

# Solvated Br<sup>-</sup> Disrupting Interfacial Proton Transfer in Alkaline Water Oxidation

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## Article

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# Solvated Br<sup>-</sup> Disrupting Interfacial Proton Transfer in Alkaline Water

## Oxidation

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## Abstract

For alkaline oxygen evolution reaction (OER) on Ni-based electrocatalysts, surface Ni(OH)<sub>2</sub> moiety is transformed to NiOOH before OER, both of which involve proton-coupled electron transfer. Herein, we report the rapid, dramatic, and partially reversible poisoning of Br<sup>-</sup> toward the OER activity of Ni-based catalysts, and highlight the markedly different hydration effects of interfacial Br<sup>-</sup> and Cl<sup>-</sup> in modulating interfacial water orientation and proton transfer efficiency. Water molecules surrounding Br<sup>-</sup> preferentially orient with their H termini facing the anion, opposite to those in the Cl<sup>-</sup> hydration shell. This difference in hydration shell polarity propagates to the first interfacial water layer on the electrode, where Br<sup>-</sup> enrichment substantially reduces the population of O-down-oriented interfacial water during Ni(OH)<sub>2</sub>-to-NiOOH transformation and the subsequent OER process. Consequently, compared with pure or Cl<sup>-</sup>-containing electrolytes, interfacial Br<sup>-</sup> blocks efficient transfer of surface protons into the bulk solution and disfavors OH<sup>-</sup> adsorption on the electrode. The electrode thus suffers from low surface OH<sup>-</sup> density, resulting in rapid poisoning of OER kinetics. By revealing the opposing influences of interfacial Cl<sup>-</sup> and Br<sup>-</sup> on alkaline water oxidation, this work emphasizes the distinctive and non-negligible role of anion hydration behavior in modulating the microenvironment and governing OER kinetics.

**Keywords:** Proton transfer, Hydration of halide anion, Interfacial water orientation,

## 1. Introduction

Direct seawater electrolysis for hydrogen production has attracted tremendous interest as a route to green hydrogen<sup>1,2</sup>. Compared with freshwater electrolysis, halide anions present particular concerns at the anode.  $\text{Cl}^-$ , the dominant halide species in seawater, has received the most attention<sup>3</sup>. Existing studies show that, for Ni-based electrocatalysts under alkaline conditions,  $\text{Cl}^-$  does not affect oxygen evolution reaction (OER) kinetics<sup>4,5</sup>. However, high interfacial  $\text{Cl}^-$  concentrations can coordinate with metal ions, leading to catalyst peeling or pitting corrosion<sup>6</sup>.

Meanwhile, alkaline water oxidation on Ni-based electrocatalysts involves oxidative reconstruction ( $\text{Ni}(\text{OH})_2 \rightarrow \text{NiOOH} + \text{H}^+ + \text{e}^-$ , denoted as *NiOR* hereafter) prior to OER ( $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ )<sup>7,8</sup>. In both anodic processes, electron transfer is coupled with proton transfer (PCET)<sup>9,10</sup>. Transport of  $\text{OH}^-$ , the alkaline OER reactant, also relies on proton transfer within the hydrogen-bonded water network<sup>11,12</sup>. Recently, beyond the intrinsic electronic structure of catalysts, the importance of the electrical double layer (EDL) to electrochemical reaction kinetics has regained attention<sup>13,14</sup>. For these PCET-associated processes, the efficiency of the microenvironment in transporting protons (or  $\text{OH}^-$ ) between the catalyst surface and the bulk solution is critical. Dynamic interfacial water behaviors, such as rotational flexibility and hydrogen bonding, have therefore attracted great interest<sup>15,16</sup>. Effects of interfacial cations and anions in the supporting electrolyte on this microenvironment have been actively pursued<sup>17,18</sup>.

In addition to  $\text{Cl}^-$ , seawater contains approximately 0.6 mM  $\text{Br}^-$ .<sup>19</sup> Due to its relatively low concentration, the influence of  $\text{Br}^-$  on alkaline OER has long been overlooked. Recent reports have described corrosion behaviors of  $\text{Br}^-$  toward Ni-based electrocatalysts during alkaline OER that differ from those of  $\text{Cl}^-$ : whereas  $\text{Cl}^-$  mainly induces deep, narrow pitting corrosion,  $\text{Br}^-$  tends to cause large-area corrosion<sup>6</sup>. Conversely,  $\text{Br}^-$ -containing surfactants, such as cetyltrimethylammonium bromide, have long been widely used as corrosion inhibitors capable of suppressing metal corrosion under open-circuit conditions<sup>20,21</sup>.

$\text{Cl}^-$  and  $\text{Br}^-$  differ fundamentally in ionic radius, polarizability, solvation behavior, and interfacial enrichment capability<sup>22</sup>. As early as the last century, it was reported that  $\text{Br}^-$  in water tends to reside preferentially at the gas-liquid interface rather than in the bulk solution, even at concentrations much lower than those of  $\text{Cl}^-$ . This interfacial preference of  $\text{Br}^-$  is enthalpically driven: partial desolvation of  $\text{Br}^-$  is thermodynamically more favorable for water-water interactions than that of fully solvated anions<sup>23,24</sup>. In OER electrocatalysis, these differences may profoundly influence interfacial water behavior, yet this remains unexplored.

In this work, we highlight the distinctive solvation structures of  $\text{Cl}^-$  and  $\text{Br}^-$  and their impacts on Ni electrocatalysts during *NiOR* and OER. AIMD reveals that the O termini of  $\text{H}_2\text{O}$  molecules in the first solvation shell of  $\text{Cl}^-$  tend to lean toward  $\text{Cl}^-$ , whereas in that of  $\text{Br}^-$  it is the H termini that lean toward  $\text{Br}^-$ . Owing to this differentiated solvation

structure, pre-adsorbed Br<sup>-</sup> anions on the Ni surface decrease the proportion of O-down-oriented interfacial water during NiOR and OER. This impedes timely transport of H<sup>+</sup> (formed during NiOR/OER) away from the electrode surface, disfavoring the accompanying PCET process and eventually decreasing surface OH<sup>-</sup> density, as observed by electrochemical quartz crystal microbalance (EQCM) measurements. Consequently, the presence of Br<sup>-</sup>, even when only weakly adsorbed, severely poisons alkaline OER activity, and such poisoning is partially reversible which can be removed by refreshing the electrode with Br-free electrolyte. Interfacial pre-adsorbed Br<sup>-</sup> also renders the Ni metal surface hydrophobic, slowing oxidation of the Ni metal. This study reveals, for the first time, the differentiated influence of halide anions on interfacial water orientation and highlights the importance of interfacial H<sup>+</sup>/OH<sup>-</sup> diffusion for the PCET process in alkaline water oxidation.

## 2. Results

### 2.1 Opposite kinetic effects of Cl<sup>-</sup> and Br<sup>-</sup> on alkaline OER

As shown in **Fig. 1a**, the same Ni electrode was alternately tested for OER activity in pure (1 M KOH) and halide-containing alkaline electrolytes (1 M KOH + 0.5 M NaCl or NaBr) for five cycles. The results are shown in **Figs. 1b and c**. The LSV curves from five consecutive tests in electrolytes with or without NaCl almost completely overlapped, and their overpotentials at 100 mA cm<sup>-2</sup> were nearly identical in each cycle (**Fig. 1c**) (see **Supplementary Fig. 1** for the CV activation). Consistently, switching from pure electrolyte to Cl<sup>-</sup>-containing electrolyte produced negligible change in activity throughout the activation process (**Fig. 1f**).

In sharp contrast, Br<sup>-</sup> poisons OER performance dramatically via two distinct patterns. As shown in **Figs. 1d and e**, addition of Br<sup>-</sup> to the electrolyte increases the overpotential by ~140 mV at 100 mA cm<sup>-2</sup> in each cycle. **Fig. 1g** details this overpotential increase: upon Br<sup>-</sup> introduction, the overpotential at 100 mA cm<sup>-2</sup> immediately rises by ~58 mV; with subsequent repetitive CV activation, the overpotential increases continuously, eventually reaching a total increase of 131 mV (see **Supplementary Fig. 2** for the CV activation). Interestingly, when the poisoned electrode is transferred back from Br-containing electrolyte to pure electrolyte, most of the original activity is recovered after multiple CV activation cycles. This indicates that the poisoning is reversible and likely arises from weakly adsorbed Br<sup>-</sup>; upon refreshing with Br-free alkaline solution, these species readily desorb, restoring catalytic activity.

However, with repeated alternating operation in electrolytes with and without Br<sup>-</sup>, slight irreversible poisoning was observed. As shown in **Fig. 1e**, from the 1<sup>st</sup> to the 5<sup>th</sup> cycle, the overpotential in pure alkaline electrolyte increased by 36 mV, while that in Br-containing electrolyte increased by ~56 mV. This poisoning cannot be eliminated by simply refreshing the electrode with Br-free electrolyte. Irreversible poisoning was also observed after continuous operation in Br-containing electrolyte for 24 h (**Supplementary Fig. 3**). Br<sup>-</sup> can poison the electrode even at low concentration. In a simulated electrolyte with Br<sup>-</sup> concentration close to that of seawater (1 M KOH + 0.6 mM NaBr), the overpotential at 100 mA cm<sup>-2</sup> increased by ~110 mV after continuous

operation for 24 h (Fig. 1h).

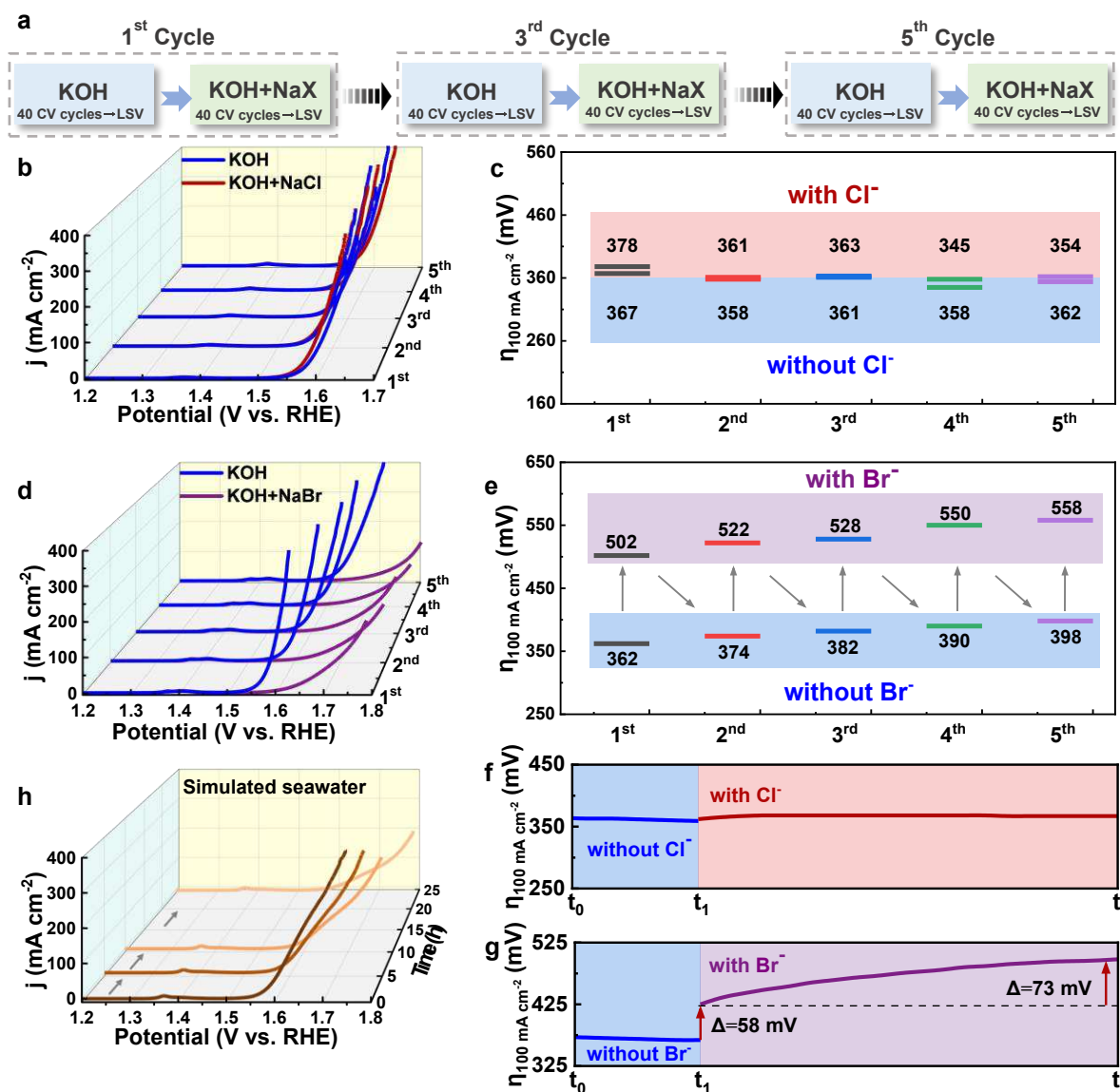


**Fig. 1 Distinctive influences of Cl<sup>-</sup> and Br<sup>-</sup> on alkaline OER activity.** (a) A scheme to show cyclic evaluation of OER activity in KOH with/without halide anions. (b, d) LSV polarization curves recorded in each cycle with/without halide anions. (c, e) evolution of overpotential at 100 mA cm<sup>-2</sup> during cyclic testing. (f, g) Overpotential evolution during the initial activation process after switching from KOH to halide-containing electrolytes. (h) evolution of OER performance in alkaline electrolyte containing 0.6 mM Br<sup>-</sup>.

## 2.2 Interfacial Br<sup>-</sup> modulates Ni(OH)<sub>2</sub>/NiOOH redox electrochemistry

To understand the distinctive impact of Br<sup>-</sup> and Cl<sup>-</sup> on OER, the mass and charge changes during the NiOR process were monitored simultaneously by EQCM. **Figs. 2a-d** present CV profiles of the NiOR process obtained at different scan rates in various electrolytes. Note that, to clarify the influence of these anions, Na<sub>2</sub>SO<sub>4</sub> was additionally

introduced as a control alongside OH<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>. In all four electrolytes, the anodic peak current scales linearly with the square root of the scan rate ( $v^{1/2}$ ) but not with the scan rate itself ( $v$ ), indicating that the NiOR process is predominantly diffusion-controlled<sup>25</sup>.

The corresponding mass-potential (MV) curves for the NiOR anodic process are shown in **Figs. 2e-h**. Interestingly, starting from the onset potential, a significant mass decrease ( $\Delta m < 0$ ) was observed in all four electrolytes, reaching a maximum at the peak potential; thereafter, the electrode mass increased with increasing potential. The maximum mass loss follows the order: KOH < KOH + NaCl  $\approx$  KOH + Na<sub>2</sub>SO<sub>4</sub> < KOH + NaBr, highlighting the non-negligible influence of Br<sup>-</sup> on the interaction between the EDL and the electrode.

For a rational comparison of mass loss, the corresponding mass-charge (MQ) curves were obtained by integrating the charge associated with NiOR in **Figs. 2a-d** (see **Supplementary Fig. 4** for the charge-potential (QV) curve). As shown in **Fig. 2i** (collected at 5 mV s<sup>-1</sup>) and **Supplementary Fig. 5**, at the same Faradaic charge  $Q$ , the electrode exhibited the smallest mass loss in pure KOH electrolyte; addition of Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> led to larger mass loss, whereas the presence of Br<sup>-</sup> produced the largest mass loss throughout the whole process, eventually displaying the largest maximum mass loss.

Note that metal corrosion and dissolution of metal cations can also cause electrode mass loss during NiOR. We therefore measured the Ni<sup>2+</sup> content dissolved in the electrolyte after multiple CV cycles (**Supplementary Note 1**). The electrode mass loss caused by Ni<sup>2+</sup> dissolution in a single CV cycle (**Supplementary Tables 1 and 2**) was two orders of magnitude lower than the maximum mass loss measured by EQCM in **Figs. 2e-h**. This excludes metal corrosion as a major cause of the mass loss observed during NiOR.

We further fitted the colored linear regions of the MQ curves in **Fig. 2i**, which falls within the early NiOR process (from the onset potential to the peak potential). From the slope, the ratio of mass change ( $\Delta m$ ) to charge change ( $\Delta Q$ )—namely the mass-per-electron (*mpe*) value—can be calculated. This *mpe* value represents the collective mass variation on an electrode associated with the transfer of one mole of electrons<sup>26,27</sup>. It provides insight into simultaneous non-Faradaic (ad)desorption events accompanying a Faradaic process. As shown in **Fig. 2j** (scan rate: 5 mV s<sup>-1</sup>), the *mpe* value obtained in Br-containing electrolyte was markedly more negative than those in the other three electrolytes, reaching -5.6 g mol<sup>-1</sup>. By comparison, the values were -4.0 g mol<sup>-1</sup> for pure KOH, -5.1 g mol<sup>-1</sup> for SO<sub>4</sub><sup>2-</sup>-containing electrolyte, and -5.2 g mol<sup>-1</sup> for Cl<sup>-</sup>-containing electrolyte.

Based on the obvious mass loss and the characteristical *mpe* values, the early NiOR process (Eq. 1) should be accompanied by a non-Faradaic desorption process. In particular, surface protons (\*H<sup>+</sup>) generated during NiOR shall be desorbed or released from the surface to the bulk solution. This PCET process can proceed via two possible pathways, depending on the source of proton acceptors. In one, surface H<sup>+</sup> combines with pre-adsorbed OH<sup>-</sup>, and the pair then desorbs as water (Eq. 2). In the other (Eq. 3), surface protons appear to detach directly from the net mass change

perspective, although this may proceed via different mechanisms. For instance, detachment could occur with assistance from interfacial water and/or free  $\text{OH}^-$  in the EDL. When  $\text{OH}^-$  adsorption occurs simultaneously with co-desorption of  $^*\text{H}^+$  and  $^*\text{OH}^-$ , the net mass change is equivalent to that of the pathway in Eq. 3.

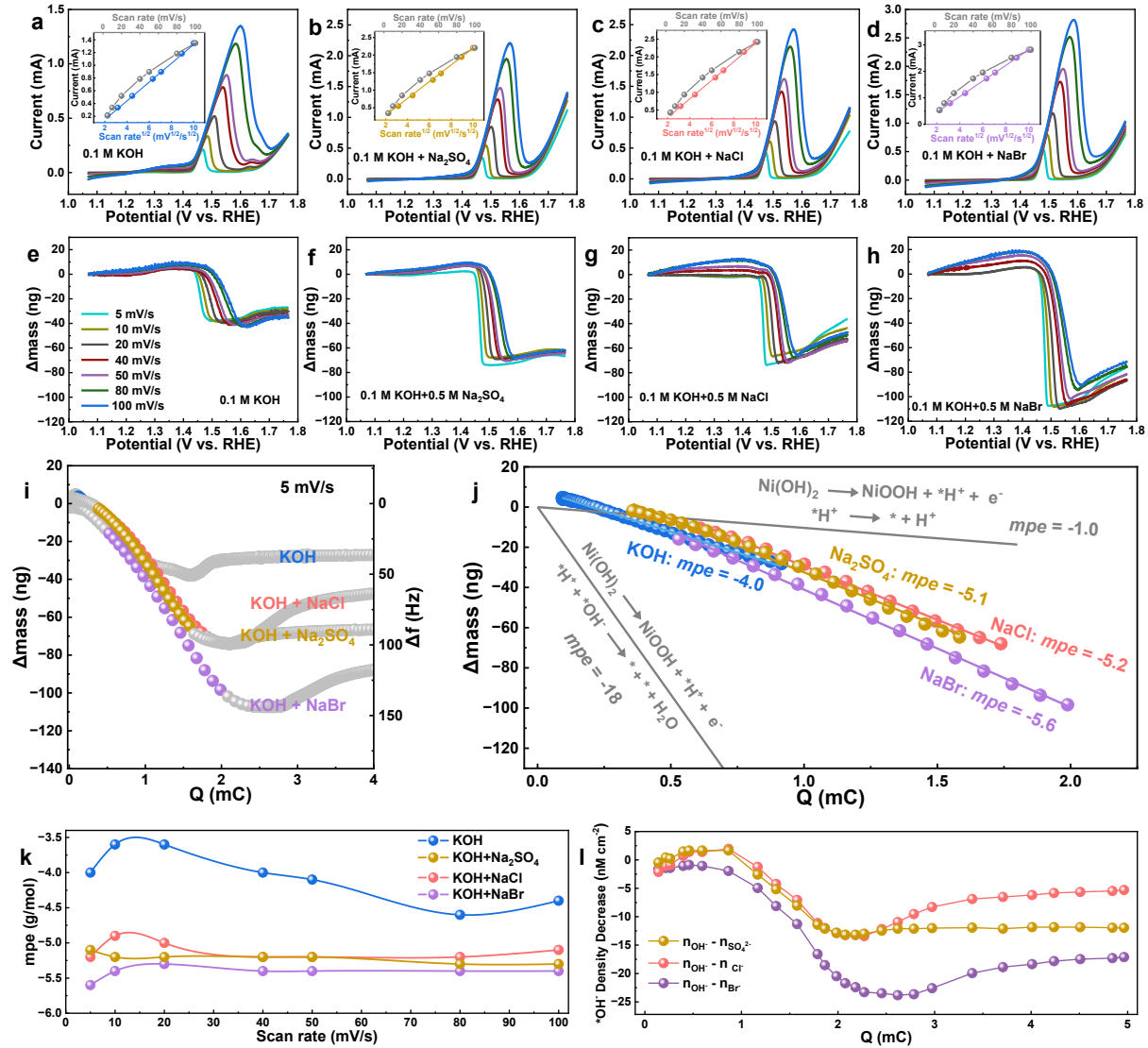
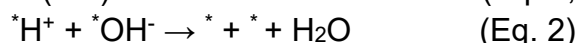
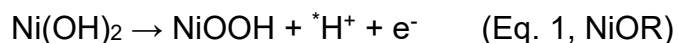


**Fig. 2 EQCM analysis of electrode mass and charge change during NiOR in different electrolytes.** (a-h) CV and relevant MV curves at different scan rates ( $v$ ,  $\text{mV s}^{-1}$ ) in (a, e) pure KOH electrolyte and those with (b, f)  $\text{Na}_2\text{SO}_4$ , (c, g)  $\text{NaCl}$ , and (d, h)  $\text{NaBr}$ , insets in (a-d) show dependence of peak current on  $v^{1/2}$  or  $v$ ; (i) the resulting MQ profile at  $5 \text{ mV s}^{-1}$  and (j) relevant mass-per-electron ( $mpe$ ) values for the early NiOR process in different electrolytes. (k)  $mpe$  for the early NiOR process under different scan rates; (l) the surface  $\text{OH}^-$  density difference between electrode in electrolyte with hybrid anions and that in pure KOH.

If the PCET process proceeds via Eq. 2, the theoretical  $mpe$  value for NiOR is  $-18 \text{ g mol}^{-1}$ ; if it proceeds via Eq. 3, the theoretical  $mpe$  value would be  $-1 \text{ g mol}^{-1}$ . As shown in **Fig. 2j**, the actual  $mpe$  values calculated from the measured MQ profiles at different

scan rates in different electrolytes all fall between -18 and -1 g mol<sup>-1</sup>, indicating that H<sup>+</sup> desorption proceeds through a combination of the two pathways, albeit with different contributions depending on the electrolyte. A more negative *mpe* value in **Fig. 2j** indicates that \*H<sup>+</sup> desorption relies more on the pathway in Eq. 2, resulting in lower surface OH<sup>-</sup> coverage. The *mpe* values in electrolytes containing Cl<sup>-</sup>, Br<sup>-</sup>, or SO<sub>4</sub><sup>2-</sup> are significantly lower than that in pure KOH. Apparently, the presence of foreign anions in the EDL hinders OH<sup>-</sup> diffusion (and subsequent adsorption) toward the Ni-based catalyst surface (**Scheme 1**). Among these anions, Br<sup>-</sup> exerts the strongest inhibitory effect, yielding the most negative *mpe* value and the largest mass loss for the NiOR process.



The above electrode mass differences can be approximately converted to differences in surface OH<sup>-</sup> density (**Supplementary Note 2**). As shown in **Fig. 2l**, compared with the electrode in pure KOH electrolyte, the presence of Br<sup>-</sup> during NiOR leads to a maximum decrease of ~25 nmol cm<sup>-2</sup> in surface OH<sup>-</sup> density, substantially larger than those in electrolytes containing Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. The peak potential marks a turning point for mass variation in the MV profile; beyond the peak potential, the electrode mass begins to increase with increasing potential, driven by electrostatically induced anion adsorption. Nevertheless, the electrode in Br-containing electrolyte exhibits lower surface OH<sup>-</sup> density than all other controls throughout the entire NiOR potential range. This is unfavorable for OER, consistent with the rapid reversible poisoning effect of Br<sup>-</sup> toward OER observed in **Fig. 1**.

Operando XAFS experiments were conducted from 1.2 to 2.0 V and then back to 1.0 V to study the NiOR and OER process. The catalyst was derived from 2 nm-thick Ni<sub>3</sub>S<sub>2</sub> precursor nanosheets; with the bulk phase minimized, the collected signals represent surface features. Prior to data collection, the catalyst was subjected to multiple CV activation cycles between 1.2 and 2.0 V. The reversible transformation Ni(OH)<sub>2</sub> → NiOOH → Ni(OH)<sub>2</sub> was observed. As shown in **Figs. 3a-d** and **m**, when the potential was increased from 1.5 V to 2.0 V, the Ni K-edge in both Br-containing and Br-free electrolytes gradually shifted to higher energy. When the potential was decreased from 2.0 V to 1.45 V and then to 1.0 V, the Ni K-edge returned to its initial oxidation state. The corresponding EXAFS results (**Figs. 3i-l** and **n**) further support these observations (See **Supplementary Fig. 6** and **Fig. 7** for data fitting). The electrocatalyst in both electrolytes exhibited shortened Ni–O and Ni–Ni bond lengths with increasing potential, reflecting the transformation from Ni(OH)<sub>2</sub> to NiOOH<sup>28</sup>.

Notably, in the NiOR region (1.45 V) and the OER potential (2.0 V), the Ni K-edge and spectral features collected in electrolytes with or without Br<sup>-</sup> overlapped almost completely in both the positive and negative scans (**Fig. 3a-c, m**). The difference spectra ( $\Delta\mu = \mu_{\text{KOH}} - \mu_{\text{KOH}+\text{NaBr}}$ ) are shown in **Figs 3e-h**. At 1.45 and 2.0 V, the difference spectra are essentially featureless (**Figs. 3e-g**). No obvious differences in Ni–O or Ni–Ni bond lengths were observed either (**Figs 3i-k**). These results reveal that the presence of Br<sup>-</sup> does not alter the local electronic structure of Ni during NiOR and

OER, ruling out change in oxidative state as the origin of the observed Br<sup>-</sup> poisoning effect on OER. This is also supported by *ex-situ* XPS analysis (**Supplementary Figs. 8-11**, see **Supplementary Fig. 12** for the XRD patterns of the corresponding samples).

Supprisingly, an influence of Br<sup>-</sup> on the oxidative state of the catalyst surface was observed at lower potentials, namely 1.0 or 1.2 V, where the oxidation state in Br<sup>-</sup>-containing electrolyte was markedly higher than that in Br<sup>-</sup>-free electrolyte (**Fig. 3d**)<sup>29,30</sup>. The XANES difference spectra ( $\Delta\mu = \mu_{\text{KOH}} - \mu_{\text{KOH+NaBr}}$ ) in **Fig. 3h** also show clear deviation near the absorption edge (**Supplementary Fig. 13a, b**). This trend is further supported by the corresponding Ni-O and Ni-Ni bond lengths at these potentials (**Fig. 3l, n** and **Supplementary Fig. 13c, d**).

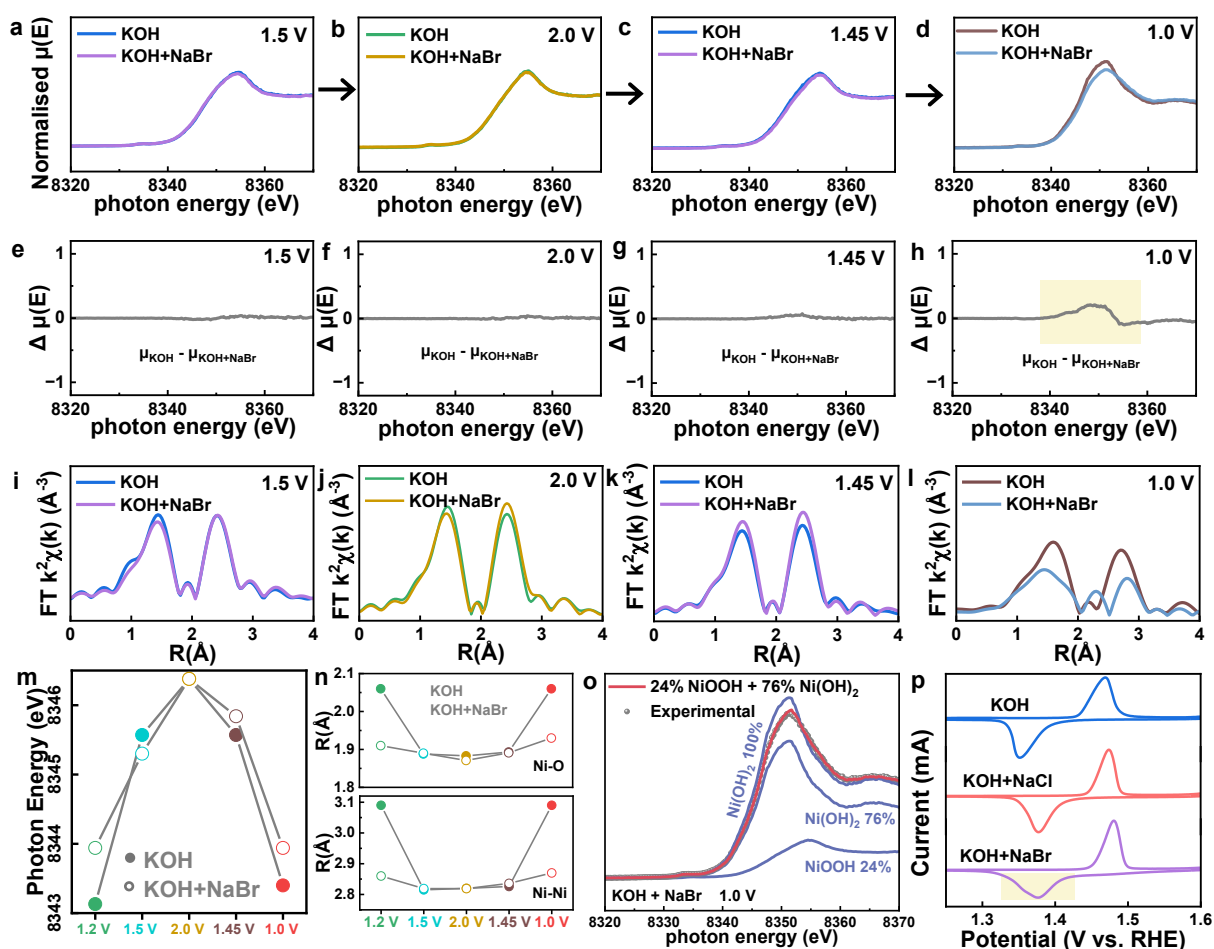


**Fig. 3 Operando XAFS analysis of Ni(OH)<sub>2</sub>/NiOOH redox electrochemistry.** (a, b, c, d) Ni K-edge XANES spectra under different potential and (e, f, g, h) the difference of the XANES spectra obtained in electrolyte with/without Br<sup>-</sup>; (i, j, k, l) the relevant *R*-space profile. (m) evolution of the Ni K-edge position (0.5 μ) and (n) evolution of Ni-O and Ni-Ni bond length versus the potential. (o) Fitting of the Ni K-edge XANES spectrum obtained in KOH+NaBr at 1.0 V with different components. (p) typical CVs of the Ni(OH)<sub>2</sub>/NiOOH conversion process (without stirring) in different electrolytes.

Meanwhile, the experimental XANES spectrum obtained in pure KOH at 1.2 V can

be well fitted using 100% Ni(OH)<sub>2</sub> as the sole component (**Supplementary Note 3**). However, as shown in **Fig. 3o** (and **Supplementary Fig. 14**), fitting of the experimental XNAES spectrum obtained in NaBr-containing electrolyte with 100% Ni(OH)<sub>2</sub> proved unsuccessful. Instead, the spectrum is best described by a linear combination fitting of 24% NiOOH and 76% Ni(OH)<sub>2</sub>. Note that the catalyst was subjected to multiple CV activation cycles between 1.0 to 2.0 V. These result clearly reveal that the presence of Br<sup>-</sup> prevents full conversion of NiOOH to Ni(OH)<sub>2</sub>, although it does not affect the oxidative state of Ni sites during NiOR and OER.

The incomplete reduction of NiOOH to Ni(OH)<sub>2</sub> induced by Br<sup>-</sup> is also evident when comparing the anodic and cathodic CV peaks of the NiOR process. As shown in **Fig. 3p**, the anodic and cathodic peaks for the Ni<sup>2+</sup>/Ni<sup>3+</sup> redox couple in pure KOH and KOH+NaCl are highly symmetric. In sharp contrast, in KOH + NaBr electrolyte, while the anodic peak remains a symmetric bell-shaped profile, the cathodic peak corresponding to NiOOH reduction becomes markedly asymmetric. Reduction of NiOOH (NiOOH + H<sup>+</sup> + e<sup>-</sup> → Ni(OH)<sub>2</sub>) consumes interfacial protons, the continuous supply of which is limited in alkaline solution. Apparently, the presence of Br<sup>-</sup> exacerbates this interfacial proton deficiency during NiOOH reduction.

The EQCM results and XAFS analysis both reveal that Br impacts interfacial proton transfer, suggesting altered interfacial proton acceptor behavior. The structural evolution of active sites and interfacial water behavior during the NiOR process were therefore investigated further. **Figs. 4a-c** present the *in-situ* Raman spectra of the Ni-based active site. The characteristic peaks at ~477 and ~556 cm<sup>-1</sup> are assigned to the bending and stretching vibrations of Ni(III)–O species, respectively<sup>31,32</sup>. With increasing potential, the intensities of both peaks gradually increased, indicating continuous conversion of Ni(OH)<sub>2</sub> to NiOOH. No noticeable differences in peak intensity or position were observed for Ni electrodes evaluated in pure KOH or in electrolytes containing Cl<sup>-</sup> or Br<sup>-</sup>. Based on the intensity ratio of E<sub>g</sub> to A<sub>1g</sub> vibration modes measured in different electrolytes, γ-NiOOH was the dominant phase formed under all conditions (**Supplementary Fig.15**)<sup>33</sup>.

In **Figs. 4d-f**, distinctive interfacial water behaviors in different scenarios was tracked using *in-situ* FTIR spectroscopy. Notably, in pure KOH, the O-H stretching signal of interfacial water intensified from 1.02 to 1.62 V, exhibiting two shoulder bands at ~3200 and ~3400 cm<sup>-1</sup>. The band at ~3400 cm<sup>-1</sup> gradually intensified and became more prominent than that at ~3200 cm<sup>-1</sup>. In comparison, introduction of Cl<sup>-</sup> and/or Br<sup>-</sup> significantly weakens the shoulder band at ~3400 cm<sup>-1</sup>, whereas the band centered at ~3200 cm<sup>-1</sup> appears unaffected. Notably, while the shoulder band at ~3400 cm<sup>-1</sup> remains discernible in Cl<sup>-</sup>-containing electrolyte, this interfacial water band nearly disappears upon introduction of Br<sup>-</sup>.

The O-H stretching envelopes were deconvoluted into two moieties, as exemplified in the insets of **Figs. 4g-i** (see also **Supplementary Figs. 16-18**). The band at ~3200 cm<sup>-1</sup> was assigned to interfacial water with symmetric hydrogen bonding (HB<sub>s</sub>), and that at ~3400 cm<sup>-1</sup> to interfacial water with asymmetric hydrogen bonding (HB<sub>as</sub>)<sup>34,35</sup>, which reflects enhanced hydrogen bonding between interfacial water and surface species (e.g., OH<sup>-</sup>)<sup>36</sup>. In pure KOH, HB<sub>as</sub> interfacial water dominates, with its

fraction increases from ~52% to ~65% as the potential increased from 1.02 to 1.62 V (**Fig. 4g**), consistent with strengthened interfacial hydrogen bonding under anodic polarization<sup>14</sup>. Upon introducing NaCl, HB<sub>as</sub> interfacial water still accounted for ~50% (**Fig. 4h**). In sharp contrast, in the presence of NaBr, the HB<sub>as</sub> moiety decreases from ~42% to ~25%, while the HB<sub>s</sub> moiety dominates at ~75% by 1.62 V (**Fig. 4i**). The marked suppression of HB<sub>as</sub> moiety by Br<sup>-</sup> indicates a fundamental disruption of the interfacial hydrogen-bonding network, influencing PCET in Ni(OH)<sub>2</sub>/NiOOH redox electrochemistry.

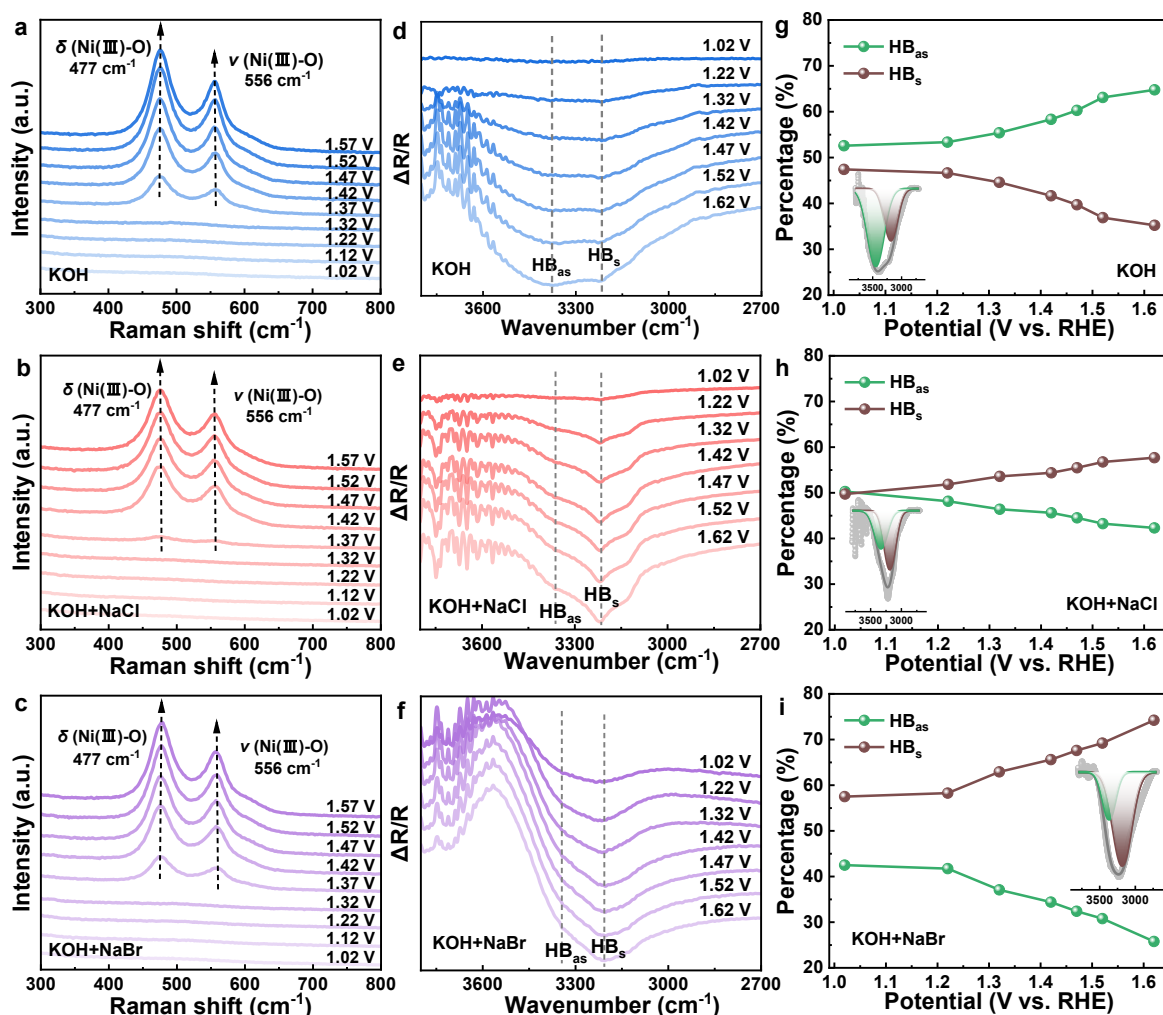


**Fig. 4** *In-situ* spectroscopic investigation of the NiOR process in pure alkaline solution or those with Cl<sup>-</sup> or Br<sup>-</sup>. (a, b, c) *In-situ* Raman spectroscopic observation of the structural evolution of the Ni-based sites; (d, e, f) *In-situ* observation of interfacial water behaviors during NiOR, and (g, h, i) the corresponding potential-dependent evolution of asymmetric (HB<sub>as</sub>) and symmetric (HB<sub>s</sub>) interfacial water fraction.

### 2.3 Br<sup>-</sup> disrupts interfacial water orientation and proton transfer during NiOR

The operando XAFS analysis and *in-situ* Raman study excludes impacts on the local electronic structure of the active site by Br<sup>-</sup> as the cause for the irreversible poisoning of OER, and both EQCM and *in-situ* FTIR study of the interfacial water

behaviors highlight the unignorable impacts of  $\text{Br}^-$  on the dynamic behaviors of the interfacial proton acceptors (that is, interfacial water/ $\text{OH}^-$ ) in the microenvironment. Herein, interaction of  $\text{OH}^-$  and halide anions with the catalyst surface was then first investigated computationally. The optimized interfacial configurations and adsorption energies of  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  are calculated. Adsorption-energy calculations are detailed in **Supplementary Note 4**. The adsorption energy of  $\text{OH}^-$  (-3.15 eV) is markedly more negative than those of  $\text{Cl}^-$  (-1.54 eV) and  $\text{Br}^-$  (-1.23 eV), indicating that  $\text{OH}^-$  adsorption is energetically preferred. Among the halide anions,  $\text{Cl}^-$  adsorption is even slightly more favourable than  $\text{Br}^-$  adsorption (**Supplementary Fig. 19a**). This adsorption energetics indicate that direct substitution of surface-bound  $\text{OH}^-$  by halide anions is thermodynamically unfavorable, thereby arguing against competitive displacement of  $\text{OH}^-$  from surface active sites as the primary origin of the reversible  $\text{Br}^-$  poisoning effect.

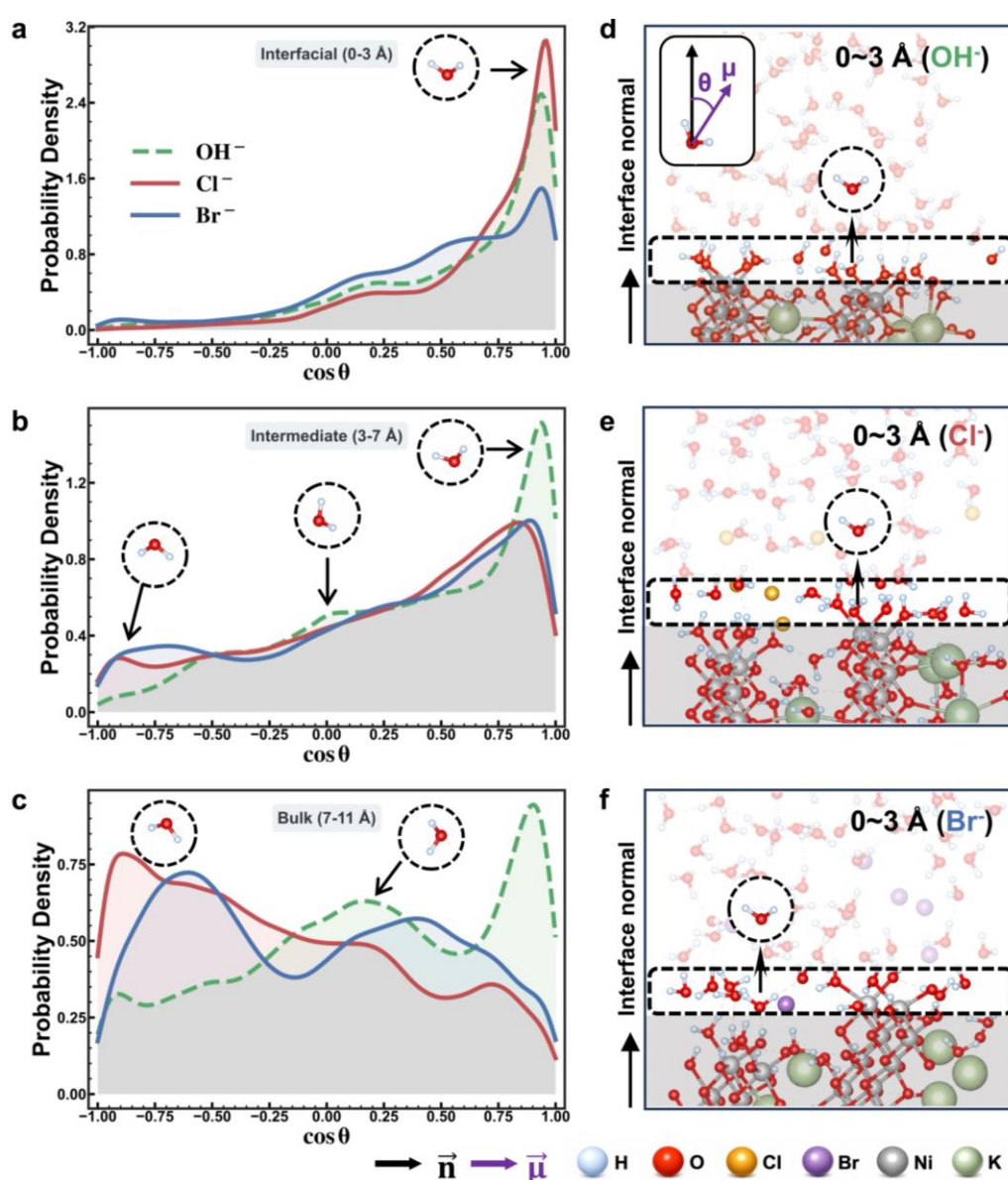


**Fig. 5 MACE-driven molecular dynamics analysis of distance-dependent water orientational ordering at the NiOOH-water interface.** (a, b, c) Probability distributions of  $\cos\theta$  for interfacial water molecules within 0-3 Å, 3-7 Å, and 7-11 Å from

the surface in OH<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>-containing systems. The representative interfacial water configurations extracted from MACE-MD trajectories for the (d) OH<sup>-</sup>, (e) Cl<sup>-</sup>, and (f) Br<sup>-</sup> systems, respectively, corresponding to the distance regions 0-3 Å identified in (a).  $\theta$  denotes the angle between the water dipole moment ( $\vec{\mu}$ ) and the surface-normal vector ( $\vec{n}$ ).

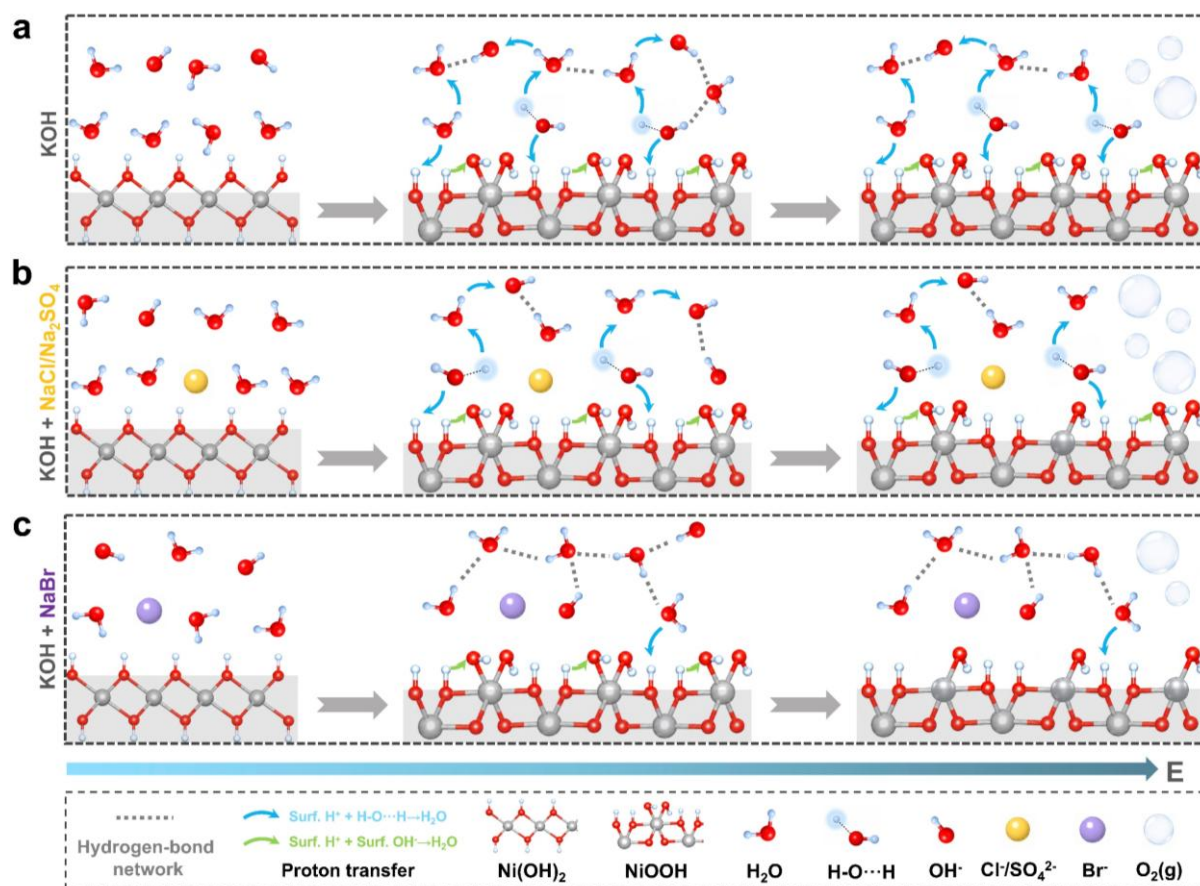
To understand the influence on the microenvironment, dynamic distributions of Cl<sup>-</sup> and Br<sup>-</sup> at the NiOOH-water interface are further characterized using MACE-driven molecular dynamics simulations, by monitoring the time evolution of their vertical distances from the interface. As shown in **Supplementary Fig. 19b and 19c**, the halide-surface distances fluctuate within finite ranges over the 180 ps MACE-MD trajectories, indicating that both Cl<sup>-</sup> and Br<sup>-</sup> remain confined to the interfacial region on the simulated timescale. The lowest  $z$  coordinate of the terminal Ni atoms is used to define the interfacial reference plane, and the time-averaged vertical distances of the six Cl<sup>-</sup> and six Br<sup>-</sup> ions relative to this plane are reported in **Supplementary Table. 5**. Compared with Br<sup>-</sup>, Cl<sup>-</sup> exhibits consistently shorter distances from the interfacial reference plane, suggesting a stronger tendency for Cl<sup>-</sup> to localize in the near-surface region.

The distinct interfacial positioning of Cl<sup>-</sup> and Br<sup>-</sup> introduces ion-specific perturbations to the local solvent environment, particularly in the orientational organization of interfacial water. To clarify this, the probability distributions of  $\cos\theta$  are statistically accumulated from the MACE-MD trajectories for water molecules located within three surface-distance intervals of 0-3, 3-7, and 7-11 Å, as shown in **Fig. 5a, 5c, and 5e**. Here,  $\theta$  is defined as the angle between the water dipole moment and the surface normal.

Within the 0-3 Å region (**Fig. 5a**), the OH<sup>-</sup>- and Cl<sup>-</sup>-containing interfaces exhibit enhanced probability densities at positive  $\cos\theta$  values, corresponding to configurations in which the water oxygen (O) atoms preferentially orient toward the NiOOH-water interface and the hydrogen (H) atoms point toward the aqueous phase, as illustrated in **Fig. 5d and 5e**. Importantly, O-down-oriented interfacial water, with the O atom directed toward the catalytic surface, provides a favorable configuration for accepting surface protons generated during the NiOR and OER processes and for promoting proton dissociation of interfacial water to form surface OH<sup>-</sup>.

In contrast, the Br<sup>-</sup>-containing system shows a broadened  $\cos\theta$  distribution, with an obviously reduced population of strongly O-down interfacial water and a larger contribution from partially aligned configurations, consistent with the representative configuration shown in **Fig. 5f**. This indicates that Br<sup>-</sup> weakens the surface-induced dipolar ordering of near-surface water. With less fraction of O-down interfacial water, desorption of surface protons has to rely more on the path 1 depicted in Eq. 2 (where the surface protons neutralize with the surface OH<sup>-</sup> and desorb together). The chance for dissociation adsorption of interfacial water ( $\text{H}_2\text{O} + * \rightarrow * \text{OH}^- + \text{H}$ ) is also decreased, which is consistent with its *in-situ* FTIR spectroscopic results in **Fig. 4f** where portion of asymmetric interfacial water is dramatically decreased compared to the other electrolyte. Therefore, the reduced population of O-down interfacial water at the Br<sup>-</sup>-

containing interface is expected to suppress the effective surface  $\text{OH}^-$  coverage, consistent with the EQCM results. This proposed interfacial-water-mediated mechanism is illustrated in **Scheme 1**.



**Scheme 1** Potential-dependent evolution of Ni hydroxide/oxyhydroxide interfaces in (a) KOH, (b) KOH + NaCl/Na<sub>2</sub>SO<sub>4</sub>, and (c) KOH + NaBr electrolytes. The scheme highlights the distinct effects of Cl<sup>-</sup> and Br<sup>-</sup> on interfacial proton transfer, hydrogen-bond network dynamics, and local solvation structures during OER.

The distance-resolved  $\cos\theta$  distributions further show that the halide-induced orientational ordering of water dipoles is spatially localized near the surface. In the 3–7 Å interval (**Fig. 5b**), the pronounced O-down preference observed in the 0–3 Å region becomes substantially weakened, and the water orientations are redistributed over a broader range of  $\cos\theta$  values. Although a positive- $\cos\theta$  population remains, especially in the OH<sup>-</sup>-containing system, the Cl<sup>-</sup>- and Br<sup>-</sup>-containing interfaces exhibit increased contributions from tilted and oppositely oriented water configurations, indicating a weaker halide-directed alignment of water dipoles away from the immediate surface region. This tendency becomes more evident in the 7–11 Å interval (**Fig. 5c**), where the distributions become broadly dispersed and no single halide-induced dipolar orientation dominates. These results indicate that, beyond the near-surface region, halide anions no longer impose a strong directional constraint on water dipoles, although residual differences among the OH<sup>-</sup>-, Cl<sup>-</sup>-, and Br<sup>-</sup>-containing systems remain.

Representative water configurations corresponding to the 3-7 and 7-11 Å intervals are provided in **Supplementary Fig. 20**.

The  $\cos\theta$  analysis reveals the spatial extent of the ion-specific orientational response but does not identify its local molecular origin. The radial organization and dipolar orientation of water around the surface-proximal halide ion are characterized using radial distribution functions (RDF) and probability density distributions. **Fig. 6a** presents the RDFs of Cl<sup>-</sup>-O and Br<sup>-</sup>-O for the six Cl<sup>-</sup> and Br<sup>-</sup> containing NiOOH-water interfacial models. The corresponding hydration-shell structures are presented in **Fig. 6b**.

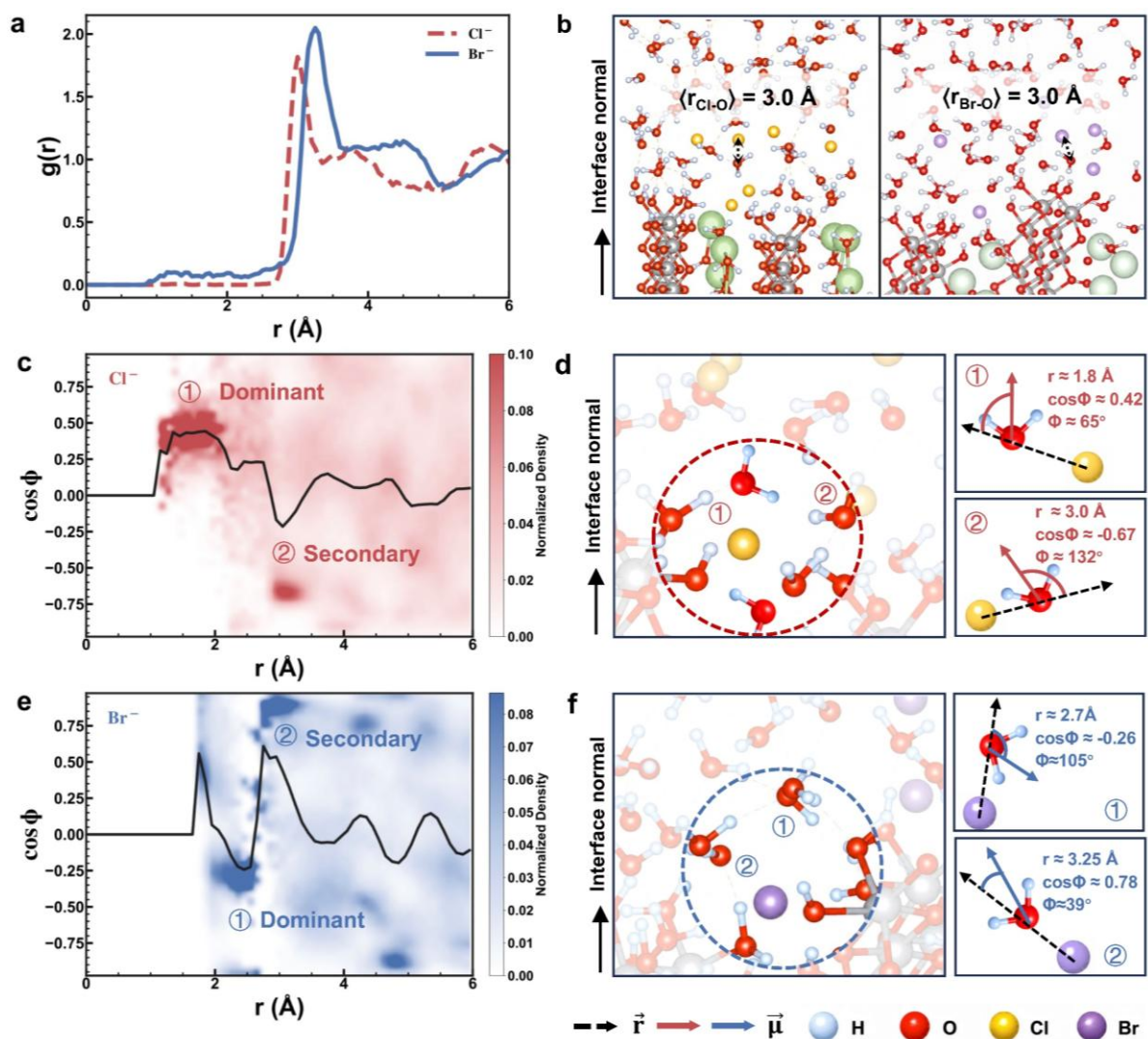


**Fig. 6 MACE-driven molecular dynamics analysis of halide-specific interfacial hydration at the NiOOH-water interface.** (a) Halide-water oxygen radial distribution functions,  $g(r)$ , for Cl<sup>-</sup> and Br<sup>-</sup> in NiOOH-water interfaces. (b) Representative hydration structures of interfacial Cl<sup>-</sup> and Br<sup>-</sup>. (c, e) Two-dimensional normalized probability density maps of the hydration configurations of surface-proximal Cl<sup>-</sup> and Br<sup>-</sup> as a function of halide-water oxygen distance ( $r$ ) and  $\cos\Phi$ . (d, f) Representative hydration structures corresponding to the dominant probability regions in (c) and (e).  $\Phi$  represents the angle between the water dipole moment ( $\vec{\mu}$ ) and the halide-water oxygen vector ( $\vec{r}$ ).

The Cl<sup>-</sup>-O RDF displays a sharper first peak at a shorter distance, whereas the Br<sup>-</sup>-O RDF is shifted outward and is more broadly distributed, indicating a more compact hydration environment around Cl<sup>-</sup> and a more diffuse solvation structure around Br<sup>-</sup>. This trend is consistent with previous neutron diffraction and first-principles simulation studies<sup>37-39</sup>.

The radial difference between Cl<sup>-</sup> and Br<sup>-</sup> solvation is further reflected in the orientational distributions of solvating water. The two-dimensional  $r$ - $\cos\Phi$  distribution of Cl<sup>-</sup> in **Fig. 6c** exhibits two dominant high-probability domains. The domain centred at  $r \approx 1.8$  Å and  $\cos\Phi \approx 0.42$  corresponds to hydration configurations in which the oxygen of water is directed toward Cl<sup>-</sup>, whereas the domain at  $r \approx 3.0$  Å and  $\cos\Phi \approx -0.67$  is associated with configurations where the hydrogen-bearing side of water faces Cl<sup>-</sup>. Representative structures assigned to these probability domains are shown in **Fig. 6d**. For Br<sup>-</sup>, the corresponding  $r$ - $\cos\Phi$  distribution in **Fig. 6e** features a high-probability domain centred at  $r \approx 2.7$  Å and  $\cos\Phi \approx -0.26$ , reflecting weakly oriented hydration configurations with the hydrogen-bearing side of water directed toward Br<sup>-</sup>. Another high-probability domain is located at  $r \approx 3.25$  Å and  $\cos\Phi \approx 0.78$ , corresponding to configurations in which the oxygen end of water is more strongly oriented toward Br<sup>-</sup>. The associated representative structures are presented in **Fig. 6f**.

The solvation analyses reveal a distinct ion-specific coupling between halide hydration and interfacial water-dipole orientation. In the Cl<sup>-</sup> hydration shell, the water oxygen atoms preferentially approach the anion, whereas water molecules surrounding Br<sup>-</sup> adopt configurations where the hydrogen atoms are directed toward the anion. This difference in hydration-shell polarity propagates into the first interfacial water layer, where Br<sup>-</sup> enrichment substantially reduces the population of O-down interfacial water configurations, impeding proton transfer away from the surface and the concomitant transport and adsorption of OH<sup>-</sup> toward the electrode, as depicted in **Scheme 1**.

## 2.4 Further evidence: distinct metal surface hydrophobicity induced by Br<sup>-</sup> and Cl<sup>-</sup> presence

The above OER, EQCM, *in-situ* FTIR, and AIMD results collectively indicate that interfacially enriched Br<sup>-</sup> suppresses OH<sup>-</sup> adsorption on the Ni surface. Because interfacial water and OH<sup>-</sup> participate in metal oxidation, the presence of Br<sup>-</sup> at the interface should influence Ni (electro)oxidation. To test this hypothesis, we evaluated metal corrosion behavior in different solutions. As expected, at pH 10.8 and 14, Br<sup>-</sup> increases the characteristic corrosion potential compared with that in pure alkaline solution, whereas Cl<sup>-</sup> lowers the corrosion potential of Ni (**Figs. 7a-d**).

Moreover, after immersion in different solution for 12 h, the Ni surface varied depending on the anion. Compared with pristine Ni metal, samples immersed in pure or Cl<sup>-</sup>-containing alkaline solutions exhibited decreased water contact angles (**Figs. 7e-g**). Severe oxidation and a higher fraction of oxidized Ni species were also found on the surfaces of these two samples, accompanied by a visibly darker appearance relative to the fresh electrode (**Supplementary Fig. 21**). In contrast, after the same

aging treatment in  $\text{Br}^-$ -containing solution, the water contact angle increased significantly, indicating a markedly more hydrophobic surface (**Fig. 7h**). The surface oxidation state of Ni remained similar to that of the fresh sample, which also retained a relatively bright metallic appearance (See **Supplementary Fig. 22** for the XRD patterns of the relevant samples). The corresponding XPS spectra are presented in **Supplementary Figs. 23 and 24**. These results collectively reflect the consistent influence of hydrated  $\text{Br}^-$  in the EDL on interfacial water behavior, which not only poisons OER but also retards the oxidative corrosion of Ni. This provides insights into the fact that Br-containing surfactants have long been used as an additive in anti-corrosion.

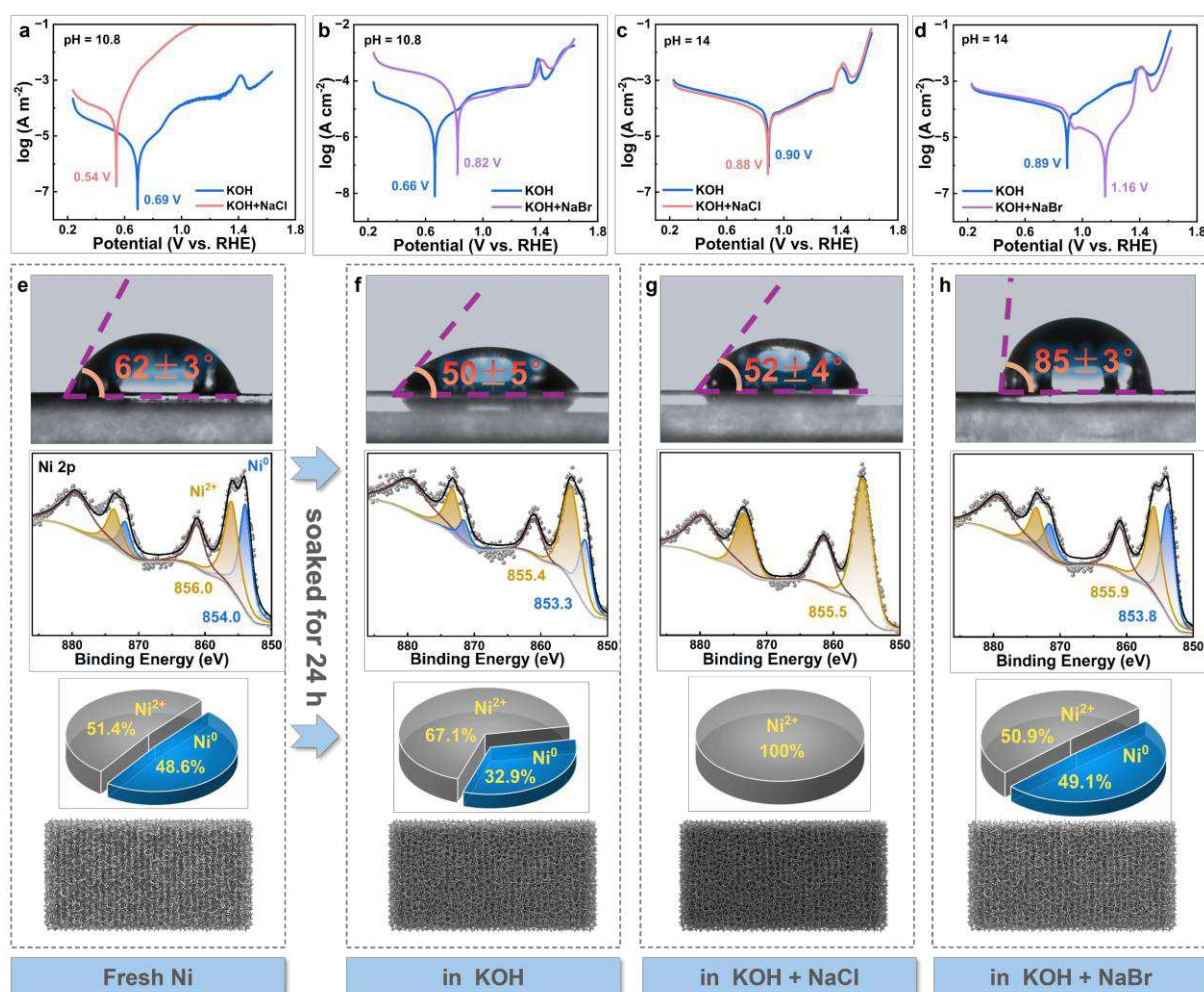


**Fig. 7 Distinctive corrosion behavior of Ni in halide-containing alkaline solution.** (a, b, c, d) Ni corrosion tafel plot in  $\text{Cl}^-$  and  $\text{Br}^-$  containing solutions at different pH values. Water contact angle, Ni 2p XPS spectra and resulting  $\text{Ni}^{2+}$ -to- $\text{Ni}^0$  ratio of different Ni foam: (e) the fresh one, (f,g,h) those being immersed in (f) pure KOH solution, (g)  $\text{Cl}^-$ - or (h)  $\text{Br}^-$ -containing alkaline solution for 24 h.

Although we have revealed that interfacial hydrated  $\text{Br}^-$  inhibits  $\text{OH}^-$  adsorption and demonstrated its reversible poisoning effect on OER, it should be clarified that prolonged contact between  $\text{Br}^-$  and the metal surface inevitably leads to covalent bonding between the two, as observed in our long-term polarization test

(Supplementary Note 5 and Supplementary Fig. 25-30)<sup>6</sup>. Though oxidative corrosion of OH<sup>-</sup> on Ni can be inhibited by hydrated Br<sup>-</sup>, covalently bonded Br<sup>-</sup> with metal itself was found to induce corrosion of the OER electrocatalyst, as reported in previous studies<sup>6</sup>.

### 3. Conclusions

In summary, this work reveals the distinct roles of Br<sup>-</sup> and Cl<sup>-</sup> in regulating the interfacial water orientation and thus the PCET process in both NiOR and alkaline OER process. Unlike Cl<sup>-</sup>, interfacial Br<sup>-</sup> adsorption reduces the population of O-down interfacial water, thereby disfavoring the PCET process during Ni(OH)<sub>2</sub>/NiOOH redox electrochemistry; as a consequence, it suppresses OH<sup>-</sup> replenishment and lowers surface OH<sup>-</sup> coverage during OER. This interfacial microenvironment modulation, rather than changes in the Ni electronic structure, accounts for the rapid, significant, and reversible poisoning of OER activity by Br<sup>-</sup>, which evolves into irreversible deactivation upon prolonged adsorption. This finding also provides insights into the role of Br<sup>-</sup> adsorption in reducing the hydrophobicity of Ni surfaces. By revealing the halide-specific interfacial impacts on alkaline OER process, we emphasize the link between solvation features of anions and interfacial water behaviors, which represents a potential motif in affecting the kinetics of PCET-relevant electrochemical processes.

### 4. Methods

#### Chemicals

Sodium bromide (NaBr, ≥99%, AR) was purchased from Aladdin. Sodium chloride (NaCl, 99.8%, GR) was purchased from Acme. Potassium hydroxide (KOH, 99.99%, GR), Nano-Nickel (20 nm-100 nm 99.9% basis Ni), Ammonium fluoride (NH<sub>4</sub>F, 96%, AR) and Urea (CO(NH<sub>3</sub>)<sub>2</sub>, AR) were purchased from Macklin. Sodium sulfide (Na<sub>2</sub>S·9H<sub>2</sub>O, AR), Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, AR) and Anhydrous ethanol (C<sub>2</sub>H<sub>5</sub>OH, AR) was purchased from XiHua. Nickel foam (NF, 99.99% purity, 1 mm thickness) and Nickel sheet (99.99% purity, 1 mm thickness) were purchased from Guangzhou Litige Co., Ltd.. All chemicals were used as received without further purification. Oxygen (99.999%) was purchased from Best Gas. Ultra-pure Milli-Q water (~18.2 MΩ cm) was used throughout the study.

#### Characterization

X-ray powder diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer (Rigaku, Japan) equipped with a Cu K $\alpha$  radiation source ( $\lambda$  = 1.5406 Å), Scan rate is 5° min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha system (USA) using monochromatic Al K $\alpha$  radiation ( $h\nu$  = 1486.6 eV) as the excitation source. Electrochemical measurements were performed using a CHI-400C series electrochemical quartz crystal microbalance (EQCM) system (Shanghai Chenhua Instrument Co., Ltd., CH Instruments). This instrument integrates a potentiostat/galvanostat with a quartz crystal microbalance, enabling the simultaneous acquisition of electrochemical responses and mass changes at the electrode surface.

### Preparation of Ni electrode

Nickel foam (99.99% purity, 1 mm thickness; Guangzhou Lithium Court Technology Co., Ltd.) was cut into rectangular pieces measuring 1.0 cm × 1.5 cm. The samples were subsequently degreased and cleaned by sequential ultrasonication in ethanol and deionized water for 10 min each, with the process repeated three times to ensure thorough removal of surface contaminants. Finally, the cleaned nickel foam pieces were dried in an oven at 60 °C for 5 h.

### Evaluation of OER activity in different electrolytes

Linear sweep voltammetry (LSV) was performed on a CHI 760E electrochemical workstation in a standard three-electrode configuration. Nickel foam (geometric area: 1.0 cm<sup>2</sup>) was used as the working electrode, a graphite rod (6 mm diameter) as the counter electrode, and an Hg/HgO electrode as the reference. The working electrode was contacted with platinum foil clips. The electrolytes: 1 M KOH, 1 M KOH + 0.5 M NaBr, 1 M KOH + 0.5 M NaCl, were each purged with O<sub>2</sub> prior to measurements. LSV curves were recorded at a scan rate of 5 mV·s<sup>-1</sup>. Prior to testing, the Ni foam electrode was electrochemically activated by cyclic voltammetry between 1.0 and 1.8 V versus the reversible hydrogen electrode (RHE) at 100 mV·s<sup>-1</sup> for 200 cycles until stable voltammograms were obtained. All potentials reported herein are referenced to the RHE according to the conversion:  $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0592 \times \text{pH}$ . All OER polarization curves were iR-corrected at 90%.

### Electrochemical quartz crystal microbalance (EQCM) measurements

EQCM measurements were performed on a CHI 440 workstation using a 7.995 MHz nickel-coated quartz crystal (Tangshan Master Electronics Co., Ltd.) as the working electrode, a platinum sheet (1 cm × 1 cm) served as the counter electrode, and an Hg/HgO electrode was used as the reference. The geometric area of the working electrode exposed to the electrolyte, defined by the cell gasket, was 0.1962 cm<sup>2</sup>. The electrolyte were 0.1 M KOH (pH ~13) with or without 0.5 M NaCl or 0.5 M NaBr.

Prior to measurements, the nickel-coated quartz crystal was electrochemically activated by 500 CV cycles between 1.0 V to 1.7 V versus RHE at 100 mV s<sup>-1</sup> in 0.1 M KOH. Subsequently, CV scans were recorded between 1.0 and 1.7 V versus RHE at scan rates of 5, 10, 20, 40, 50, 80, and 100 mV s<sup>-1</sup> (five cycles at each rate). The electrolyte was then replaced with 0.1 M KOH + 0.5 M NaCl, and the activation and CV protocols were repeated. Finally, the electrolyte was exchanged for 0.1 M KOH + 0.5 M NaBr, and the same procedures were followed.

The mass change ( $\Delta m$ ) was determined from the resonant frequency shift ( $\Delta f$ ) using the Sauerbrey equation<sup>40,41</sup>:

$$\Delta m = -C \cdot \Delta f \quad (\text{Eq. 4})$$

where  $C$  is the integral sensitivity of the quartz crystal ( $1.34 \pm 0.02 \text{ ng Hz}^{-1}$  for a 7.995 MHz crystal).

The charge ( $Q$ ) passed during the electrochemical process was obtained by

integrating the current ( $I$ ) over time:

$$Q = \int I dt \quad (\text{Eq. 5})$$

The mass change per mole of electrons transferred ( $mpe$ ) was calculated according to:

$$mpe = \frac{\Delta m \cdot F}{Q} \quad (\text{Eq. 6})$$

where  $F$  is the Faraday constant ( $96\,485\text{ C mol}^{-1}$ ). The  $mpe$  value provides the net mass change associated with one mole of electron transfer.

### **Operando XAFs measurements**

Operando X-ray absorption spectroscopy (XAS) measurements were conducted at the Ni K-edge on 2 nm-thick  $\text{Ni}_2\text{S}_3$  deposited onto carbon paper by magnetron sputtering, serving as the working electrode, at Beamline B18 of the Diamond Light Source (Didcot, UK). A custom-designed in-house electrochemical cell was employed for these experiments. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively, in 1 M KOH electrolyte. All electrochemical measurements were performed under computer control using an electrochemical workstation. XAS spectra were acquired continuously in fluorescence mode while the sample was subjected to chronoamperometry at various applied potentials. A Si (111) double-crystal monochromator was used for energy selection, with the energy calibrated against the first inflection point of a Ni metal foil reference (Ni K-edge = 8333 eV). Data processing and analysis were performed using the ATHENA software package.

### ***in-situ* Raman measurements**

Raman spectra were collected on a confocal Raman microscope (Xplora, Jobin-Yvon, France) using a 638 nm He-Ne laser. A 50 $\times$  objective lens (numerical aperture of 0.55) was used for all measurements. Wavenumber calibration was verified against the silicon Raman peak at 520.7  $\text{cm}^{-1}$ . Spectra were recorded over the range of 200–2000  $\text{cm}^{-1}$  with an acquisition time of 15 s.

*In-situ* electrochemical Raman measurements were performed in a dedicated Raman electrochemical cell (Warwick, Reach Co.) using a conventional three-electrode configuration. Nickel foam, a platinum wire, and an Hg/HgO electrode (1 M KOH) served as the working, counter, and reference electrodes, respectively. Electrochemical control was maintained with an Autolab PGSTAT30 potentiostat (Metrohm).

### ***in-situ* FTIR measurements**

*In-situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) measurements were performed on a Thermo Nicolet 8700 FTIR spectrometer coupled to a PAR-263 potentiostat via an in-house-developed control program. The spectrometer was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT-A) detector and a Globar infrared source. A custom-made Si prism coated with a chemically deposited gold nanofilm served as the ATR

element. The working electrode was prepared by drop-casting a catalyst ink onto the Au nanofilm. The ink was prepared by dispersing 1 mg of nickel nanoparticles and 1 mg of conductive carbon black in 900  $\mu\text{L}$  of ethanol and 100  $\mu\text{L}$  of deionized water, followed by sonication for 30 min. Subsequently, 30  $\mu\text{L}$  of the ink was drop-cast onto the prism and dried under ambient conditions.

*In-situ* IR measurements were conducted in a custom-designed spectroelectrochemical cell using 1 M KOH, 1 M KOH + 0.5 M NaCl, and 1 M KOH + 0.5 M NaBr as electrolytes. Spectra were collected over 400-4000  $\text{cm}^{-1}$ .

## Theoretical computation details

### Computational model

Complex redox phase transitions mediate the catalytic behavior of Ni-based materials, with  $\gamma$ -NiOOH widely accepted as the active phase for the oxygen evolution reaction (OER). This layered oxyhydroxide exhibits a substantial interlayer expansion, facilitating the intercalation of cations, anions, and water from the electrolyte<sup>42-45</sup>. The stoichiometry of  $\gamma$ -NiOOH is experimentally determined as  $\text{M}_{0.33}\cdot\text{NiO}_2\cdot 0.67\text{H}_2\text{O}$  ( $\text{M}^+$  = monovalent cation), based on electrochemical, iodometric, and spectroscopic evidence<sup>46-50</sup>.  $\gamma$ -NiOOH exhibits mixed  $\text{Ni}^{3+}/\text{Ni}^{4+}$  oxidation states (average oxidation state +3.67)<sup>47-50</sup> and ferromagnetic ordering arising from low-spin  $\text{Ni}^{3+}(\text{t}_{2g}^6\text{e}_g^1)$  and  $\text{Ni}^{4+}(\text{t}_{2g}^6\text{e}_g^0)$ <sup>51-55</sup>. To model the  $\gamma$ -NiOOH(010)-water interface, the surface is first saturated with a monolayer of chemisorbed water, hereafter denoted  $\gamma$ -NiOOH(010)-ml. The adsorption energies of  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  are calculated on the  $\gamma$ -NiOOH(010)-ml surface. The  $\gamma$ -NiOOH(010)-water interface is represented by a periodic supercell measuring 14.869, 9.998, and 46.110  $\text{\AA}$  and angles  $\alpha = \beta = 90^\circ$ ,  $\gamma = 105.769^\circ$ , with bulk lattice parameters taken from experiment ( $a = 4.975 \text{ \AA}$ ,  $b = 8.648 \text{ \AA}$ ,  $c = 14.740 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 104.05^\circ$ )<sup>56</sup>. At this interface, chemisorbed water is fully dissociated.  $\text{K}^+$  is employed as the intercalating cation. It is solvated by interlayer water and lattice oxygens, preserving a bulk-like coordination environment. To investigate the effect of halide anions on the interfacial properties, the initial configuration for  $\text{Cl}^-$  and  $\text{Br}^-$ -containing systems corresponds to an equilibrium frame of the  $\sim 30$  ps AIMD trajectory. Six  $\text{Cl}^-$  or  $\text{Br}^-$  anions are introduced into the interfacial aqueous region at randomized positions, with charge neutrality ensured by adjusting the interfacial protonation state. More details of the computational models are provided in **Supplementary Table 6**. As show in **Supplementary Fig. 31**, the resulting charge-neutral configurations define the initial geometries for MLMD simulations.

### DFT settings

DFT calculations are performed with spin polarization using the CP2K/Quickstep package<sup>57,58</sup>. Core electrons are represented by analytic Goedecker-Teter-Hutter (GTH) pseudopotentials, and the valence states of H (1s), O (2s, 2p), and Ni (3d, 4s, 4p) are treated explicitly<sup>59</sup>. Complete basis-set and pseudopotential specifications are provided in **Supplementary Table 7**. The valence orbitals are expanded in a double- $\zeta$  polarized (DZVP) basis set, and the electron density is expanded in plane waves with a cutoff of 500 Ry<sup>60</sup>. Only the  $\Gamma$ -point is sampled in the Brillouin zone. PBE+U method

is employed to correct strong correlation and self-interaction errors in the Ni 3d states of  $\gamma$ -NiOOH<sup>61,62</sup>. An effective  $U_{\text{eff}}$  of 3.5 eV on  $\text{Ni}^{3+}$  recovers the correct localized electronic configurations for both  $\text{Ni}^{3+}$  and  $\text{Ni}^{4+}$ . Grimme-D3 dispersion corrections are included<sup>63</sup>. The orbital transformation (OT) method is used for SCF optimization with a convergence threshold of  $3.0 \times 10^{-7}$ .<sup>64</sup> Ab initio molecular dynamics (AIMD) simulations are performed in the NVT ensemble at 330 K under Nosé-Hoover thermostat control<sup>65,66</sup>, with a time step of 0.5 fs. For the  $\gamma$ -NiOOH-water interface, the system is sampled for  $\sim 30$  ps.

### **Machine learning molecular dynamics**

Molecular dynamics simulations are performed for the  $\text{Cl}^-$ - and  $\text{Br}^-$ -containing  $\gamma$ -NiOOH(010)-water interfaces using the MACE-MPA-0-medium machine-learning interatomic potential<sup>67</sup>. These simulations are employed to elucidate the distinct roles of  $\text{Cl}^-$  and  $\text{Br}^-$  in perturbing the interfacial solvation structure of the corresponding halide-containing  $\gamma$ -NiOOH-water interfaces, with particular focus on the local structuring of interfacial water molecules and their interactions with solvated halide ions. The MACE-MPA-0-medium model is built upon the MACE architecture, a higher-order E(3)-equivariant message-passing neural network potential that encodes the requisite Euclidean and permutational symmetries of atomic systems. This framework enables an efficient representation of many-body interatomic interactions and is therefore well suited for extended molecular dynamics sampling of heterogeneous interfacial systems<sup>68</sup>. The total potential energy is decomposed into a sum of local atomic energy contributions, and the corresponding atomic forces are obtained analytically as the negative gradients of the energy with respect to atomic coordinates<sup>67,69</sup>. Each MD simulation is performed for 200 ps, including 20 ps of equilibration and 180 ps of production sampling. Atomic configurations are saved every 10 fs for subsequent analysis of interfacial water orientation, hydrogen-bond network evolution, and  $\text{Cl}^-/\text{Br}^-$  solvation motifs at the corresponding halide-containing NiOOH-water interfaces.

### **Credit authorship contribution statement**

H.H., and J.H. contributed equally to this work. Y.Z., C.W., Y.H., J.L., J.C. and S.S. supervised the project and provided guidance on the project. Y.Z., H.H. and J.H. conceived and designed the study. H.H., H.C., and W.L. performed the experiments. J.H., and J.C. performed the AIMD studies. F. E. O., G. G., conducted Operando XAFs measurements. H.H., J.H., C.W., Y.H. and Y.Z. wrote and revised the paper. All authors contributed to the analysis.

### **Declaration of Competing Interest**

The authors declare that there is no conflict of interest.

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