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View Journal | View Issue Cite this: *J. Mater. Chem. A*, 2018, 6, 16959Activity enhancement *via* borate incorporation into a NiFe (oxy)hydroxide catalyst for electrocatalytic oxygen evolution†Ning Wang,^{‡ab} Zhen Cao,^{‡c} Xiangbin Kong,^{‡ab} Junhui Liang,^{ab} Qixing Zhang,^{ab} Lirong Zheng,^{id e} Changchun Wei,^{ab} Xinliang Chen,^{ab} Ying Zhao,^{ab} Luigi Cavallo,^{id c} Bo Zhang^d and Xiaodan Zhang^{id *ab}

The oxygen evolution reaction (OER) is a key process in electrocatalysis and is critical for achieving the cost-effective conversion of renewable electricity to chemicals and fuels. However, the high overpotential (η) originates from poor charge-transfer ability and low catalytic activity may lead to high power consumption. Herein, we alleviate these issues by introducing borate into the NiFe (oxy)hydroxide framework. Our density functional theory (DFT) calculations demonstrated that the borate could be efficiently adsorbed onto the Ni/NiFe (oxy)hydroxide surface. Microscopically, the adsorbed borate can induce a favorable electronic structure for the Ni active sites. Meanwhile, the macroscopic charge-transfer ability of this synthesized catalyst has been dramatically increased. Hence, the catalytic performance of this material is improved compared with its NiFe counterpart: we achieved a higher OER activity with an ultralow η of only 230 mV at 10 mA cm⁻² on a glassy carbon electrode (GCE) and of 200 mV at 10 mA cm⁻² on Ni foam in alkaline medium. Moreover, this borate mediated NiFe (oxy)hydroxide is very stable: no appreciable degradation is observed after more than 110 hours of operation.

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Introduction

Water oxidation, or the oxygen evolution reaction (OER), is a pivotal reaction in diverse energy conversion and storage technologies, such as electrolyzers,^{1,2} regenerative fuel cells,^{3,4} metal–air batteries⁵ and photoelectrochemical cells. In water-alkali electrolytes, the OER is a complex process, where hydroxide anions are oxidized to produce oxygen molecules ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$).^{6,7} Noble materials, such as iridium oxide (IrO_2), have shown great benefits in anodic-half cell reactions, while the requirement of cost-effective conversion

may limit their practical applications. Therefore, earth-abundant, economical alternatives possessing catalytic activities comparable to or even higher than those of noble metal oxides are needed. During the last decade, significant advances have been made in the development of OER electrocatalysts, such as perovskite oxides,^{8,9} 3d M (Ni, Co, Fe, Mn)-based compounds,^{10–13} metal–organic frameworks^{14,15} and carbon nanomaterials.^{16,17} In particular, 3d metal-based alloys,¹⁸ oxides,¹⁹ nitrides,²⁰ phosphides,²¹ and sulfides²² have gained broad attention due to their attractive catalytic activities and scalable preparation strategies.

Among these catalysts, NiFe (oxy)hydroxides have been recognized as promising water-splitting electrocatalysts due to their inherent octahedral structures,^{23,24} which provide interfacial active sites exposed to electrolytes. The urgent problems that limit these catalysts originate from their low charge-transfer ability and high overpotential in basic media. Current strategies of performance enhancement typically include doping with heterometal-atoms,^{25,26} embedding into a nano-carbon matrix²⁷ or combining with other catalysts.²⁸ However, employing these methods, the overpotential (η) is still quite high. Possible explanations attribute this phenomenon to the inhomogeneous distribution of the newly introduced elements,²⁹ which leads to a poor charge-transfer ability that remains to be improved.

On the other hand, borate is known to be an efficient proton-accepting species that enables the formation of a catalyst with

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sustainable activity. Investigating this material, Nocera *et al.*^{30,31} achieved better OER performance of the Ni–borate catalyst. Thereafter, Li *et al.*³² attributed the improved catalytic activity to the fact that borate can assist the proton coupled electron transfer (PCET). Despite these advances, investigations of borate in NiFe-based catalysts, a family of catalysts with much better OER performance, have rarely been reported.

Thus, we hypothesized that the NiFe (oxy)hydroxide (NiFe) combined with borate may also lead to a high-performance catalyst. Herein, using a room temperature sol–gel method, we synthesized a homogeneous NiFe–borate (oxy)hydroxide (NiFe–borate) catalyst. Then, the detailed atomic structure and catalytic behavior of this material were carefully investigated. Our results demonstrate that borate can be introduced to generate stable NiFe–borate catalysts, leading to better OER efficiency.

Results and discussion

The NiFe–borate catalyst was synthesized from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, FeCl_3 and $\text{Na}_2\text{B}_4\text{O}_7$ through a room temperature sol–gel procedure (Fig. 1). The precursors were mixed and hydrolyzed at a controlled rate to achieve atomic homogeneity. Fig. 2a displays a typical transmission electron microscopy (TEM) image

image of the product, indicating that the synthesized material possesses a porous nanostructure consisting of aggregated nanoparticles and exposed underlying active sites. Scanning electron microscopy (SEM, Fig. 1) confirmed this nanostructure. Electron energy loss spectroscopy (EELS, Fig. 2b) elemental mapping confirmed that the doped B is uniformly distributed in the NiFe host. Selected area electron diffraction (SAED, Fig. 2c) and X-ray diffraction (XRD, Fig. S1†) analyses indicated that the prepared catalyst possessed a weakly crystalline phase.

Thereafter, we performed density functional theory (DFT) calculations to evaluate the binding energy (E_b) of the borate onto the Ni–Fe catalyst surface, and compared it with the E_b of borate onto the Ni (oxy)hydroxide following the proposed structure³⁰ (details in the ESI†). The borate can strongly bind onto the surface of the catalyst, while the binding energy decreases a lot after the surface Fe is introduced into the system. Considering the benefits in charge transfer brought about by the incorporated borate, this calculation result is consistent with the below experimental characterization of different types of Ni–Fe catalysts (R_{ct} : NiFe > NiFe–borate > Ni–borate). Even though E_b decreases after introducing the surface Fe, it is still large enough to maintain the stable NiFe–borate structure. Interestingly, even starting from the same configuration, the optimized NiFe (oxy)hydroxides exhibit different protonated states compared with the Ni (oxy)hydroxides, indicating that the enhancement in the charge-transfer ability does not change the relative activity between the Ni or Ni–Fe systems and the role of borate is only to assist the electron transfer rather than the whole OER cycle.

Next, the detailed electronic environment of the Ni sites was investigated through experiments. Firstly, the bonding structures centered at Ni were characterized through the Raman spectrum. Broad peaks for both catalysts demonstrate weakly crystalline properties (Fig. 4a).³³ After borate incorporation, the

Fig. 1 Schematic illustration of the NiFe–borate preparation through a sol–gel method; the SEM image demonstrates the morphology of the product.

Fig. 2 Morphological and compositional characterization of the NiFe–borate catalyst. Representative (a) TEM image and (b) electron energy loss spectroscopy (EELS) elemental mapping of the NiFe–borate catalyst showing the uniform, uncorrelated spatial distribution of Ni, Fe, B and O. (c) Selected area electron diffraction (SAED) analysis.

Fig. 3 Schematic view of the borate incorporated OER catalysts: (a) borate incorporated Ni (oxyhydroxide) and (b) borate incorporated Ni–Fe (oxyhydroxide).

Ni–O peak of the NiFe is shifted from 523 cm^{-1} toward higher wavenumbers, indicating a contracted Ni–O distance and a modified chemical activity of the center Ni elements.

Then, the chemical states of the synthesized samples were further investigated using X-ray photoelectron spectroscopy (XPS). The peak at 192 eV is correlated with the B–O bonds of the

boron-oxo species (borate), confirming the presence of B atoms (Fig. S2†).³⁴ The Ni 2p spectrum contains two main peaks, located at ~ 855.8 (Ni $2p_{3/2}$) and ~ 873.4 (Ni $2p_{1/2}$) eV, respectively (Fig. 4b). The two peaks were slightly shifted toward 856 and 873.6 eV for the NiFe–borate catalyst. Thereafter, we activated these catalysts in 1 M KOH at 1.6 V vs. RHE for 30 min to

Fig. 4 Structural and chemical states of the catalysts. (a) Raman spectra of NiFe and NiFe–borate. XPS analysis of NiFe and NiFe–borate in the (b) Ni 2p and (c) Fe 2p bonding energy region after the OER process at 1.6 V vs. RHE for 30 min in 1 M KOH . (d) Ni K-edge X-ray absorption spectra of the catalysts. (e) Fourier-transformed k^3 -weighted EXAFS oscillations of the catalysts at the Ni K-edge, and NiO and Ni_2O_3 as references. (f) Fe K-edge X-ray absorption spectra of the catalysts.

observe the quasi-*in situ* variation of the Ni 2p peak, and these two peaks can further shift to higher energies (857.2 eV for Ni 2p_{3/2} and 875 eV for Ni 2p_{1/2}), suggesting that the incorporated B can stimulate the Ni sites toward the correct direction (higher chemical oxidation states).³⁵ Different from the chemically active Ni sites, the Fe 2p binding energies of both catalysts remained nearly unchanged (Fig. 4c). This result may be consistent with the statement that the Ni sites act as the OH[−] acceptors that accelerate water oxidation through discharge and desorption.³⁶

To precisely evaluate the effects of borate mediation toward the active Ni sites, we performed Ni K-edge X-ray absorption spectroscopy (XAS) on the NiFe–borate and NiFe samples immediately after oxidation at 1.6 V (vs. RHE). The Ni K-edge X-ray absorption near edge structure (XANES) spectra are shown in Fig. 4d. The pre-edge centroid and the photoionization threshold of the (oxy)hydroxides occurred at significantly higher energies compared with those in the Ni(II) and Ni(III) references, suggesting that the Ni active sites possess higher oxidation states.²³ Moreover, NiFe–borate exhibits the most noticeable shifts toward higher energies among the samples, illustrating that the incorporated borate can enhance the oxidation state of Ni during the OER processes. This enhanced oxidation state can also be clearly seen in the extended X-ray fine structure (EXAFS, Fig. 4e): the NiFe–borate has a shorter Ni–O bond length than the control samples. Consistent with the XPS results, the Fe K-edge XANES spectra do not show a clear variation of NiFe–borate (Fig. 4f).

Then, we explored the effect of incorporated borate on the catalytic performance of the NiFe catalyst. This was first studied

using linear sweep voltammetry (LSV) on a glassy carbon electrode (GCE) in a three-electrode design (details in the ESI†). The bare GCE was inactive in the basic electrolyte (1 M KOH) and functioned only as a current collector. Compared with NiFe, addition of borate can remarkably reduce the η at 10 mA cm^{−2} from 253 to 230 mV, which is comparable to the η of the previous IrO₂ catalyst (Fig. 5a). The high catalytic activity mainly originates from the higher oxidation state and the contracted Ni–O bond distance. The better performance of NiFe compared with the Ni–borate is mainly due to the fact that incorporated Fe ions can optimize the NiOOH electronic structure²⁴ and the enhancement in the charge-transfer ability does not change the relative activity between the Ni or Ni–Fe systems. Further evaluation of the reaction kinetics was achieved from the Tafel slope (Fig. 5b). The Tafel slope of NiFe–borate was calculated to be 32 mV dec^{−1}, which is clearly lower than those of IrO₂ (60 mV dec^{−1}), NiFe (67 mV dec^{−1}) and Ni–borate (181 mV dec^{−1}). The smaller Tafel slope reveals that NiFe–borate exhibited faster reaction kinetics. The enhancement in the charge transfer and the interfacial reaction by the NiFe–borate catalyst were confirmed by EIS measurements under the OER operating conditions (Fig. 5c). Notably, the Nyquist plots revealed a decrease in the charge-transfer resistance (R_{ct} , 2463.4 → 994.3 Ω) after the incorporation of borate into NiFe, which indicates that this catalyst exhibited much faster charge transfer than its counterparts. Besides, the NiFe–borate shows a higher resistance compared with the Ni–borate system, indicating that the amount of incorporated borate in NiFe–borate is lower than that in the Ni–borate. This is consistent with the DFT

Fig. 5 Characterization of the electrochemical OER activities of the catalysts on the GCE and Ni foam in 1 M KOH. (a) LSV polarization curves with a scan rate of 1 mV s^{−1} and (b) the corresponding Tafel plots and (c) Nyquist plots of NiFe–borate and the controls by EIS at a 100 mV over-potential. The inset is the equivalent circuit. R_s : series resistance; R_{ct} : charge-transfer resistance; CPE: constant-phase element related to the double-layer capacitance. (d) LSV polarization curves with a scan rate of 1 mV s^{−1}; and (e) chronopotentiometry curve obtained with NiFe–borate on a Ni foam electrode with a constant current density of 10 mA cm^{−2}.

Table 1 Parameters for each catalyst investigated on a GCE in 1 M KOH

Samples	η (mV, 10 mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	R_s (Ω)	Mass activity (A g ⁻¹)
NiFe	253	67	9.1	128.5
Ni-borate	370	181	9.4	21.7
NiFe-borate	230	32	9.6	228.7

calculations (Fig. 3) that the binding energy for the borate is smaller in the NiFe-borate compared with that in the Ni-borate catalyst.

Next, we sought to confirm whether the OER performance of NiFe-borate originated from the intrinsic catalytic activity or exclusively from the enhanced surface area. The Brunauer–Emmett–Teller (BET, Fig. S3†) surface area of the samples was evaluated to determine the specific activity, and it was normalized by the kinetic current density as a function of the potential *vs.* RHE.³⁷ The intrinsic activity of NiFe-borate was notably higher than that of the controls (Fig. S4†), which is consistent with the LSV, Tafel and EIS results. The mass activities were also tested to further examine the intrinsic properties of NiFe-borate. The result of these tests suggested that an enhancement in the mass activity, from 128.5 A g⁻¹ for NiFe to 228.7 A g⁻¹ for NiFe-borate at $\eta = 200$ mV, was obtained with the addition of borate (Table 1).

We also measured the electrocatalytic performance of NiFe-borate in the OER on a Ni foam substrate and compared its activity with that of the controls (Fig. 5d and S5†). The three catalysts exhibited similar activity trends, and NiFe-borate showed the lowest η of 200 mV at 10 mA cm⁻² on the Ni foam. Hence, the synthesized NiFe-borate catalyst exhibited better activity in anodic oxidation reactions than most other Ni-based electrocatalysts reported to date (Table S1†).

A long-term oxidation process utilizing the NiFe-borate was performed for 110 hours at a constant current density of 10 mA cm⁻² (Fig. 5e), and the catalyst exhibited remarkable durability with no appreciable increment in potential. In addition, we examined the sample after the OER experiment by SEM and EDS to determine whether the catalyst remained physically intact. A similar porous nanostructured morphology was maintained (Fig. S6†). Thus, this NiFe-borate catalyst prepared by a sol-gel method showed exceptionally stable performance in an alkaline electrolyte.

Conclusions

In conclusion, we reported the preparation of a highly efficient OER catalyst with enhanced charge-transfer ability and catalytic activity *via* the incorporation of borate into a NiFe (oxy) hydroxide host by a sol-gel method. The good performance is mainly derived from the fact that borate can produce a favorable Ni electronic structure and provide fast charge transfer. This NiFe-borate (oxy)hydroxide catalyst possesses excellent activity, superior stability and low-cost characteristics, and therefore, it can be applied as a cost-effective electrocatalyst in water splitting systems.

Conflicts of interest

There are no conflicts to declare.

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