FI SEVIER



Materials Today Physics



journal homepage: www.journals.elsevier.com/materials-today-physics

Efficient alkaline seawater oxidation by a three-dimensional core-shell dendritic NiCo@NiFe layered double hydroxide electrode

Fanghao Zhang ^{a,b}, Yifei Liu^c, Libo Wu^{a,d}, Minghui Ning ^a, Shaowei Song ^a, Xin Xiao ^a, Viktor G. Hadjiev^e, Donglei Emma Fan^{c,f}, Dezhi Wang ^a, Luo Yu^{a,*}, Shuo Chen^{a,**}, Zhifeng Ren^{a,***}

^a Department of Physics and Texas Center for Superconductivity at the University of Houston (TcSUH), University of Houston, Houston, TX, 77204, USA

^b Department of Chemistry, University of Houston, Houston, TX, 77204, USA

^c Materials Science and Engineering Program, Texas Materials Institute, The University of Texas at Austin, Austin, TX, 78712, USA

^d Materials Science and Engineering Program, University of Houston, Houston, TX, 77204, USA

e Department of Mechanical Engineering and Texas Centre for Superconductivity at the University of Houston (TcSUH), University of Houston, Houston, TX, 77204, USA

^f Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX, 78712, USA

ARTICLE INFO

Keywords: Oxygen evolution reaction Seawater Large surface area Core-shell structure

ABSTRACT

Seawater electrolysis for hydrogen generation has received increasing attention recently due to the scarcity of freshwater and the additional prospect of seawater desalination. The development of non-noble-metal-based oxygen evolution reaction (OER) electrocatalysts with high catalytic activity, long-term durability, and high OER selectivity is crucial for large-scale seawater electrolysis but remains a significant challenge. Here we develop a three-dimensional core-shell dendritic catalyst by vertically growing NiFe layered double hydroxide (LDH) nanosheets on dendritic NiCo branches (denoted as NiCo@NiFe LDH). The dendritic NiCo@NiFe LDH is highly active and stable in alkaline seawater due to its large surface area, fast charge transfer and effective mass transfer, and excellent corrosion resistance. It requires only a small overpotential of 222 mV to achieve current densities of 100 mA cm⁻² in 1 M KOH seawater. To deliver a large current density of 500 mA cm⁻², the NiCo@NiFe LDH is headen of ClO⁻ in the electrolyte following seawater electrolysis indicate the high OER selectivity of our catalyst. The stability of NiCo@NiFe LDH in seawater is proven by its small overpotential fluctuation at a constant current density of 500 mA cm⁻² over 100 h.

1. Introduction

Hydrogen, due to its high energy density and the absence of pollution in its use, has become the most attractive renewable energy carrier [1–3]. One sustainable way to produce hydrogen is electrolysis of water, which involves two half-reactions, the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) [4,5]. Between these, OER is the bottleneck because of its sluggish four-electron transfer process [6]. In the past few years, extensive effort has been devoted to developing efficient OER catalysts, including transition-metal oxides [7], layered double hydroxides (LDHs) [8–10], oxyhydroxides [11], nitrides [12–14], phosphides [15,16], sulfides [17], and selenides [18], to improve the efficiency of freshwater electrolysis. However, the shortage of freshwater is an urgent issue, especially for arid zones [19], while seawater is the most abundant resource on Earth. In addition, seawater electrolysis offers a possibility for seawater desalination. However, direct electrolysis of seawater faces the significant challenges of selectivity and stability, as discussed in recent representative reports [20–24]. Due to the presence of Cl⁻ in seawater, the undesired chlorine evolution reaction (ClER) and hypochlorite formation would occur on the anode in acidic and alkaline conditions, respectively, and either would compete with the OER and decrease overall seawater-splitting efficiency [25]. In addition, the impurities in seawater would degrade the catalyst by blocking some active sites. Due

https://doi.org/10.1016/j.mtphys.2022.100841

Received 29 July 2022; Received in revised form 1 September 2022; Accepted 3 September 2022 Available online 7 September 2022 2542-5293/© 2022 Elsevier Ltd. All rights reserved.

^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: yuluoke8@gmail.com (L. Yu), schen34@uh.edu (S. Chen), zren@uh.edu (Z. Ren).

to the high corrosivity of Cl⁻, catalysts' stability in seawater is also a major issue compared with that in freshwater electrolytes [19,26]. To address the aforementioned challenges, some strategies have been proposed [27–30]. Dionigi et al. suggested that high pH enables OER to be preferred rather than chloride oxidation reactions [31]. Our group developed three-dimensional (3D) porous structured catalysts for seawater electrolysis, proving that hierarchical structure accelerates electron and mass transport [20]. Dai et al. demonstrated that sulfate-and carbonate-ion co-intercalated NiFe LDH could improve corrosion resistance against Cl⁻ [21,22,32,33]. Therefore, a good seawater OER catalyst should have the following properties: 1) be chemically stable in alkaline conditions; 2) have a hierarchical structure with a large surface area; and 3) have a protective layer with high anti-corrosion ability.

Here we designed a 3D core-shell dendritic NiCo@NiFe LDH catalyst, in which NiFe LDH nanosheets were vertically grown on dendritic NiCo branches. The NiFe LDH outer layer serves as an OER-active and largesurface-area catalyst. The dendritic NiCo core not only serves as a largesurface-area, high-conductivity substrate, but also optimizes the electronic structure of the surface NiFe LDH for better catalytic performance. This NiCo@NiFe LDH was found to require extremely low overpotentials of 209 and 244 mV to achieve current densities of 100 and 500 mA cm⁻², respectively, in 1 M KOH. Benefiting from its large surface area with sufficient active sites, the NiCo@NiFe LDH still required only small overpotentials of 222 and 266 mV to achieve current densities of 100 and 500 mA cm⁻², respectively, in alkaline natural seawater (1 M KOH + seawater). The catalyst also exhibited impressive stability in seawater over 100 h at a current density of 500 mA cm⁻², in which the high corrosion resistance was found to play an important role.

2. Results and discussion

The dendritic NiCo core was first fabricated on Ni foam (Fig. 1a-c) by electrodeposition (synthesis details are provided in the Experimental Section of the ESI), and the dendritic structure contributes additional porosity to commercial Ni foam (Fig. S1, ESI) [34,35]. Following a second electrodeposition step, abundant NiFe LDH nanosheets were



Fig. 1. Microscopic and structural characterizations of catalysts. Scanning electron microscopy (SEM) images of (a–c) NiCo foam and (d–f) NiCo@NiFe LDH. (g and h) TEM images, (i) HRTEM image, and (j) SAED pattern of NiCo@NiFe LDH. (k) Raman spectra and high-resolution XPS spectra of (l) Ni 2p and (m) Fe 2p for NiCo@NiFe LDH and Ni@NiFe LDH.

homogeneously and vertically deposited on the branches of the dendritic NiCo foam, generating a favorable 3D core-shell nanostructure (Fig. 1d-f). The transmission electron microscopy (TEM) image displayed in Fig. 1g shows the core-shell nanostructure in greater detail, from which it can be seen that the core and shell are 1.14 and 0.59 μ m thick, respectively. Fig. 1h further reveals the mesoporous surface structure of the NiFe LDH nanosheets, showing that the thickness of each nanosheet is around 8.86 nm. A high-resolution TEM (HRTEM) image of the nanosheets (Fig. 1i) shows distinctive lattice fringes with interplanar spacings of 0.20 and 0.23 nm, which are assigned to the (018) and (015) planes, respectively, of NiFe LDH [36]. A selected area electron diffraction (SAED) pattern (Fig. 1j) recorded from the nanosheet shell also confirms the existence of the NiFe LDH phase.

To determine the chemical states of NiCo@NiFe LDH, Raman and Xray photoelectron spectroscopy (XPS) spectra were obtained. As shown in Fig. 1k, NiCo@NiFe LDH displays a Raman spectrum similar to that of Ni@NiFe LDH (pure NiFe LDH nanosheets grown on commercial Ni foam) and features vibration bands at 295, 442, 538, and 710 cm^{-1} . which are attributed to lattice vibrations of β -Ni_{1-x}Fe_x (OH)₂ [37], demonstrating successful fabrication of NiFe LDH on the surfaces of the NiCo foam. In the high-resolution XPS spectra of Ni 2p for NiCo@NiFe LDH and Ni@NiFe LDH (Figure 11), two doublet peaks (856.1 and 873.8 eV) belonging to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, as well as two satellite peaks, are detected, indicating the presence of the Ni²⁺ state in the two catalysts [38,39]. Similarly, as shown in Figure 1m, two doublet peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are located at 710.9 and 724.1 eV, respectively, which suggests that Fe^{3+} is the main oxidation state of Fe [40]. The slight peak shift for both Ni 2p and Fe 2p between the spectra for Ni@NiFe LDH and NiCo@NiFe LDH confirms that the NiCo substrate interacts with the outer layer of NiFe LDH. Two doublet peaks of $Fe^{2+} 2p_{3/2}$ (708.9 eV) and $Fe^{2+} 2p_{1/2}$ (722.4 eV) are observed in the spectrum for NiCo@NiFe LDH but are absent from that for Ni@NiFe LDH, which indicates that NiCo helps stabilize the Fe²⁺ ions in NiFe LDH. The existence of stable Fe²⁺ has been proved to be beneficial for oxygen evolution [41,42].

The electrocatalytic OER performance of the as-prepared catalysts

was evaluated in both 1 M KOH and 1 M KOH + natural seawater electrolytes using a standard three-electrode system. Backward cyclic voltammetry (CV) performed under a scan rate of 2 mV s⁻¹ was chosen to avoid oxidation peaks in the resulting curves during the OER process. As shown in Fig. 2a and b, NiCo@NiFe LDH exhibits outstanding OER activity in 1 M KOH, with very low overpotentials of 209 and 244 mV required to achieve current densities of 100 and 500 mA cm^{-2} , much better than those required by Ni@NiFe LDH (312 and 388 mV, respectively) and the benchmark commercial IrO2 (Fig. S2, ESI; 397 mV at a curretn density of 100 mA cm⁻²) under the same conditions. Such good performance is well maintained after 1000 polarization cycles (Fig. S3, ESI). The corresponding Tafel slope of 46.1 mV dec⁻¹ for NiCo@NiFe LDH (Fig. 2c) indicates its faster kinetics during the OER process in comparison to Ni@NiFe LDH (103.4 mV dec^{-1}). Mostly due to the existence of Cl⁻ and solids such as Mg(OH)₂ and bacteria in seawater, activity degradation has been a major challenge when OER catalysts are operated in alkaline natural seawater [43]. As shown in Fig. 2a, NiCo@NiFe LDH shows slight activity decay in 1 M KOH + seawater, but it still requires overpotentials of only 222 mV to achieve a current density of 100 mA cm⁻². To deliver a larger current density of 500 mA cm⁻², the overpotential required is still as low as 266 mV, which is significantly lower than that required to trigger hypochlorite formation (>490 mV in pH of 14) [31]. To the best of our knowledge, this is the best OER activity in alkaline seawater reported to date (see Table S1, ESI, for a detailed comparison between NiCo@NiFe LDH and other recently reported OER electrocatalysts in 1 M KOH and 1 M KOH + seawater electrolytes). Notably, the OER activity of Ni@NiFe LDH is significantly degraded in the seawater electrolyte in comparison with that of NiCo@NiFe LDH. At a current density of 100 mÅ cm^{-2} , the overpotential required by Ni@NiFe LDH increases by 74 mV between the freshwater and seawater electrolytes, while the corresponding increase for NiCo@NiFe LDH is only 13 mV, indicating that the 3D dendritic core-shell structure of the latter catalyst plays a crucial role in suppressing OER activity degradation in seawater electrolyte. More importantly, NiCo@NiFe LDH exhibits high Faradaic efficiency for OER in seawater (Fig. 2d) and no



Fig. 2. (a–b) OER activity and (c) corresponding Tafel slopes of NiCo@NiFe LDH and Ni@NiFe LDH in 1 M KOH + seawater electrolytes. (d) Faradaic efficiency of NiCo@NiFe LDH in 1 M KOH + seawater tested at 500 mA cm⁻². (e) Double-layer capacitance of the NiCo@NiFe LDH and Ni@NiFe LDH catalysts and the NiCo foam substrate. (f) ECSA-normalized activity of the NiCo@NiFe LDH and Ni@NiFe LDH catalysts.

hypochlorite ions were detected in the electrolyte following electrolysis (Fig. S4, ESI), demonstrating the catalyst's high selectivity for OER over hypochlorite formation reaction.

To investigate the exposure of active sites in the as-prepared catalysts, their double-layer capacitance (C_{dl}), an indicator of the electrochemically active surface area (ECSA), was measured using CV cycling (Fig. S5, ESI) in 1 M KOH. As shown in Fig. 2e, the C_{dl} of NiCo@NiFe LDH is nearly 4.14 mF cm^{-2} , while that of Ni@NiFe LDH is only 0.22 mF cm⁻², indicating that dendritic NiCo successfully increases the ECSA with greater exposure of active sites. Furthermore, compared with that of the NiCo foam substrate (1.84 mF cm⁻²), the C_{dl} of the NiCo@NiFe LDH catalyst increases by 225% after growth of the NiFe LDH nanosheets, suggesting that these vertically grown nanosheets are also beneficial for high ECSA. Based on polarization curves normalized by ECSA in 1 M KOH, the intrinsic activity of the as-prepared catalysts was determined and is shown in Fig. 2f. In 1 M KOH, NiCo@NiFe LDH exhibits better performance than Ni@NiFe LDH, which indicates its higher intrinsic activity and demonstrates that the apparent promotion in activity does not benefit only from its enlarged surface area with a greater number of active sites. In 1 M KOH + seawater, both NiCo@NiFe LDH and Ni@NiFe LDH show degradation of activity due to the decreased number of active sites, but the activity degradation of NiCo@NiFe LDH is less significant compared with that of Ni@NiFe LDH, especially at large current densities, which proves that having sufficient active sites is extremely useful for alleviating degradation in seawater electrolyte. The factors that may improve intrinsic activity have been taken into consideration. As discussed above, the XPS results for NiCo@NiFe LDH suggest the existence of stable Fe^{2+} , which may contribute to its promoted OER activity [41,42]. The robust contact between the NiFe LDH shell and the NiCo core accelerates charge transfer, as proved by the results of electrochemical impedance spectroscopy (EIS). As shown in Fig. S6, ESI, the charge-transfer resistance (R_{ct}) of NiCo@NiFe LDH is only 0.98 Ω , which is much smaller than that of Ni@NiFe LDH (2.75 Ω). Surface wettability is also an important factor affecting catalytic activity in water electrolysis at high current densities. The hydrophilic property (Fig. S7, ESI) and large surface area of NiCo@NiFe LDH synergistically contribute to its promoted mass transport, which further boosts the OER activity.

Stability is another vital parameter for evaluating a catalyst's suitability for water electrolysis, especially in seawater electrolytes since these contain aggressive chlorine ions. We conducted long-term stability tests of the two as-prepared catalysts at a constant current density of 100 mA cm⁻² in 1 M KOH + seawater. NiCo@NiFe LDH exhibits a small fluctuation in overpotential of 18 mV, much less than that of Ni@NiFe LDH (86 mV), proving its good stability in alkaline seawater electrolysis (Fig. S8, ESI). As shown in Fig. 3a, NiCo@NiFe LDH exhibits good stability throughout 100 h testing at a large current density of 500 mA ${\rm cm}^{-2}$ in 1 M KOH + seawater. To explore the origins of such enhanced stability, we obtained corrosion polarization curves for Ni@NiFe LDH and NiCo@NiFe LDH in natural seawater (Fig. S9, ESI). As shown in Fig. 3b, NiCo@NiFe LDH has a lower corrosion current density of 1.995 µA cm⁻² than Ni@NiFe LDH (12.023 $\mu A \ \text{cm}^{-2})$ and a higher corrosion potential (-0.104 V vs. -0.198 V for Ni@NiFe LDH), indicating higher corrosion resistance ability in seawater that contributes to its good stability.

Surface reconstruction of catalysts during OER has been widely reported previously [32,35,44], and NiCo@NiFe LDH is no exception. A clear color change from yellow to black was observed in the catalyst after OER stability testing (Fig. S10, ESI). Based on Raman spectroscopy analysis, the NiFe LDH outer layer partly changes to Ni_{1-x}Fe_xOOH during OER [45]. As shown in Fig. 3c, two bands at 466 and 534 cm⁻¹ become pronounced after 24 h stability testing, which indicates the formation of Ni_{1-x}Fe_xOOH [37]. The XPS spectra of Ni 2p and Fe 2p were also obtained after 24 h OER stability testing. As shown in Fig. 3d and e, the oxidation states of Ni and Fe remain unchanged. Additionally, although the outer layer of the catalyst is reconstructed, its core-shell dendritic structure is maintained (Fig. S11, ESI) during seawater electrolysis. Given that Ni_{1-x}Fe_xOOH has also been proved to be an efficient OER catalyst [46,47], the performance of our catalyst showed negligible degradation during stability testing.

3. Conclusion

In summary, we developed a large-surface-area 3D core-shell NiCo@NiFe LDH electrode that shows efficient and stable OER performance in alkaline seawater electrolyte. Large surface area, fast charge transfer, and high corrosion resistance were found to contribute to its good



Fig. 3. (a) Stability testing of NiCo@NiFe LDH for 100 h at a current density of 500 mA cm⁻² in 1 M KOH + seawater. (b) Corrosion current densities and potentials of NiCo@NiFe LDH and Ni@NiFe LDH in natural seawater. (c) Raman spectra and high-resolution XPS spectra of (d) Ni 2p and (e) Fe 2p for NiCo@NiFe LDH before and after 24 h stability testing.

performance. By comparing the as-prepared NiCo@NiFe LDH catalyst with NiFe LDH grown on commercial Ni foam, the importance of a large surface area in seawater electrolysis has been investigated. Our study highlights an effective strategy of large-surface-area construction for the rational design of OER catalysts toward efficient and stable seawater electrolysis.

Credit author statement

Fanghao Zhang: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Visualization. Yifei Liu: Investigation, Resources. Libo Wu: Validation, Formal analysis, Investigation. Minghui Ning: Validation, Formal analysis, Investigation. Shaowei Song: Validation, Formal analysis, Investigation. Donglei Emma Fan: Resources. Dezhi Wang: Resources, Investigation, Formal analysis. Luo Yu: Conceptualization, Methodology, Writing - Review & Editing. Shuo Chen: Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision. Zhifeng Ren: Conceptualization, Methodology, Resources, Writing -Review & Editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data supporting the findings of this work are available from the corresponding author upon reasonable request.

Acknowledgements

Element, LLC funded part of the work. D. Emma Fan and Yifei Liu acknowledge the support of the Welch Foundation (F1734) and the National Science Foundation (CMMI-1563382). The authors thank Mr. Troy J. Christensen at TcSUH for revisions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtphys.2022.100841.

References

- Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Norskov, T.F. Jaramillo, Combining theory and experiment in electrocatalysis: insights into materials design, Science 355 (2017): eaad4998, https://doi.org/10.1126/science.aad4998.
- [2] H. Sun, Z. Yan, F. Liu, W. Xu, F. Cheng, J. Chen, Self-supported transition-metalbased electrocatalysts for hydrogen and oxygen evolution, Adv. Mater. 32 (2020): e1806326, https://doi.org/10.1002/adma.201806326.
- [3] Q. Zhou, L. Liao, H. Zhou, D. Li, D. Tang, F. Yu, Innovative strategies in design of transition metal-based catalysts for large-current-density alkaline water/seawater electrolysis, mater, Today Phys 26 (2022): 100727. https://doi:10.1016/j.mtph ys.2022.100727.
- [4] Q. Zhou, Q. Bian, L. Liao, F. Yu, D. Li, D. Tang, H. Zhou, In situ electrochemical dehydrogenation of ultrathin Co(OH)₂ nanosheets for enhanced hydrogen evolution. chin. Chem. Lett. (2022). https://doi.10.1016/j.cclet.2022.02.053.
- [5] L. Wu, F. Zhang, S. Song, M. Ning, Q. Zhu, J. Zhou, G. Gao, Z. Chen, Q. Zhou, X. Xing, T. Tong, Y. Yao, J. Bao, L. Yu, S. Chen, Z. Ren, Efficient alkaline water/ seawater hydrogen evolution by a nanorod-nanoparticle-structured Ni-Mon catalyst with fast water-dissociation kinetics, Adv. Mater. 34 (2022): 2201774, https://doi.org/10.1002/adma.202201774.
- [6] C.C. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, T.F. Jaramillo, Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices, J. Am. Chem. Soc. 137 (2015) 4347–4357, https://doi.org/10.1021/ja510442p.
- [7] Q. Wang, X. Huang, Z.L. Zhao, M. Wang, B. Xiang, J. Li, Z. Feng, H. Xu, M. Gu, Ultrahigh-loading of Ir single atoms on NiO matrix to dramatically enhance oxygen

evolution reaction, J. Am. Chem. Soc. 142 (2020) 7425–7433, https://doi.org/10.1021/jacs.9b12642.

- [8] J. Jiang, A. Zhang, L. Li, L. Ai, Nickel–cobalt layered double hydroxide nanosheets as high-performance electrocatalyst for oxygen evolution reaction, J. Power Sources 278 (2015) 445–451, https://doi.org/10.1016/j.jpowsour.2014.12.085.
- [9] M. Gong, Y. Li, H. Wang, Y. Liang, J.Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, An advanced Ni-Fe layered double hydroxide electrocatalyst for water oxidation, J. Am. Chem. Soc. 135 (2013) 8452–8455, https://doi.org/10.1021/ ia4027715.
- [10] L. Yang, Z. Liu, S. Zhu, L. Feng, W. Xing, Ni-Based layered double hydroxide catalysts for oxygen evolution reaction, mater, Today Phys 16 (2021): 100292, https://doi.org/10.1016/j.mtphys.2020.100292.
- [11] C.W. Liang, P.C. Zou, A. Nairan, Y.Q. Zhang, J.X. Liu, K.W. Liu, S.Y. Hu, F.Y. Kang, H.J. Fan, C. Yang, Exceptional performance of hierarchical Ni-Fe oxyhydroxide@ NiFe alloy nanowire array electrocatalysts for large current density water splitting, Energy Environ. Sci. 13 (2020) 86–95, https://doi.org/10.1039/C9EE02388G.
- [12] R.Q. Yao, H. Shi, W.B. Wan, Z. Wen, X.Y. Lang, Q. Jiang, Flexible Co-Mo-N/Au electrodes with a hierarchical nanoporous architecture as highly efficient electrocatalysts for oxygen evolution reaction, Adv. Mater. 32 (2020): e1907214, https://doi.org/10.1002/adma.201907214.
- [13]] X.H. Chen, Q. Zhang, L.L. Wu, L. Shen, H.C. Fu, J. Luo, X.L. Li, J.L. Lei, H.Q. Luo, N.B. Li, Regulation of the electronic structure of Co4N with novel Nb to form hierarchical porous nanosheets for electrocatalytic overall water splitting, mater, Today Phys 15 (2020): 100268, https://doi.org/10.1016/j.mtphys.2020.100268.
- [14] F. Cai, L. Liao, Y. Zhao, D. Li, J. Zeng, F. Yu, H. Zhou, Large-current-stable bifunctional nanoporous Fe-rich nitride electrocatalysts for highly efficient overall water and urea splitting, J. Mater. Chem. A. 9 (2021) 10199–10207. https://doi i10.1039/d1ta00144b.
- [15] C. Huang, S. Cheng, L. Yu, W. Zhang, J. Zhou, Y. Zhang, Y. Yu, Electrolyzer with hierarchical transition metal sulfide and phosphide towards overall water splitting, Mater. Today Phys. 11 (2019): 100162, https://doi.org/10.1016/j. mtphys.2019.100162.
- [16] H. Zhou, F. Yu, J. Sun, R. He, S. Chen, C. Chu, Z. Ren, Highly active catalyst derived from a 3D foam of Fe(PO₃)₂/Ni₂P for extremely efficient water oxidation, Proc. Natl. Acad. Sci. U.S.A. 114 (2017) 5607–5611. https://doi.10.1073/pnas.1701 562114.
- [17] J. Zeng, L. Zhang, Q. Zhou, L. Liao, Y. Qi, H. Zhou, D. Li, F. Cai, H. Wang, D. Tang, F. Yu, Boosting alkaline hydrogen and oxygen evolution kinetic process of tungsten disulfide-based heterostructures by multi-site engineering, Small 18 (2021): 2104624. https://doi:10.1002/smll.202104624.
- [18] S. Song, L. Yu, X. Xiao, Z. Qin, W. Zhang, D. Wang, J. Bao, H. Zhou, Q. Zhang, S. Chen, Z. Ren, Outstanding oxygen evolution reaction performance of nickel iron selenide/stainless steel mat for water electrolysis, Mater. Today Phys. 13 (2020): 100216, https://doi.org/10.1016/j.mtphys.2020.100216.
- [19] S. Dresp, F. Dionigi, M. Klingenhof, P. Strasser, Direct electrolytic splitting of seawater: opportunities and challenges, ACS Energy Lett. 4 (2019) 933–942, https://doi.org/10.1021/acsenergylett.9b00220.
- [20] L. Yu, L.B. Wu, B. McElhenny, S.W. Song, D. Luo, F.H. Zhang, Y. Yu, S. Chen, Z. F. Ren, Ultrafast room-temperature synthesis of porous S-doped Ni/Fe (oxy) hydroxide electrodes for oxygen evolution catalysis in seawater splitting, Energy Environ. Sci. 13 (2020) 3439–3446, https://doi.org/10.1039/D0EE00921K.
- [21] Y. Kuang, M.J. Kenney, Y. Meng, W.H. Hung, Y. Liu, J.E. Huang, R. Prasanna, P. Li, Y. Li, L. Wang, M.C. Lin, M.D. McGehee, X. Sun, H. Dai, Solar-driven, highly sustained splitting of seawater into hydrogen and oxygen fuels, Proc. Natl. Acad. Sci. U.S.A. 116 (2019) 6624–6629, https://doi.org/10.1073/pnas.1900556116.
- [22] P. Li, S. Wang, I.A. Samo, X. Zhang, Z. Wang, C. Wang, Y. Li, Y. Du, Y. Zhong, C. Cheng, W. Xu, X. Liu, Y. Kuang, Z. Lu, X. Sun, Common-ion Effect Triggered Highly Sustained Seawater Electrolysis with Additional NaCl Production, Research (Wash D C), 2020: 2872141, https://doi.org/10.34133/2020/2872141, 2020.
- [23] M. Ning, L. Wu, F. Zhang, D. Wang, S. Song, T. Tong, J. Bao, S. Chen, L. Yu, Z. Ren, One-step spontaneous growth of NiFe layered double hydroxide at room temperature for seawater oxygen evolution, mater, Today Phys 19 (2021): 100419, https://doi.org/10.1016/j.mtphys.2021.100419.
- [24] S. Khatun, H. Hirani, P. Roy, Seawater electrocatalysis: activity and selectivity, J. Mater. Chem. 9 (2021) 74–86, https://doi.org/10.1039/D0TA08709B.
 [25] S. Dresp, T.N. Thanh, M. Klingenhof, S. Bruckner, P. Hauke, P. Strasser, Efficient
- [25] S. Dresp, T.N. Thanh, M. Klingenhof, S. Bruckner, P. Hauke, P. Strasser, Efficient direct seawater electrolysers using selective alkaline nife-LDH as OER catalyst in asymmetric electrolyte feeds, Energy Environ. Sci. 13 (2020) 1725–1729, https:// doi.org/10.1039/D0EE01125H.
- [26] F.F. Cheng, X.L. Feng, X. Chen, W.G. Lin, J.F. Rong, W.S. Yang, Synergistic action of Co-Fe layered double hydroxide electrocatalyst and multiple ions of sea salt for efficient seawater oxidation at near-neutral pH, Electrochim. Acta 251 (2017) 336–343, https://doi.org/10.1016/j.electacta.2017.08.098.
- [27] J.E. Bennett, Int. Electrodes for generation of hydrogen and oxygen from seawater, J. Hydrog. Energy 5 (1980) 401–408, https://doi.org/10.1016/0360-3199(80) 90021-X.
- [28] H. Chen, Y. Zou, J. Li, K. Zhang, Y. Xia, B. Hui, D. Yang, Wood aerogel-derived sandwich-like layered nanoelectrodes for alkaline overall seawater electrosplitting, Appl. Catal., B 293 (2021): 120215, https://doi.org/10.1016/j. apcatb.2021.120215.
- [29] T. Ma, W. Xu, B. Li, X. Chen, J. Zhao, S. Wan, K. Jiang, S. Zhang, Z. Wang, Z. Tian, Z. Lu, L. Chen, The critical role of additive sulfate for stable Alkaline seawater oxidation on nickel-based electrodes, Angew. Chem. Int. Ed. 60 (2021) 22740–22744, https://doi.org/10.1002/anie.202110355.
- [30] A.A. Bhardwaj, J.G. Vos, M.E.S. Beatty, A.F. Baxter, M.T.M. Koper, N.Y. Yip, D. V. Esposito, Ultrathin silicon oxide overlayers enable selective oxygen evolution

F. Zhang et al.

from acidic and unbuffered pH-neutral seawater, ACS Catal. 11 (2021) 1316–1330, https://doi.org/10.1021/acscatal.0c04343.

- [31] F. Dionigi, T. Reier, Z. Pawolek, M. Gliech, P. Strasser, Design criteria, operating conditions, and nickel-iron hydroxide catalyst materials for selective seawater electrolysis, ChemSusChem 9 (2016) 962–972, https://doi.org/10.1002/ cssc.201501581.
- [32] L.B. Wu, L. Yu, F.H. Zhang, B. McElhenny, D. Luo, A. Karim, S. Chen, Z.F. Ren, Heterogeneous bimetallic phosphide Ni2P-Fe2P as an efficient bifunctional catalyst for water/seawater splitting, Adv. Funct. Mater. 31 (2020): 2006484, https://doi. org/10.1002/adfm.202006484.
- [33] L. Wu, L. Yu, B. McElhenny, X. Xing, D. Luo, F. Zhang, J. Bao, S. Chen, Z. Ren, Rational design of core-shell-structured CoP @FeOOH for efficient seawater electrolysis, Appl. Catal., B 294 (2021): 120256, https://doi.org/10.1016/j. apcatb.2021.120256.
- [34] W. Li, M.C. Tekell, C. Liu, J.A. Hethcock, D. Fan, Flexible all-solid-state supercapacitors of high areal capacitance enabled by porous graphite foams with diverging microtubes, Adv. Funct. Mater. 28 (2018): 1800601, https://doi.org/ 10.1002/adfm.201800601.
- [35] Y. Liu, W. Li, Y. Ma, D. Fan, Core-shell dendritic superstructural catalysts by design for highly efficient and stable electrochemical oxygen evolution reaction, Adv. Mater. Interfac. 7 (2020): 2000777, https://doi.org/10.1002/admi.202000777.
- [36] B.M. Hunter, W. Hieringer, J.R. Winkler, H.B. Gray, A.M. Müller, Effect of interlayer anions on [NiFe]-LDH nanosheet water oxidation activity, Energy Environ. Sci. 9 (2016) 1734–1743, https://doi.org/10.1039/C6EE00377J.
- [37] F. Tang, T. Liu, W. Jiang, L. Gan, Windowless thin layer electrochemical Raman spectroscopy of Ni-Fe oxide electrocatalysts during oxygen evolution reaction, J. Electroanal. Chem. 871 (2020): 114282, https://doi.org/10.1016/j. jelechem.2020.114282.
- [38] A.N. Mansour, C.A. Melendres, Characterization of slightly hydrated Ni(OH)2 by XPS, Surf. Sci. Spectra 3 (1994) 247–254, https://doi.org/10.1116/1.1247753.
- [39] Y. Yang, L. Dang, M.J. Shearer, H. Sheng, W. Li, J. Chen, P. Xiao, Y. Zhang, R. J. Hamers, S. Jin, Highly active trimetallic NiFeCr layered double hydroxide electrocatalysts for oxygen evolution reaction, Adv. Energy Mater. 8 (2018): 1703189, https://doi.org/10.1002/aenm.201703189.

- [40] W. Temesghen, P.M. Sherwood, Analytical utility of valence band X-ray photoelectron spectroscopy of iron and its oxides, with spectral interpretation by cluster and band structure calculations, Anal. Bioanal. Chem. 373 (2002) 601–608, https://doi.org/10.1007/s00216-002-1362-3.
- [41] Z. Čai, D. Zhou, M. Wang, S.-M. Bak, Y. Wu, Z. Wu, Y. Tian, X. Xiong, Y. Li, W. Liu, S. Siahrostami, Y. Kuang, X.-Q. Yang, H. Duan, Z. Feng, H. Wang, X. Sun, Introducing Fe2+ into nickel–iron layered double hydroxide: local structure modulated water oxidation activity, Angew. Chem. Int. Ed. 57 (2018) 9392–9396, https://doi.org/10.1002/ange.201804881.
- [42] B. Zhang, L. Wang, Z. Cao, S.M. Kozlov, F.P. García de Arquer, C.T. Dinh, J. Li, Z. Wang, X. Zheng, L. Zhang, Y. Wen, O. Voznyy, R. Comin, P. De Luna, T. Regier, W. Bi, E.E. Alp, C.-W. Pao, L. Zheng, Y. Hu, Y. Ji, Y. Li, Y. Zhang, L. Cavallo, H. Peng, E.H. Sargent, High-valence metals improve oxygen evolution reaction performance by modulating 3d metal oxidation cycle energetics, Nat. Catal. 3 (2020) 985–992, https://doi.org/10.1038/s41929-020-00525-6.
- [43] F. Zhang, L. Yu, L. Wu, D. Luo, Z. Ren, Rational design of oxygen evolution reaction catalysts for seawater electrolysis, Trends Chem 3 (2021) 485–498, https://doi. org/10.1016/j.trechm.2021.03.003.
- [44] Y. Hao, Y. Li, J. Wu, L. Meng, J. Wang, C. Jia, T. Liu, X. Yang, Z.P. Liu, M. Gong, Recognition of surface oxygen intermediates on NiFe oxyhydroxide oxygenevolving catalysts by homogeneous oxidation reactivity, J. Am. Chem. Soc. 143 (2021) 1493–1502, https://doi.org/10.1021/jacs.0c11307.
- [45] S. Klaus, M.W. Louie, L. Trotochaud, A.T. Bell, Role of catalyst preparation on the electrocatalytic activity of Ni1–xFexOOH for the oxygen evolution reaction, J. Phys. Chem. C 119 (2015) 18303–18316, https://doi.org/10.1021/acs. jpcc.5b04776.
- [46] J. Chi, H. Yu, B. Qin, L. Fu, J. Jia, B. Yi, Z. Shao, Vertically aligned FeOOH/NiFe layered double hydroxides electrode for highly efficient oxygen evolution reaction, ACS Appl. Mater. Interfaces 9 (2017) 464–471, https://doi.org/10.1021/ acsami.6b13360.
- [47] H. Zhou, F. Yu, Q. Zhu, J. Sun, F. Qin, L. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, Water splitting by electrolysis at high current densities under 1.6 volts, Energy Environ. Sci. 11 (2018) 2858–2864, https://doi.org/10.1039/C8EE00927A.