)₂, consistent with the deposition process described above³². This is further supported by the O 1s region of NiCeO_x-Au (Supplementary Fig. 1b), where the peak at 531.5 eV corresponds to hydroxyl bonds³³. The Ce 3d spectrum is more complicated and can be deconvoluted into 10 different peaks indicative of Ce in both 3+ and 4+ states, as observed in previous bulk studies^{34, 35}. Lastly, the lack of any Ni or Ce X-ray diffraction (XRD) peaks (Supplementary Fig. 1c) suggests absence of long-range crystallinity in NiCeO_x-Au.

Electrochemical evaluation of NiCeO_x-Au

Electrochemical testing of NiCeO_x-Au was carried out using a three-electrode electrochemical cell in a Fe-free alkaline environment (1 M NaOH, verified by ICP analysis). The measured cyclic voltammograms (Supplementary Fig. 2) indicate that NiCeO_x-Au is a highly active OER catalyst, requiring only 271 mV overpotential to reach 10 mA/cm² and achieving 13.3 mA/cm² at 280 mV overpotential (Fig. 2a inset). This current density is significantly higher than that obtained with pure NiO_x-GC (Fig. 2a). We note that the performance of our NiO_x-GC is comparable to that of Fe-free NiO_x in literature and that the activity of NiCeO_x-Au in an unpurified and Fe-free environment is similar (Supplementary Fig. 3), which suggests that Fe does not play a significant role in our NiCeO_x-Au system²⁸. Figure 2a also reveals that the presence of both Ce and Au is required for the significant enhancement; we will examine this point more thoroughly further below. All 4 tested catalysts (NiCeO_x-Au, NiCeO_x-GC, NiO_x-Au, NiO_x-GC) exhibit comparable Ni^{2+/3+} peak areas on their first anodic sweep (Supplementary Fig. 4a), which implies that the activity difference is not due to variations in material loading. Subsequent optimization studies reveal that an 80 nm catalyst film with a 100 nm gold support delivers the highest performance, possibly due to an optimal amount of electrolyte-accessible metal oxide-gold interfacial sites (details in Supplementary Information). We also find only a modest Au substrate effect on CoCeO_x, possibly due to overshooting the optimal binding energy region, which suggests that for the NiCeO_x-Au system, Ni is a critical component of the active site. Hence, the most significant catalyst-substrate interaction is found for NiCeO_x, with NiCeO_x-Au exhibiting the highest OER activity.

To put the above results in context, in Fig. 2b we compare the performance of NiCeO_x-Au with state-of-the-art OER catalysts reported in a recent benchmarking study²⁶. The initial activity of each film is compared to its activity after 2 hours of continuous OER at 10 mA/cm² using the benchmarking protocol (details in Supplementary Information). Previously benchmarked OER catalysts were categorized into three groups based on their composition, namely those that are Ni-based, Co-based or precious-metal-

based. NiCeO_x-Au clearly outperforms all other catalysts, both before and after the stability test on a geometric surface area basis. In addition, we also electrodeposited our own NiFeO_x films, generally acknowledged to be the best binary non-precious metal oxide OER catalyst, using the exact same conditions as that for NiCeO_x-Au for further controlled benchmarking. Optimization of the Ni to Fe molar ratio in the deposition solution (97:3 Ni:Fe) led to the NiFeO_x-Au catalyst with the best performance, requiring 279 mV overpotential to reach 10 mA/cm² (Supplementary Fig. 5). We note that this performance is consistent with those obtained by electrodeposited NiFeO_x catalysts synthesized by others^{28, 30, 36}, and is comparable to that achieved by our NiCeO_x-Au catalyst (Fig. 2b inset).

To study the intrinsic activity of NiCeO_x-Au, we estimated the turnover frequency (TOF) by normalizing the rate of O₂ generation to the total number of metal ions present, as determined by ICP analysis, a methodology described previously³⁶. By this method, the TOF of NiCeO_x-Au at 280 mV overpotential was determined to be 0.080 /s, reflecting a highly active catalyst, more than an order of magnitude higher than that of NiCeO_x-GC and approximately double that of NiFeO_x-Au, 0.046 /s (Fig. 2b inset, details in Methods section). We note that the true TOF of the most active sites in NiCeO_x-Au would be even higher, as the use of ICP for TOF normalization provides a lower-bound limit on TOF since it presumes every metal cation in the film performs identically, turning over the reaction at exactly the same rate. In reality, there will likely be a distribution of site-specific activities amongst the metal cations, thus the true TOF of the most active sites would be even higher. These comparisons of intrinsic activity confirm the outstanding OER activity of NiCeO_x-Au, as well as the significant enhancement effect arising from catalyst-substrate interactions.

Understanding NiCeO_x-Au through theoretical calculations

A key question, however, remains as to how Ce-doping and the Au support significantly improve the OER activity of NiO_x. To shed light on this, we performed density functional theory plus Hubbard U (DFT+U) calculations using a well-established procedure that has been demonstrated to deliver a basis for interpreting the relationship between catalyst composition and OER overpotential (details in the computational methods section)^{37, 38}. In particular, we investigated a series of distinct representative model Ni-based catalysts with and without a Ce dopant, and with and without a gold support. The calculated OER activities are summarized in the volcano plot (Fig. 2c), with the most active system near the volcano peak consisting of a Ce-doped finite NiO_x film, forming stripes of NiO_x, adsorbed on-top of an Au(111) surface. This catalyst exposes under-coordinated edge sites with two possible active sites: the Ce dopant atom positioned at the substrate-catalyst interface (denoted Ce_{edge} (▲)) and a neighbouring Ni atom (denoted Ni_{edge} (▲)). For the Ce_{edge} (▲) site, calculations predict an overpotential of 0.44 V, whereas for the Ni_{edge} (▲) site an even lower overpotential of 0.37 V is found. Importantly, this value is reasonably close to the experimental value of 0.271 V at 10 mA/cm² (Fig. 2b), which would explain the OER activity enhancement observed experimentally. In contrast, the pure NiOOH(01 $\bar{1}$ 2) surface is associated with much higher overpotentials of 0.67 and 1.02 V for bridge (Ni_{bridge} (●)) and on-top (Ni_{top} (●)) sites, respectively, in agreement with previous theoretical findings^{29, 39}. The other modelled systems include Ce-doped NiOOH(01 $\bar{1}$ 2) surface (denoted Ce_{top} (●)), undoped (denoted Ni_{basal} (□)) and Ce-doped (denoted Ce_{basal} (■)) infinite Au-supported NiO_x films, and undoped finite Au-supported NiO_x (denoted Ni_{edge} (▲)), which were found to have moderate overpotentials ranging from

0.53 to 0.82 V. Therefore, calculations reveal that the coexistence of both Ce and Au in the vicinity of under-coordinated Ni edge sites is necessary to explain the improved OER activity of NiCeO_x-Au.

To deconvolute the individual contributions from Ce, Au, and the catalyst's active site geometry on the OER performance of NiCeO_x-Au, we present in Fig. 3a the changes in OER descriptor $\Delta G_O - \Delta G_{OH}$ values for the distinct model catalysts considered. The shaded region at *ca.* 1.6 eV indicates the optimal region for the OER descriptor value based on scaling relations and is associated with the volcano peak³⁷. We probed different types of active sites to design an active site motif with the optimal descriptor value. First, we find that Ce incorporation into any of the investigated host NiO_x catalyst systems alters the electronic properties of the active sites resulting in an OER descriptor value lower in magnitude, which could be attributed to the oxophilicity of Ce. Interestingly, this influence of Ce doping is rather similar for the three main model catalysts (Fig. 3a), namely, unsupported NiOOH(01 $\bar{1}$ 2) surface (Ni_{top} (●) → Ce_{top} (●) sites), finite NiO_x on Au (Ni_{edge} (▲) → Ce_{edge} (▲)), and infinite NiO_x on Au (Ni_{basal} (□) → Ce_{basal} (■) sites). We note that a smaller OER descriptor value can result in a lower overpotential, as in the case of the unsupported NiOOH(01 $\bar{1}$ 2) and the finite Au-supported NiO_x systems, though smaller descriptor values do not always translate to a lower overpotential since this can cause a transition from the right to the left leg of the volcano (Fig. 2c), as is the case for the infinite Au-supported NiO_x film. Overall, the theoretical findings of NiCeO_x-Au agree well with experimental observations that the addition of small amounts of Ce to NiO_x, supported on either GC or Au, leads to strong electronic interactions and a significant improvement in the OER activity (Fig. 3b and Supplementary Fig. 2). The electronic interactions within the Ni_{1-x}Ce_xO_y-Au systems can be observed experimentally by means of cyclic voltammetry (Supplementary Fig. 2a), where an anodic shift of the Ni(OH)₂/NiOOH peak at *ca.* 1.4 V vs. RHE is observed with increasing Ce content, suggesting a strong interaction between Ni and Ce arising from the substitutional incorporation of Ce into Ni sites. These features are consistent with experimental observations from related studies on Ni-Fe and Co-Fe oxides whereby strong electronic interactions were also observed^{21, 27}.

Next, we examined the effect of gold, which may modify the binding energies of the OER intermediates in different ways: by perturbing the electronic properties of the active sites, enabling existence of certain active site geometries, or directly participating in the bond with the intermediates giving rise to bidentate sites^{22-25, 40}. Simulations reveal that the presence of Au leads to a similar lowering of the OER descriptor value for both pure and doped finite and infinite Au-supported NiO_x films *i.e.* Ni_{top} (●) → Ni_{basal} (□) or Ni_{edge} (▲), and Ce_{top} (●) → Ce_{basal} (■) or Ce_{edge} (▲) in Fig. 3a. Nevertheless, this is not sufficient to explain the significant enhancement of the OER performance found experimentally for NiCeO_x-Au since none of the 4 aforementioned Au supported sites exhibits an optimum OER descriptor value.

Additionally, we considered geometric effects by focusing on finite Au-supported NiO_x films, as these structures feature both the Ni_{basal} (□) sites and under-coordinated sites at the catalyst-substrate interface. Indeed, the OER descriptor value for the undoped finite film, Ni_{edge} (▲), lies between those of the undoped NiOOH(01 $\bar{1}$ 2) surface, Ni_{top} (●), and the undoped infinite NiO_x film, Ni_{basal} (□) (Fig. 3a). Introduction of Ce into finite Au-supported NiO_x results in a strengthening of the OER descriptor towards

the optimum region, with the Ni_{edge} (▲) site at the substrate-catalyst interface possessing a slightly more ideal value than the Ce_{edge} (▲) site, though both values are excellent. Thus, theory shows that NiCeO_x-Au contains highly active sites, Ni_{edge} (▲) and Ce_{edge} (▲), whose binding energies for key OER intermediates are tuned appropriately. Experimental evidence for the effects of Au comes from the observation that NiCeO_x-GC displays neither a cathodic Ni^{2+/3+} peak on the first sweep nor an anodic Ni^{2+/3+} peak on the second sweep, unlike NiCeO_x-Au (Supplementary Fig. 4). The much smaller drop in the cathodic peak observed for the latter suggests that, similar to Ni systems, the outer NiCeO_x film may be trapped by insulating Ni(OH)₂ at the electrode-catalyst interface and the presence of Au may enhance the electrochemical accessibility of the active sites through either geometrical structure changes or enhanced conductivity^{20, 27}. The Ni, Ce and Au all play important roles in achieving such well-tuned binding energies through electronic and geometric effects. The DFT calculations of Fig. 3a elucidate the different contributions. Figure 3b represents an experimental analogue to Fig. 3a, where catalytic activity is directly compared among NiO_x-GC, NiO_x-Au, NiCeO_x-GC and NiCeO_x-Au, by means of the overpotential required to reach 10 mA/cm². Consistent with theory, we see that Ce doping and the use of an Au support each individually lead to improved catalytic activity; combining both effects simultaneously leads to the highest performance.

Overall, we find that a combination of the local active site geometry, under-coordinated edge sites, and the presence of both Au and Ce in finite NiO_x films provides the right synergetic balance between electronic and geometric effects, resulting in a near-optimal OER descriptor value (Fig. 3a). This, accompanied by the right energetics of the OER intermediates, places NiCeO_x-Au at the top of the OER activity volcano and explains the experimentally measured activity enhancement over bare NiO_x.

Evaluation of NiCeO_x-Au in a water electrolysis setup

Finally, to test the viability of NiCeO_x-Au for larger-scale water electrolysis, we constructed a high surface area electrode with this catalyst and incorporated it into an electrolyser (Fig. 4a inset). The anode was fabricated by first electrodepositing a thin layer of gold followed by NiCeO_x onto a Ni foam support, while the cathode was made via electrodeposition of NiMo onto a Ni foam support²⁶. SEM imaging and visual inspection of the electrodes (Supplementary Fig. 6) confirm successful catalyst deposition. The electrodes were first tested separately in a three-electrode setup to assess their individual performance for the relevant reactions. Both electrodes displayed high activity in 6 M KOH electrolyte, with the NiCeO_x-based anode requiring 244 mV overpotential to drive the OER at 100 mA/cm² and the NiMo-based cathode requiring 103 mV overpotential to drive the same amount of cathodic HER current (Fig. 4b). Both electrodes also exhibited higher performance than a bare Ni foam (Supplementary Fig. 7). The electrodes were then loaded into individual compartments of an H-cell separated by a membrane (Supplementary Fig. 8) to ensure that the current generated is due to water splitting rather than fuel crossover. The resultant electrolyser exhibited excellent performance at room temperature, delivering 50 mA (equivalent to 10 mA/cm²) at approximately 1.5 V consistently over a 24-hour period (Fig. 4a). This result provides an initial assessment of the feasibility for using NiCeO_x-Au in operational water electrolysis systems.

Conclusions

In summary, we have leveraged a combination of electronic, geometric and support effects in complex multi-component catalytic systems to engineer a catalyst operating in base that is competitive with the best OER electrocatalysts to date. Our experimental observations and theoretical calculations show that this outstanding performance can be attributed to geometric and electronic effects between the Ni-oxide host and the Ce dopant, which modifies the local electronic environment resulting in favourable binding energies of the OER intermediates, and the Ni-oxide host and gold, which facilitates access to highly active geometrically under-coordinated Ni sites. We emphasize that this new catalyst is very close to the theoretically predicted optimal activity based on scaling relations between OOH and OH; approaches to break this relation would allow for further activity enhancements as discussed in a recent perspective⁴¹. Future work will be focused on utilizing advanced spectroscopic techniques to probe the electronic interactions between the various components in this system, and exploring the effects of Ce and Au on other 3d-transition metals to provide a general guideline for designing multi-component electrocatalytic systems.

This work highlights the potential of combining multiple approaches simultaneously to tune binding energies of reaction intermediates to achieve improvements in catalyst performance. Based on experimental observations and theoretical modelling, we have illustrated that a combination of catalyst-doping and catalyst-support interactions can be utilized to enhance the OER activity of NiO_x, and have demonstrated that NiCeO_x-Au is promising for alkaline OER catalysis in an operational device environment. These findings represent an important advance towards the development of high-performance OER electrocatalysts.

Methods

Synthesis of NiCeO_x-Au. NiCeO_x-Au was synthesized by electrodepositing Ni and Ce onto an Au-coated substrate which was prepared by sputter-coating 10 nm of Ti followed by 100 nm of gold onto a GC disk (Sigradur G HTW Hochtemperatur-Werkstoffe GmbH). Electrodeposition was carried out in a 100 mL beaker with a carbon rod counter electrode and an Ag/AgCl reference electrode. The beaker, carbon rod, and GC disk holder were cleaned in aqua regia, and the Ag/AgCl reference electrode was cleaned in 1 M HCl to avoid metal contamination. The deposition electrolyte (95:5 Ni:Ce by mol %) consisted of 1.105 g of nickel nitrate (99.9985 %, Strem Chemicals) and 0.087 g of cerium nitrate (99.99 %, Sigma-Aldrich) dissolved in 40 mL of Millipore water. The deposition current of -16 mA/cm² was held for 10 seconds. Ni_{1-x}Ce_xO_y-Au of differing Ni to Ce ratios, gold thickness and catalyst thickness, NiCeO_x (95:5) on bare GC, and NiFeO_x of various Ni to Fe ratios and CoCeO_x (95:5 Co:Ce by mol %) on Au-coated GC and bare GC were also prepared with the same amount of charge passed for each sample.

Physical and chemical characterization. The morphology of the NiCeO_x-Au catalyst was assessed by using SEM (FEI Magellan 400 XHR) with a 5 kV beam voltage and a 25 pA beam current. The thickness of the NiCeO_x-Au catalyst was imaged by cross-sectional SEM. Prior to imaging, the sample was prepared by focused ion beam (FIB, FEI Strata 235DB dual-beam FIB/SEM) milling. First, 1 μm of Pt was deposited on a 3 μm x 3 μm area using an electron beam voltage of 2 kV and spot 5 (~640 pA) to protect the catalyst's surface from ion-beam damage. Then, coarse milling was carried out by high current ion-beam

(300 pA, 30 kV), followed by a cleaning cross section with low current ion-beam (10 pA, 30 kV) to preserve catalyst features. The cross-sectional image was subsequently taken using SEM with a 45 degree angle tilt-correction. The reported thickness is the average of 5 measurements taken at different points.

The elemental composition of NiCeO_x-Au was examined using XPS (PHI 5000 VersaProbe) with Al K α 1486.6 eV radiation. Survey XPS spectra were obtained in a binding energy range from 0 to 1100 eV. High resolution spectra of Ni-2p and Ce-3d peak regions were obtained in a binding energy range from 846 to 914 eV with 50 scans of 0.1 eV energy step and 40 ms per step parameters. The binding energies of the peaks were calibrated to that of adventitious carbon at 284.5 eV. Elemental mapping of the NiCeO_x-Au catalyst was carried out using Auger electron spectroscopy (PHI 700 Scanning Auger Nanoprobe) with beam parameters of 10 kV and 10 nA. The Auger peaks used for Ni, Ce, and Au were 849, 87, and 2022 eV respectively.

Mass loading and elemental analysis of NiCeO_x-Au and NiFeO_x-Au were determined by ICP-OES (Thermo Scientific ICAP 6300 Duo View Spectrometer). Prior to analysis, the catalyst films deposited on GC disks were dissolved in Aqua Regia, which consists of 3 parts HCl (Fisher Scientific) and 1 part HNO₃ (Fisher Scientific), overnight before dilution to 5% acid with Millipore water. The elemental composition of a blank GC disk, the Ni(NO₃)₃ precursor, and the Fe-free NaOH electrolyte were also analysed. Ni, Ce, Au, and Fe standards (Sigma Aldrich) were used for calibration.

The crystallinity of the NiCeO_x-Au catalyst was examined using XRD (Phillips PANanalytical X'Pert Pro) with Cu K α radiation and operated at 45 kV and 40 mA. The scan parameters were a scan range of 10 to 90 degrees and 0.05 degrees step intervals with each step held for 1 second.

Electrochemical characterization. Fundamental electrochemical testing in a 1 M Fe-free sodium hydroxide (99.99%, Sigma-Aldrich) electrolyte was carried out in an acid-cleaned three-electrode setup, consisting of each OER catalyst as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl reference electrode in a polypropylene electrochemical cell. Electrolyte purification was carried out following a procedure similar to that of Trotochaud *et al.* by using Ni(OH)₂ powder to precipitate trace Fe²⁸. The Pt wire was cleaned in aqua regia for 30 s prior to OER testing. The Ag/AgCl electrode was cleaned in 1 M HCl, and the polypropylene electrochemical cell was cleaned and stored in 1 M H₂SO₄ prior to the experiment. For the rotating disk electrode measurements, the potential was cycled between 1.2 V and 1.65 V vs. RHE (or higher for low-activity catalysts) at 10 mV/s with a shaft rotation rate of 400 rpm. The OER catalysts were tested immediately after insertion into the test electrolyte and we only show the initial scans to reduce the possibility of Fe contamination. A stability test was performed by holding the working electrode at 10 mA/cm² for 2 hours. The reference potential scale was calibrated to the RHE using a Pt wire (Sigma-Aldrich) as the working electrode in a H₂-saturated electrolyte, and a value of 1.01 V was obtained.

TOF calculations. The turnover frequency (TOF) at 280 mV overpotential was calculated using the following formula:

$$TOF = \frac{\text{number of } O_2 \text{ turnovers}}{\text{number of metal ions}}$$

The number of O₂ turnover was calculated using the current density at 280 mV overpotential via:

#O₂ turnover

$$= \left(j \frac{mA}{cm^2} \right) (0.196 cm^2) \left(\frac{1C/s}{1000mA} \right) \left(\frac{1mol e^-}{96485C} \right) \left(\frac{1mol O_2}{4mol e^-} \right) \left(\frac{6.02 \times 10^{23} molecules O_2}{1mol O_2} \right)$$

$$= 3.06 \times 10^{14} O_2/s \text{ per } \frac{mA}{cm^2}$$

The number of metal ions was determined from ICP analysis.

For NiCeO_x-Au:

13.3 mA/cm² at 280 mV overpotential, ICP: 5.12*10¹⁶ metal ions (4.64*10¹⁶ Ni and 4.77*10¹⁵ Ce)

Therefore, TOF of NiCeO_x-Au = **0.0795 s⁻¹**

For NiFeO_x-Au:

10.9 mA/cm² at 280 mV overpotential, ICP: 7.23*10¹⁶ metal ions (6.31*10¹⁶ Ni and 9.21*10¹⁵ Fe)

Therefore, TOF of NiFeO_x-Au = **0.0461 s⁻¹**

For NiCeO_x-GC:

1.0 mA/cm² at 280 mV overpotential, ICP: 5.85*10¹⁶ metal ions (5.36*10¹⁶ Ni and 4.90*10¹⁵ Ce)

Therefore, TOF of NiCeO_x-Au = **0.0052 s⁻¹**

Computational methods. Density functional theory calculations within the Hubbard *U* approach (DFT+*U*) were carried out using projector-augmented wave (PAW) pseudopotentials⁴² and the Perdew-Burke-Ernzenhof⁴³ (PBE) exchange correlation functional, as implemented in the VASP code^{44, 45}. For a better description of the Ni(3d) and Ce(4f) electrons, the Hubbard effective terms $U_{eff}(Ni) = 6.45$ eV and $U_{eff}(Ce) = 4.5$ eV were added to the PBE functional through the rotationally invariant approach proposed by Dudarev *et al*⁴⁶. The $U_{eff}(Ni)$ value was taken from the Materials Project database⁴⁷, while the $U_{eff}(Ce)$ value was adopted from self-consistent calculations by Fabris *et al*.⁴⁸ using the linear response approach.

All periodic slab calculations were carried out using a plane wave kinetic energy cutoff of 500 eV and a vacuum spacing of at least 15 Å. In these calculations, the Brillouin zone was sampled in each direction on a Monkhorst-Pack⁴⁹ k-point grid of size $\text{int}(20/a)$, where *a* corresponds to the unit cell length. To model the unsupported NiOOH (01 $\bar{1}$ 2) surfaces, four Ni–O layers with a (2x2) periodicity were employed as reported in our previous work²⁹. In these structures, the two topmost layers were allowed to relax, whereas the rest of atoms were kept fixed at their bulk positions. On the other hand, the infinite Au-supported NiO_x thin films were simulated as an O–Ni–O trilayer adsorbed on-top of three layers of an Au(111) surface with an optimized lattice constant of $a_{lat} = 4.157$ Å. This structure with a (2x2) periodicity is similar to the one proposed in a combined experimental and theoretical work on Au-supported CoO_x thin films⁵⁰. From the infinite Au-supported NiO_x thin films, the analogue finite NiO_x thin films with a (2x4) periodicity were constructed. During geometry optimizations of the NiO_x thin films, the oxide layer and the first atomic layer of the Au(111) surface were allow to relax. Spin-polarized calculations were performed when needed, and geometries were relaxed until a maximum threshold

force of 0.02 eV/Å was fulfilled. The magnetic moments for the most energetically favourable and active OER catalyst in this work, *i.e.* finite Au-supported NiO_x, are reported in Supplementary Fig. 9.

The Gibbs free energies of the OER intermediates were calculated at T = 300 K by adding the potential energy, the zero point energy (ZPE) and the vibrational enthalpy and entropy contributions obtained by means of the harmonic approximation (see Supplementary Table 1).

The overpotential for the considered model NiO_x-based catalysts was determined assuming the OER mechanism occurs in an acidic environment with the following elementary steps⁵¹:

where * indicates an active surface site.

The computational hydrogen electrode model³⁸ allows for the expression of the chemical potentials of protons and electrons at any given pH and applied potential. As a result, the theoretical overpotential, η_{theory} , can be obtained from the Gibbs free energy differences at each step, ΔG_i ($i = 1, \dots, 4$), as:

$$\eta_{\text{theor}} = \max[\Delta a_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23[\text{V}] \quad (5)$$

It is worth highlighting that this definition is independent of pH, and therefore, is also applicable to an alkaline environment. The surface termination under relevant OER conditions was determined by calculating the surface Pourbaix diagram (see Supplementary Fig. 10).

Electrolyser testing. Two separate electrodes were prepared via electrodeposition. For the anode, a thin layer of gold was first electrodeposited on a 5 cm² Ni foam substrate (Goodfellow) at -0.8 V vs. Ag/AgCl for 1 minute, using a deposition solution with 0.136 g of gold chloride (Aldrich) and 5.682 g of sodium sulphate (Sigma-Aldrich) dissolved in 80 mL of water. NiCeO_x was then electrodeposited on the Au-coated Ni foam substrate at a deposition current of -16 mA/cm² for 1 minute. For the cathode, NiMo was electrodeposited in the same cell setup at -80 mA/cm² for 20 minutes. The deposition solution consisted of 3.16 g of nickel sulphate (Sigma-Aldrich), 1.92 g of sodium molybdate (Sigma-Aldrich), and 3.52g of sodium citrate (Sigma-Aldrich) dissolved in 80 ml water and mixed with 4 ml NH₄OH (Fisher Scientific). The electrodes were first tested separately in a three-electrode electrochemical cell setup at room temperature in 6 M KOH electrolyte. Cyclic voltammetry runs were performed at a scan rate of 10 mV/s and at potential ranges of -0.15 to 0.075 V and 1.15 to 1.51 V vs. RHE for the NiMo and NiCeO_x electrodes respectively. A bare Ni foam substrate was also tested for comparison. Next, the electrodes were integrated into a two-electrode setup as shown in Supplementary Fig. 8 and a chronopotentiometry run at 50 mA was carried out over 24 hours. Prior to the run, the cell was held at 50 mA for 5 minutes for the Ni on the anode to be fully oxidized to the 3+ state. All runs were 100 % iR compensated.

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Author contributions

J.W.D.N and T.F.J. conceived and designed the experiments. J.W.D.N., P.C., and C.K. carried out material synthesis. J.W.D.N. and P.C. performed physical and chemical characterization. J.W.D.N., P.C., and C.K. conducted the electrochemical measurements. M.G.-M., M.B. and A.V. formulated, defined and designed the computational part of the paper. M.G.-M. and M.B. performed all the DFT calculations under supervision from A.V. All authors discussed the results and co-wrote the paper.

Additional information

Supplementary information is available online. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to A.V. and T.F.J.

Competing interests

The authors declare no competing financial interests.

Figure 1. Physical and chemical characterization of NiCeO_x-Au. (a) Top-down SEM image of NiCeO_x-Au. The inset shows a bare Au-coated glassy carbon substrate. (b) Cross-sectional SEM image of the NiCeO_x-Au film. The top Pt layer was deposited to protect the catalyst from ion beam damage during the milling process and is present for cross-section imaging purpose only. (c) XPS depth profile of NiCeO_x-Au. The initial scan prior to sputtering is represented by the black solid line, and subsequent scans were taken after additional 1 minute Ar sputters. (d) High resolution XPS spectra of the Ni 2p and Ce 3d regions of NiCeO_x-Au, NiO_x-Au, and CeO_x-Au.

Figure 2. Experimental and theoretical OER performance of NiCeO_x-Au. (a) Activity difference between NiCeO_x supported on either Au-coated or bare GC disk. The substrate-activity relationship for NiO_x and CoCeO_x (95:5) is also shown. (b) OER performance of NiCeO_x-Au compared to those of the catalysts reported in the benchmarking work by McCrory *et al.*²⁶. The catalysts are color-coded based on their composition. The dotted line represents points for which the activity did not change after being held at 10 mA/cm² for 2 hours. The inset displays the current density and TOF at 280 mV overpotential for NiCeO_x-Au and our optimized NiFeO_x-Au catalyst. (c) Representation of the theoretical overpotential as a function of O* and HO* adsorption Gibbs energies. Green circles, gold squares and gold triangles refer to the NiOOH (011̄2) surface, and infinite and finite NiO_x-Au thin films, respectively. Grey filled markers indicate Ce-doped structures. Insets of the different type of structures are shown. Colour coding is as follows: Au (gold), Ni (green), Ce (grey), O (red), H (white).

Figure 3. Deconvolution of the various effects modifying the OER performance of NiCeO_x-Au. (a) Effects due to Ce-doping, gold support and geometry based on DFT+*U* calculations. The region shaded in red indicates ideal binding energy of the intermediates. Green circles, gold squares and gold triangles refer to the NiOOH (011̄2) surface, and infinite and finite NiO_x-Au thin films, respectively. Grey-filled markers indicate Ce-doped structures, while grey and gold arrows show the effects of Ce-doping and the gold support. A zoomed-in view of the different active sites (marked with black circles) is also shown. (b) Experimental overpotentials for NiO_x and NiCeO_x supported on either bare or Au-coated GC substrates, with the same colour coding as used in (a).

Figure 4. Evaluation of the performance of NiCeO_x-Au in an electrolyser setup. (a) Performance of the electrolyser held at 50 mA for 24 hours at room temperature. Inset: schematic of the electrolyser, which utilizes a NiCeO_x on Au-coated Ni foam anode and a NiMo on Ni foam cathode, separated by an anion-exchange membrane in a 6 M KOH electrolyte. (b) Performance of the individual electrodes tested in a three-electrode electrochemical cell setup. The counter and reference electrodes were a carbon rod and Ag/AgCl respectively.