Water splitting by electrolysis at high current densities under 1.6 volts†

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Splitting water into hydrogen and oxygen by electrolysis using electricity from intermittent waste heat, wind, or solar energies is one of the easiest and cleanest methods for high-purity hydrogen production and an effective way to store the excess electrical power. The key dilemma for efficient large-scale production of hydrogen by splitting of water via the hydrogen and oxygen evolution reactions (HER and OER, respectively) is the high overpotential required, especially for the OER. We report an exceptionally active and durable OER catalyst yielding current densities of 500 and 1000 mA cm⁻² at overpotentials of only 259 mV and 289 mV in alkaline electrolyte, respectively, fulfilling the commercial criteria of the OER process. Together with a good HER catalyst, we have achieved the commercially required current densities of 500 and 1000 mA cm⁻² at 1.586 and 1.657 V, respectively, with very good stability, dramatically lower than any previously reported voltage. This discovery sets the stage for large-scale hydrogen production by water splitting using excess electrical power whenever and wherever available.

Broader context

Water electrolysis for hydrogen production is one of the easiest and cleanest routes to store the considerable intermittent clean energy resources (wind, waste heat, solar, etc.) on a large scale. At present, mass production in industry remains challenging (<5%) due to the high cost of noble metals as catalysts in acid and low energy conversion efficiency of non-noble metal catalysts in base. Although many water electrolyzers have been constructed experimentally by designing robust electrocatalysts, most of them still need cell voltages significantly larger than 1.8 V to deliver 200 mA cm⁻², unsatisfactory for the commercial requirements. In particular, for H₂ to play an important role in the energy sector, water splitting at current density ≥500 mA cm⁻² under 1.6 V is required, in which the OER is the main bottleneck with poor efficiency. Here we develop a straightforward room-temperature strategy to fabricate a robust and durable OER catalyst yielding current densities of 500 and 1000 mA cm⁻² at overpotentials of only 259 mV and 289 mV in alkaline electrolyte, respectively, fulfilling the commercial criteria of the OER process. Integrating it into a water electrolyzer can realize the commercial electrolysis current of 500 and 1000 mA cm⁻² at around 1.6 V with excellent durability. This discovery is an advanced development toward large-scale H₂ production using excess electrical power whenever and wherever available.

Increasing the fraction of clean energy over fossil fuels including coal, petroleum, and natural gas will certainly reduce pollution,† but large-scale utilization of the considerable intermittent clean energy resources, such as wind, wave power, waste heat, and solar energies, requires reliable storage of electrical power, and the same applies to the oversupply of the electrical power from sources such as nuclear power plants during the night. Hydrogen is a good energy carrier for energy storage. Water electrolyzers are a promising commercial apparatus to produce high-purity hydrogen with unlimited water resources, among which alkaline water electrolyzers are more appealing than those based on proton exchange membranes (PEMs) in acid.²,³ This is primarily because low-cost electrocatalysts, instead of noble metal-based catalysts, can be utilized in alkaline media. However, efficient and mass hydrogen production in industry has not been widely deployed at present (<5% hydrogen production) due to the high cost of the noble metals as catalysts in acid and the low energy conversion efficiency of the non-noble metal catalysts in base. Although a variety of alkaline water electrolyzers have been constructed by designing robust electrocatalysts,²,³ most of them...
require cell voltages significantly larger than 1.8 V to deliver 200 mA cm\(^{-2}\), unsatisfactory for the commercial requirements of 1.8–2.4 V for current densities of 200–400 mA cm\(^{-2}\). In particular, the key challenge is to employ the overall water splitting durably at high current densities above 500 mA cm\(^{-2}\). Thus, it is of high desire to develop robust electrocatalysts to substantially expedite the strongly uphill water splitting process\(^6\)-\(^8\) and to maintain the activity at high current densities, so as to greatly improve the electrolysis efficiency for large-scale water splitting.

Essential to the full water splitting reaction is the half reaction called the oxygen evolution reaction (OER), which is the bottleneck due to the sluggish kinetics arising from the rigid O–O double bond formation and the multiproton-coupled electron transfer steps.\(^9\)-\(^11\) Although substantial advancements have been accomplished in the development of robust OER catalysts, neither the benchmark noble IrO\(_2\) and RuO\(_2\) catalysts,\(^12\) nor the non-precious OER electrocatalysts, including transition metal oxides,\(^5\)-\(^11\) nitrides,\(^14\) selenides,\(^15\) phosphides,\(^16\) and phosphate,\(^17\)-\(^18\) are effective enough for an efficient anodic OER. In particular, very few catalysts can satisfy the strict industrial criteria that the OER process should be energetically catalyzed over a long period at extremely high current densities (\(\geq 500\) mA cm\(^{-2}\)) with overpotentials \(\leq 300\) mV,\(^10\),\(^17\) which hinders the widespread implementation of these available electrocatalysts. It is noted that iron metaphosphate is the only OER catalyst satisfying the strict criteria;\(^17\) however, the preparation method is complicated, and neither environmentally friendly nor safe, since toxic PH\(_3\) is involved. In addition, the stability of this catalyst operated at a high current density of 500 mA cm\(^{-2}\) is still not satisfactory, not to mention at even higher current densities. Aiming at commercially practical high-performing and environmentally friendly OER catalysts, we report an outstanding oxygen-evolving electrocatalyst constructed by three-dimensional porous interwoven (Ni,Fe) oxyhydroxide nanorod arrays, which are mainly derived from amorphous Ni/Fe (oxy)hydroxide mesoporous films on Ni foams synthesized by a simple yet industrially compatible strategy based on room-temperature mechanical stirring. Then an outstanding alkaline water electrolyzer was constructed by pairing this OER catalyst with another robust MoNi\(_4\) catalyst for the HER, which exhibits a record low voltage of about 1.6 V for efficient overall-water-splitting activity and can be driven by different power sources, such as an AA battery or a commercial thermoelectric power generator.

The key in pursuing efficient OER electrocatalysts is to design catalysts with large surface area and high-density active sites directly grown on three-dimensional conductive porous scaffolds,\(^19\)-\(^21\) so that multiple levels of porosity with high-density active sites and good conductivity can be simultaneously integrated in the same device. Here we employed commercial Ni foams as the conductive support,\(^22\) and synthesized amorphous mesoporous Ni/Fe (oxy)hydroxide [(Ni,Fe)OOH] film on their surface by room-temperature mechanical stirring processing, which is normally used for preparing amorphous FeOOH for use in supercapacitors.\(^23\) Different from this conventional process, we creatively introduced a new chemical reaction between metallic Ni and FeCl\(_3\) during mechanical stirring, and synthesized amorphous FeOOH and Ni(OH)\(_2\) simultaneously, which is further evolved into a robust OER electrocatalyst during electrocatalysis as discussed below. This approach is very simple yet effective not involving any complicated procedures or poisonous chemicals relative to other growth procedures for preparing efficient OER catalysts, and is also different from traditional methods for preparing an OER catalyst by means of electrodeposition or hydrothermal synthesis of transition metal Ni/Fe oxides on Ni foam, since the Ni foam used here was etched and reacted with the solution to form Ni(OH)\(_2\) particles simultaneously.

After growth, deionized water cleaning and drying in air overnight are all that is required, and the as-prepared multiporous catalysts were then directly utilized as a self-supported anode for water oxidation reaction (Fig. 1a) using a three-electrode configuration in 1 M KOH as reported previously.\(^14\),\(^17\) For comparison, bare Ni foam, NiFe layered double hydroxide (LDH) nanosheets (Fig. S1, ESf), and the benchmark IrO\(_2\) catalysts on Ni foam were also included here. Apparently, as revealed in Fig. 1b, this amorphous (Ni,Fe)OOH electrode exhibited significantly enhanced catalytic OER activity. It requires an overpotential as low as 174 mV to achieve a current density of 50 mA cm\(^{-2}\) (Fig. 1c), which is 75, 165, and 179 mV less than the state-of-the-art NiFe nanosheets/Ni foam (249 mV), the benchmark IrO\(_2\) electrode (339 mV), and the Ni foam (353 mV), respectively. This overpotential is also substantially lower than that of any of the non-precious OER catalysts (Fig. 1d and Table S1, ESf) including recently reported excellent electrocatalysts Fe(PO\(_3\))\(_2\)-derived oxyhydroxide (213 mV),\(^17\) G-FeCoW oxyhydroxide/gold foam (234 mV),\(^12\) NiFe\(_1\)-Se\(_2\)-derived hydroxide nanosheets (209 mV),\(^15\) and NiFe LDH/graphene (335 mV),\(^24\) and so forth. At the overpotential of 300 mV, this catalyst can deliver a current density up to 1251 mA cm\(^{-2}\) (Fig. 1e and Table S1, ESf). In particular, our OER catalyst requires overpotentials of only 259 and 289 mV to achieve 500 and 1000 mA cm\(^{-2}\), respectively (Table S1, ESf). The outstanding catalytic behavior toward water oxidation is primarily due to the amorphous (Ni,Fe)OOH film, rather than the Ni foam support.

The operating durability is another essential performance index to assess the application in catalysis. To characterize the performance stability of this OER catalyst, we carried out water oxidation continuously at constant current densities (Fig. 1f). Notably, this catalyst withstood accelerated degradation tests, and the overpotential needed to reach a current density of 10 mA cm\(^{-2}\) varies very little at 154 mV for over 42 h, corroborating that the catalytic activity can be sustained upon OER testing. For applications, the catalyst must survive over a long period under high-current operation conditions (\(\geq 500\) mA cm\(^{-2}\)).\(^10\),\(^17\) This catalyst also shows sustainable capability of being operated continuously at 500 and 1000 mA cm\(^{-2}\) over 44 h with no significant decay (the overpotentials increase by merely 11 mV, 14 mV and 59 mV for current densities of 10, 500 and 1000 mA cm\(^{-2}\) after 44 h electrolysis), as shown in Fig. 1f, verifying its durability during OER electrocatalysis, which is far better than the previously reported Fe(PO\(_3\))\(_2\)-derived catalyst\(^17\) with higher catalyst loading and NiFe LDH/Cu nanowire arrays.
(Fig. S2, ESI†). The long-term robustness is probably attributed to the absence of polymer binder and to the strong interconnection between the topmost catalyst and the Ni foam support. To the best of our knowledge, this catalyst is adequate to fulfill the aforementioned strict criteria (low overpotential for high current density) toward commercial utilization of alkaline water electrolyzers, outperforming most non-noble OER catalysts reported thus far, as well as the benchmark precious IrO₂ catalysts. Although Ni/Fe (oxy)hydroxides are well known as promising OER electrocatalysts, most of the reported electrocatalysts, specifically the best one from NiFe LDH/rGO, still require 229 mV overpotentials to reach 50 mA cm⁻². In particular, there are no OER electrocatalysts made of Ni/Fe oxyhydroxides reporting good durability over a long time at large current densities like 500 and 1000 mA cm⁻², meaning that there is no such kind of OER catalyst fulfilling the aforementioned commercial criteria. Thus, although the active sites of our OER catalysts still originate from Ni/Fe (oxy)hydroxide evolved from a mixed composite of Ni(OH)₂ and FeOOH, it is interesting to point out that our catalyst is the first Ni/Fe (oxy)hydroxide-based OER catalyst satisfying the commercial criteria hitherto. This film is further confirmed to be a mixture of mainly amorphous FeOOH and Ni(OH)₂ by elaborate X-ray photoelectron spectroscopy (XPS) analysis (Fig. 3a–c). The Raman frequencies appearing at 140.2, 307.7, 413.6, 534.7, 720.9, and 1395.4 cm⁻¹ in the original samples (Fig. 3d) also indicated that the original samples were mainly composed of amorphous FeOOH at the surface.²⁷,²⁸ The strong binding between these catalysts and Ni foams, ensuring good electrical contact and efficient charge transfer between the catalyst and current collector Ni foam, was further indicated by the low series and charge-transfer resistances obtained via electrochemical impedance spectroscopy (EIS) (Fig. S4, ESI†). After the OER testing, due to the partial dissolution of FeOOH in concentrated KOH solution, an amorphous film is evolved into porous interwoven nanorod arrays, as shown in Fig. 2b, which exposed more active sites for the OER. These arrays are confirmed to be predominantly amorphous NiOOH mixed with a small amount of FeOOH nanoparticles by the high-resolution TEM image and
elemental mapping (Fig. 2d and Fig. S3, ESI†), energy-dispersive X-ray spectroscopy (EDS) (Fig. S5, ESI†), XPS (Fig. 3a–c), and Raman spectrum (Fig. 3d), in which two new strong modes located at 478.6 and 556.5 cm⁻¹ belonging to the Ni–O vibrations in NiOOH, rather than amorphous FeOOH, 27,30 were detected. The electrochemical double-layer capacitance (Cdl), estimated using a simple cyclic voltammetry method, directly manifests the electrochemically active surface area. 8,17,21 As shown in Fig. S6–S8 (ESI†), this amorphous (Ni,Fe)OOH electrode has a smaller Cdl value (5.9 mF cm⁻²) compared to the NiFe LDH nanosheets/ Ni foam (9.0 mF cm⁻²), but a slightly larger values than pristine Ni foam electrodes (5.0 mF cm⁻²), meaning that the active surface area of this (Ni,Fe)OOH electrode has no significant difference relative to the other two reference electrodes. Thus, the change of surface area cannot account for the 4.3- and 261.3-fold enhancement of its current density relative to the two reference materials, respectively, at 300 mV (Fig. 1b), unambiguously corroborating that this material has a higher intrinsic catalytic activity for water oxidation.15,17 To support this point, we roughly calculated the turnover frequencies (TOFs) at 300 mV to compare the intrinsic activities among amorphous (Ni,Fe)OOH, NiFe LDH, and IrO₂ catalysts based on the formula: TOF = j / A(F x n), where j, A, F, and n represent the current density (A cm⁻²), electrode area, Faraday constant (~96 485 C mol⁻¹), and the active site density of the catalysts (mole), respectively. It is demonstrated that this amorphous (Ni,Fe)OOH electrode still exhibits a much larger TOF value of 0.073 s⁻¹ at 300 mV overpotential, compared to that of the noble IrO₂ and NiFe LDH catalysts (0.0023 s⁻¹ and 0.018 s⁻¹, respectively). It is noted that this TOF for the (Ni,Fe)OOH electrode is probably underestimated, considering that not every metal atom is electrochemically active and exposed for the OER, and a small amount of FeOOH is soluble in KOH, but it is enough to confirm the better intrinsic activity of the (Ni,Fe)OOH catalyst than the other two catalysts. Its high intrinsic activity may originate from the possible incorporation of Fe cations in solution into NiOOH nanorod arrays, forming Ni₁₋ₓFeₓOOH nanorods with a 30-fold enhancement of the electrical conductivity and improved electronic structures, 29,31–33 which are stable in alkaline electrolyte. Meanwhile, we further extracted the Tafel slopes and exchange current densities of the electrocatalysts (Fig. S9, ESI†) including (Ni,Fe)OOH, IrO₂, and NiFe LDH on Ni foams. It is demonstrated that this (Ni,Fe)OOH catalyst exhibits the lowest Tafel slope (41.5 mV dec⁻¹) and the largest exchange current density (9.9 μA cm⁻²). After normalization by the active surface area, 34,35 it still has a larger exchange current density than NiFe LDH on Ni foam (Table S2, ESI†). Furthermore, FeOOH itself exhibits a very poor electrical conductivity, 20 limiting its electrocatalytic performance. In our case, the predominant compound of conductive NiOOH in the (Ni,Fe)OOH catalyst,
strong adhesion between the catalyst and the support, and the good conductivity of Ni foam facilitated the charge transfer between the catalyst and the support as highlighted in Fig. S4 (ESI†), which clearly revealed that the charge-transfer resistance of this amorphous electrode (1.29 Ω) is extremely small. These observations demonstrated that the real active sites for the OER may be associated with the porous nanorod arrays of Ni(OH)2-derived amorphous NiOOH mixed with FeOOH on Ni foam, which provides the final catalyst with high intrinsic catalytic activity, high electrochemically active surface area, highly exposed active sites, good electrical conductivity, and fast mass transport pathways.

To go a step further toward industrial applications, it is desirable to investigate full-cell water splitting that converts water to hydrogen at the cathode and oxygen at the anode simultaneously in a two-electrode configuration. Since this amorphous catalyst exhibits a record activity for OER catalysis, it is promising to integrate it with another robust HER electrolyzer. Here we paired our new OER electrolytocalysts with a MoNi4/MoO2 cuboid array, a robust non-noble metal-based HER electrocatalyst (Fig. S10 and S11, ESI†) to make an alkaline electrolyzer in 1 M KOH as shown in Fig. 4a. The steady-state potential polarization curves of this coupled (Ni,Fe)OOH(+)//MoNi4(−) water alkaline electrolyzer are shown in Fig. 4b and c. Impressively, the overall-water-splitting activity of this electrolyzer is far superior to the state-of-the-art IrO2(+)//Pt wire(−) coupled electrolyzer. At room temperature, our electrolyzer requires only a cell voltage of 1.464 V to achieve a water-splitting current density of 50 mA cm−2, suggesting ~84% electrical-to-fuel efficiency. In particular, this electrolyzer can generate extremely high current densities of 500 and 1000 mA cm−2 at only 1.586 and 1.657 V, respectively, surpassing even the industrial scale (200–400 mA cm−2 at 1.8–2.4 V) for hydrogen production, and outperforming the standard Ni and stainless-steel pair used in industrial alkaline electrolyzers by 495 mV and 474 mV at room temperature, respectively. This overpotential difference corresponds to ~24% and ~22% savings of voltage and energy, respectively. These two values of 1.464 and 1.586 V are record performance indices for overall alkaline water splitting, among the very best inexpensive bifunctional electrocatalysts or heterogeneous catalysts for overall water splitting (Fig. 4d, e and Table S3, ESI†).

Electrochemical durability is an important metric to assess the catalytic properties. It is remarkable that this electrolyzer can sustain its outstanding overall-water-splitting performance with no sign of decay for over 40 h when operated at constant current densities of 30, 500, 1000, and 1500 mA cm−2 (Fig. 4f). To the best of our knowledge, this is the only electrolyzer ever reported to achieve 50 mA cm−2 at a voltage of 1.464 V, and to maintain stability at high current densities of 500 and 1000 mA cm−2 at voltages of 1.586 and 1.657 V, respectively, for water electrolysis in a two-electrode configuration. Given its impressive activity, this electrolyzer can be easily promoted by a 1.5 V single-cell AA battery (Fig. S12, ESI†). Additionally, the kinetics and thermodynamics of this electrolyzer can be further boosted by increasing the reaction temperature to 40 °C, which requires a lower voltage of 1.562 V for 500 mA cm−2 (Fig. S13, ESI†), meaning further improvement of its catalytic activity at higher cell temperature as required by industrial use. Finally, the Faradaic efficiency for H2 and O2 generation by this electrolyzer was evaluated (Fig. S14, ESI†). We found that H2 and O2 gases were the only products from the electrolyzer with their volume ratio close to 2:1, and the efficiency was determined to be nearly 100% during water electrolysis over 1 h and beyond. Overall, these electrochemical results imply that our alkaline electrolyzer has great potential to be utilized for scale-up industrial implementation of hydrogen production with high efficiency and low cost.

In addition to the excellent overall-water-splitting activity, we propose to power the electrolyzer using a thermoelectric (TE) module (bismuth telluride) that converts heat to electricity (ESI†). At present, it is estimated that around 20 to 50% of industrial energy input is turned into waste heat ejected into the surrounding environment. Thus, capturing and storing the
Conclusions

In conclusion, a robust and durable OER catalyst composed of amorphous interwoven Ni/Fe (oxy)hydroxide nanowire arrays was fabricated at room temperature using a simple method. This OER catalyst requires the lowest overpotentials of 259 and 289 mV to achieve current densities of 500 and 1000 mA cm\(^{-2}\), respectively, in 1 M KOH with excellent electrochemical durability for over 40 h. In addition, by pairing it with another robust HER catalyst, an outstanding alkaline water electrolyzer was demonstrated with record low voltages of 1.586 and 1.657 V for current densities of 500 and 1000 mA cm\(^{-2}\), respectively, for overall water splitting, and can be potentially driven by a TE module using waste heat at temperatures below 100 °C. Our preparation method is simple and safe without any hydrothermal procedures or poisonous materials involved. All of the experiments were performed at room temperature without any high-temperature treatment to save energy, making it very promising and economically viable for large-scale industrial hydrogen production.

Conflicts of interest

The authors declare no competing financial interests.

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References


