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Scalable synthesis of hetero-structured Ni/NiO@RE₂O₃/C for high-performance industrial-scale HER catalysis by AEMWE

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Abstract: Actualizing mass production of high-performance Ni-based nanocatalysts and industrial-scale HER catalysis via AEMWE is significant yet challenging. Herein, we develop a scalable method to generally produce Ni/NiO@RE₂O₃/C with 500 g-scale for unprecedented HER catalysis of AEMWE. The hetero-structured Ni/NiO@La₂O₃/C consists of *fcc* Ni metal as the core, *fcc* NiO as the sub-surface layer and *bcc* La₂O₃ adhered on the local surface. Its remarkable HER performance of 32 mV overpotential at 10 mA cm⁻² and 29.2 mV dec⁻¹ Tafel slope is significantly better than those of Pt/C, Raney Ni, Ni/NiO/C and other Ni/NiO@RE₂O₃/C. More importantly, it can realize industrial-scale current densities of 1 A cm⁻² and 2 A cm⁻² at 1.6 V and 1.7 V for AEMWE, respectively, exceeding the U.S. DOE's target in 2025 specifications, along with a long-term lifetime of 250 h with voltage decay rate of only 76 μ V h⁻¹, demonstrating a large potential for industrial-scale AEMWE application.

Introduction

Hydrogen energy has the advantages of high energy density, wide source, environmental protection and renewability, which can be considered as an ideal energy carrier to solve the global fossil energy shortage and environmental pollution problems¹⁻³. From the perspective of its source, the use of water electrolysis (WE) technology to produce green hydrogen has very important basic research value and practical application significance⁴⁻⁶. Among various WE technologies, anion exchange membrane WE (AEMWE) as the 3rd generation of WE technology is very promising, and has multiple advantages such as low cost, high efficiency, mild operating conditions, safety, environmental protection and strong flexibility⁷⁻⁹. This is due to the fact that it can use the cheap non-precious metal-based catalysts, which greatly reduces the overall cost. Simultaneously, it can operate at lower temperatures and pressures, reducing the equipment investment costs and operational risks. Moreover, AEM has good selective permeability to hydroxide ions, which can realize the rapid ion transport and improve the electrolysis reaction rate, thus enhancing the hydrogen production efficiency. Furthermore, AEMWE is

environmentally friendly and reduces the wastewater discharge and product purification steps, making it to be one of the most promising green hydrogen production technologies in the future¹⁰⁻¹². To achieve high performance of AEMWE device, it is firstly necessary to significantly enhance the catalytic performances of alkaline hydrogen evolution reaction (HER) catalysts¹³. From the perspective of HER mechanism, the use of highly active and stable catalysts is beneficial to improve the kinetics of Vollmer step and the efficiency of hydrogen production under alkaline conditions¹⁴⁻¹⁶. Generally, precious metals-based and non-precious metals-based nanomaterials are two types of alternative alkaline HER catalysts. However, the precious metals are expensive and scarce in reserves, while non-precious metals-based catalysts tend to exhibit low activity and stability, seriously hindering the process of sustainable hydrogen production and practical application of AEMWE¹⁷⁻¹⁹. Developing completely non-precious metals-based catalysts with high alkaline HER performance and electrolytic device performance is the key to the large-scale commercialization of AEMWE technology at the current and future stages.

In recent years, a great deal of efforts were put into the development of various non-precious metals-based HER catalysts²⁰⁻²². Numerous studies have shown that those nickel (Ni)-based nanomaterials with high electrical conductivity, low cost and high storage capacity can effectively promote the adsorption and dissociation of H₂O. They are highly expected as efficient and practical non-precious metals-based HER catalysts, or even for replacing the platinum (Pt) group metals (PGM)-based catalysts²³⁻²⁵. However, the Ni-based nanomaterials have a relatively strong affinity with OH* produced by water dissociation, which can hinder the subsequent H₂O adsorption and lead to the slow kinetics of alkaline Vollmer step, thus inhibiting the WE reaction. Accordingly, the nanostructures and electronic structures of Ni-based materials need to be further regulated and optimized²⁶⁻²⁸. By far, a variety of methods for the modification of Ni-based HER nanomaterials have been successfully reported, such as the doping of nonmetallic elements (N, P, S, etc.), the modulation of crystalline phases, the construction of core-shell or

heterojunction structures, the modulation of metal-carrier interactions, the introduction of oxygen vacancy defects and so forth²⁹⁻³¹. Unfortunately, the vast majority of these Ni-based nanomaterials adopt the combined types of Ni with those metals/nonmetals having only 3*d* orbital or shielded *f*-orbital energy levels, while the centralized distribution of *d*-orbital electrons may lead to a low electron transfer efficiency, making it difficult to desorb the H* dissociated from H₂O, thus reducing the HER rate. There is still a large room for the performance improvement in both HER and corresponding membrane electrode assembly (MEA) media. It remains the current research focus and difficulty to reasonably select the effective elements with higher orbital energy level and combine them with Ni to form a new type of Ni-based nanocatalysts for greatly improving the alkaline HER efficiency. Among them, the nanomaterials of rare earth (RE) elements combined with Ni may break the performance bottleneck of those traditional Ni-based nanocatalysts, which is even less considered in the relevant literatures reported to date³². Inherently, the RE elements except of scandium (Sc) and yttrium (Y) have unique advantages such as special electronic configurations of partially occupied 4*f* orbitals ([Xe]4*f*^{*n*-1}5*d*⁰⁻¹6*s*², *n* = 1-15), various crystal structures and relatively low electronegativity. When integrating with Ni, the RE elements with smaller electronegativity and stronger ability to provide the electrons are beneficial for modulating the surface electronic environment of Ni atoms, lowering the activation energy of HER and thus enhancing its reaction rate³³⁻³⁵. Hence, developing a new class of Ni-RE-based nanomaterials with high alkaline HER and MEA performances is very significant and cutting-edge^{36,37}. Unfortunately, it is still a challenging research task by far.

Based on these considerations, herein, we adopt a dual rare earth and nickel oxides assistance strategy to construct 16 kinds of non-radioactive RE oxides adhered Ni/NiO nanomaterials grown on carbon support (Ni/NiO@RE₂O₃/C) as the high-performance non-noble metal-based catalysts for alkaline HER and MEA catalysis. The detailed structure analyses demonstrate that the representative Ni/NiO@La₂O₃/C

consists of face-centered cubic (*fcc*)-Ni as the core, *fcc*-NiO as the sub-surface layer and body-centered cubic (*bcc*)-La₂O₃ as the local surface composition. Impressively, the optimized Ni/NiO@La₂O₃/C exhibits an outstanding alkaline HER performance with a low overpotential of 32 mV at 10 mA cm⁻² and a competitive Tafel slope of 29.2 mV dec⁻¹, largely exceeding those of commercial Pt/C, Raney Ni, Ni/NiO/C and other Ni/NiO@RE₂O₃/C, even much better than those of majority of currently reported Ni-based catalysts. Moreover, it also realizes a satisfactory HER stability over 130 h, which is far superior to the commercial Pt/C (nearly inactivation after 24 h). More importantly, the Ni/NiO@La₂O₃/C can achieve an industrial-scale alkaline MEA electrolysis with 1.6 V@1 A cm⁻² and 1.7 V@2 A cm⁻² for AEMWE, which can exceed the U.S. Department of Energy (DOE)'s target in 2025 specifications for hydrogen production (1.8 V@2 A cm⁻²). Meanwhile, a remarkable MEA lifetime with only 9.3% voltage decay can be readily achieved at 1 A cm⁻² for 250 h, which is better than those of Ni/NiO@La₂O₃/C, Ni/NiO/C and commercial Pt/C. This work creates a new type of Ni-based non-precious metal nanocatalysts that can simultaneously achieve the state-of-the-art performance improvement in both alkaline HER and industrial-scale MEA media, accelerating the commercialization proceeding of AEMWE technology.

Results

Synthesis and structure characterizations for various Ni/NiO@RE₂O₃/C. In this work, 16 kinds of Ni/NiO@RE₂O₃/C nanocatalysts (RE = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) can be obtained by using a scalable one-step annealing synthesis method. Take the representative Ni/NiO@La₂O₃/C as an example, its synthetic process has been displayed (details in the Materials synthesis section). It is noted that its mass production amount can be magnified to 500 g for a batch, which is very difficult to be afforded by many state-of-the-art HER catalysts, revealing the robustness of this scalable synthesis method (Fig. 1a, b). We firstly analyze its structure by many characterization techniques. The transmission electron microscopy (TEM) image shows that the uniform nanoparticles (NPs) with an

average diameter of 11.2 ± 1.9 nm highly distribute on the commercial C powder (Fig. 1c and its inset). As measured by TEM energy-dispersive X-ray spectroscopy (TEM-EDS), its atomic ratio of Ni/La is measured to be 93.3/6.7, indicating that Ni is the dominant component and La is the doped component for this nanomaterial (Fig. 1d). To study its crystalline phase and crystal structure, the X-ray diffraction (XRD) measurement was conducted. Three diffraction peaks in the XRD pattern locate at $2\theta = 44.48^\circ$, 51.81° and 76.33° , which is very close to the standard (111), (200) and (220) crystal planes of *fcc*-Ni with Fm-3m (225) space group ($2\theta = 44.51^\circ$, 51.85° and 76.37° , JCPDS, No. 04-0850) (Fig. 1e). The slight shifts can be attributed to the partial substitution of La with larger atomic radius into the Ni lattices, which can induce the local lattice distortion, resulting in the Ni lattice expansion. This phenomenon was also verified by the high-resolution TEM (HRTEM) image of Ni/NiO@La₂O₃/C, showing that the lattice spacing of (111) plane is 0.206 nm, a little higher than that of the theoretical value (0.203 nm) (Fig. 1f).

To make clear the element distributions of Ni and La in the bulk and on the surface of Ni/NiO@La₂O₃/C, the high-angle annular dark-field scanning TEM (HAADF-STEM) image, HAADF-STEM-EDS elemental mappings and detailed X-ray photoelectron spectroscopy (XPS) techniques were performed. The HAADF-STEM image with elemental mappings display that the Ni element is enriched in the core, while the La element mainly locates at the partial edge of this NP, revealing the presence of heterostructure interface (white dotted line) and the local existence of La element (Fig. 1g). Particularly, we analyzed the compositions and valence states of elements for Ni/NiO@La₂O₃/C before and after different etching degrees (S₀-S₅) by XPS in detail. As for the initial Ni/NiO@La₂O₃/C (S₀), the surface content of La₂O₃ is measured to be 30.3%, which is the highest one among all the samples of S₀-S₅. With the increased etching degrees, the content of La₂O₃ on the surface displays a sharp decline (Fig. 1h, Supplementary Fig. 1 and Supplementary Table 1). Simultaneously, the La element nearly all exists as the oxidation state based on the fitting results of peaks, that is, from surface and sub-surface to interior, the

content of La_2O_3 gradually drops, and the La element with the form of La_2O_3 mainly exists on the surface (Supplementary Figs. 1a, 3a, 4a, 5a, 6a, 7a and Supplementary Table 1). By contrast, the Ni element exhibits a different situation. The measured content of NiO in the sub-surface (S_1) is even higher than the case on the surface (S_0). However, with the etching degree increases, the content of Ni shows an increasing trend from 28.4% (S_2) to 37.8% (S_5). It is demonstrated that the compositions of NiO and Ni mainly locate in the sub-surface and in the interior, respectively (Fig. 1i, Supplementary Figs. 2b, 3b, 4b, 5b, 6b, 7b and Supplementary Table 1). Based on these above analyses, we can logically construct the corresponding atomic model and crystal structures for the surface, subsurface and interior parts of $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$ (Fig. 1j). The *bcc*-phased La_2O_3 mainly distributes on the local surface. The *fcc*-phased NiO mostly locates in the sub-surface (a little higher) and on the surface (a little lower), but shows a gradually decreased trend from sub-surface to interior. Moreover, the content of *fcc*-phased Ni becomes higher from sub-surface to interior. These three parts collectively construct the well-defined $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$ with a unique tri-phase heterostructure.

Atomic-level structure analysis of $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$. In order to accurately analyze the structural features of $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$, the aberration-corrected HAADF-STEM (AC-HAADF-STEM) technique with atomic-level resolution was then performed. The AC-HAADF-STEM image of $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$ shows that its single NP presents the different degrees of crystallinity and obvious lattice boundaries (white dotted lines). Especially, the lattice orientations at the edge are largely different from those in the center (Fig. 2a). According to the fast Fourier transform (FFT) analysis, three planes belonging to different phases can be clearly distinguished, and no diffraction loop of polycrystalline material was observed, further indicating that the $\text{Ni/NiO@La}_2\text{O}_3/\text{C}$ has a single-crystal dominated heterostructure (Fig. 2b). To further certify the different compositions of this hetero-structure, the atomic-level analyses were performed separately for the labeled regions in Fig. 2a. At the edge of this NP, the clear atom arrangement

with lattice spacing of 0.224 nm can be observed, corresponding to the standard atom arrangement of (002) plane in *bcc*-phased La_2O_3 with *Im-3m* (229) space group along the $\langle 001 \rangle$ zone axis (Fig. 2c, d). Meanwhile, in the adjacent areas between edge and interior, the atom arrangement of (200) plane in *fcc*-phased NiO with lattice spacing of 0.210 nm can also be found (Fig. 2e, f). Moreover, the case of *fcc*-phased Ni is similar to that of *fcc*-phased NiO with *Fm-3m* (225) space group along the $\langle 100 \rangle$ zone axis, excepting for the lattice spacing of (200) plane (0.174 nm) (Fig. 2g, h). These analyses of lattice planes and atom arrangements are consistent well with those of above structure results (Fig. 1c-g and Fig. 2a-h). Based on these coupled analyses at the atomic-scale, we can confirm the distinctive hetero-structure of Ni/NiO@ La_2O_3 /C featured with three different components, including the main *bcc*- La_2O_3 attached on the local surface, the main *fcc*-NiO located in the sub-surface and on the surface, along with the main *fcc*-Ni located in the interior. It is also noted that two types of lattice boundaries exist between *bcc*- La_2O_3 and *fcc*-Ni as well as between *fcc*-NiO and *fcc*-Ni, forming two types of metallic oxide/metal interfaces ($\text{La}_2\text{O}_3/\text{Ni}$ and NiO/Ni). These three components of *bcc*- La_2O_3 , *fcc*-NiO and *fcc*-Ni can expose their respective roles to the surface-adsorbed reagents and reaction intermediates, which is beneficial for the improvement of targeted catalytic performance.

Local electronic structure and coordination environment analysis of Ni/NiO@ La_2O_3 /C. To elucidate the local electronic structure and coordination environment for Ni/NiO@ La_2O_3 /C, we used the X-ray absorption spectroscopy (XAS) technique. From the Ni K-edge X-ray absorption near-edge structure (XANES) spectra of different samples, it is observed that the spectrum of Ni/NiO@ La_2O_3 /C is more inclined towards both of referenced Ni foil (metallic state) and NiO (oxidized state) under different intensities, indicating the coexistence of Ni^0 and Ni^{2+} in Ni/NiO@ La_2O_3 /C, corresponding to the Ni and NiO components, respectively (Fig. 2i). Simultaneously, we also analyzed the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra of different samples in R spaces. The

referenced Ni foil and NiO display the standard radial distances (R values) of Ni-Ni bond (2.95 Å) and Ni-O bond (2.08 Å), respectively. By contrast, the Ni/NiO@La₂O₃/C mainly exhibits a lower R value of Ni-Ni bond at 2.49 Å (Fig. 2j). This result can be ascribed to the coexistence of La₂O₃ and NiO in Ni/NiO@La₂O₃/C with lattice distortions. Moreover, we measured the coordination number (CN) for Ni/NiO@La₂O₃/C by FT-EXAFS spectrum, since the CN can be considered as a significant descriptor for nanostructure analysis and electrocatalytic property. Accordingly, the CN of Ni-Ni bond for Ni/NiO@La₂O₃/C is fitted to be about 7.4, which is between the cases of Ni foil (12) and NiO (6), further demonstrating the presence of low-coordination defect sites (Fig. 2j, k, Supplementary Fig. 8a, c and Supplementary Table 2). Furthermore, the wavelet transform (WT) analyses of Ni K-edge FT-EXAFS data were performed to verify the Ni-Ni/Ni-O bonds differences for Ni/NiO@La₂O₃/C, Ni foil and NiO, especially reflecting the characteristic coordination center of Ni/NiO@La₂O₃/C (Fig. 2l and Supplementary Fig. 8b, d). These results from its unique local electronic structures of *bcc*-La₂O₃ and *fcc*-NiO will affect the evolution of electrocatalytic property for *fcc*-Ni. Based on these detailed analyses, the distinctive nanostructure and electronic structure are expected to endow the Ni/NiO@La₂O₃/C with satisfactory HER and MEA performances for AEMWE.

Alkaline HER performance of Ni/NiO@La₂O₃/C. In this work, to comprehensively evaluate the alkaline HER performances of designed Ni-based nanocatalysts affected by the parameters of different types of RE₂O₃ species, different contents of La₂O₃, Sm₂O₃ and NiO, we prepared various catalysts in comparison with Ni/NiO@La₂O₃/C (Fig. 1c-g), including 15 kinds of other Ni/NiO@RE₂O₃/C (Supplementary Figs. 9-23), 3 kinds of Ni/NiO@La₂O₃/C with different amounts of La₂O₃ (Supplementary Figs. 24-27), 4 kinds of Ni/NiO@La₂O₃/C with different amounts of NiO (Supplementary Figs. 28-31), along with Ni/NiO/C (Supplementary Fig. 32), Raney Ni (Supplementary Fig. 33) and commercial Pt/C (Supplementary Fig. 34). The alkaline HER performance of each catalyst was then tested

by linear scanning voltammetry (LSV) with an accurate calibration of reference electrode (Supplementary Fig. 35) and the corresponding polarization curve measured in 1 M KOH electrolyte was obtained. As a result, the Ni/NiO@La₂O₃/C only needs a low overpotential of 32 mV to achieve the current density of 10 mA cm⁻², much better than those of Ni/NiO@Sm₂O₃/C (45 mV@10 mA cm⁻²), Ni/NiO/C (216 mV@10 mA cm⁻²), Raney Ni (99 mV@10 mA cm⁻²) and commercial Pt/C (59 mV@10 mA cm⁻²) (Fig. 3a, b). Simultaneously, the Ni/NiO@La₂O₃/C also displays a much lower Tafel slope of 29.2 mV dec⁻¹ in comparison with Ni/NiO@Sm₂O₃/C (63.4 mV dec⁻¹), Ni/NiO/C (162.8 mV dec⁻¹), Raney Ni (139.3 mV dec⁻¹) and commercial Pt/C (67.3 mV dec⁻¹), indicating the faster alkaline HER kinetics (Fig. 3c, d). Moreover, the HER performances of Ni/NiO@La₂O₃/C with different contents of La₂O₃ and NiO were also evaluated. Compared with other samples with different contents of La₂O₃ (3.0%, 9.9% and 18.2%) and NiO (67.0%, 73.1%, 86.6% and 91.9%), the Ni/NiO@La₂O₃/C with 6.7% La₂O₃ and 82.9% NiO (initial Ni/NiO@La₂O₃/C) still exhibits the lowest overpotential, indicating the most suitable La₂O₃ and NiO contents for optimized HER catalysis (Fig. 3e, f, Supplementary Figs. 36, 37 and Supplementary Table 3). Actually, the overpotential of 32 mV for Ni/NiO@La₂O₃/C is the lowest one among 16 kinds of Ni/NiO@RE₂O₃/C, Ni/NiO/C, Raney Ni and commercial Pt/C (Fig. 3g, Supplementary Fig. 38a and Supplementary Table 4). The Tafel slope of 29.2 mV dec⁻¹ for Ni/NiO@La₂O₃/C is also the lowest one among all the catalysts investigated (Fig. 3h, Supplementary Fig. 38b and Supplementary Table 4). It should be mentioned that both of the HER overpotential at 10 mA cm⁻² and Tafel slope of Ni/NiO@La₂O₃/C measured in 1 M KOH have outperformed vast majority of state-of-the-art HER catalysts reported in recent five years (more than 60 kinds of HER catalysts), demonstrating the unprecedented alkaline HER kinetics (Fig. 3i and Supplementary Table 5). Furthermore, to test the stabilities of different HER catalysts, their voltage-time curves at the current density of 10 mA cm⁻² were recorded. It is observed that the Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C, Raney Ni and

commercial Pt/C display the overpotential decay of 89 mV, 50 mV, 61 mV, 379 mV and 238 mV after different durations, respectively (Fig. 3j). The corresponding residual overpotentials of Ni/NiO@La₂O₃/C (121 mV) and Ni/NiO@Sm₂O₃/C (95 mV) after 130 h durability tests are obviously better than those of Ni/NiO/C (277 mV after 130 h), Raney Ni (478 mV after 24 h) and commercial Pt/C (400 mV after 24 h), revealing the much enhanced HER stability for Ni/NiO@La₂O₃/C and Ni/NiO@Sm₂O₃/C. In addition, these five HER catalysts after the durability tests were characterized. The spent Ni/NiO@La₂O₃/C can largely maintain its NP morphology without obvious size change (11.6 ± 1.8 nm) and lattice distance of (111) plane (0.207 nm), except for the elemental mappings of Ni and La and atomic ratio of Ni/La (98.7/1.3) (Supplementary Fig. 39). The composition evolution of La₂O₃ and catalyst exfoliation from the electrode are the main reasons for the presence of active sites loss and performance degradation. The case of spent Ni/NiO@Sm₂O₃/C except for the large size increase (14.3 ± 1.4 nm) is similar to that of spent Ni/NiO@La₂O₃/C (Supplementary Fig. 40). By contrast, the Ni/NiO/C, Raney Ni and commercial Pt/C after the HER stability tests exhibit the obvious aggregations and evolutions in their shapes and average diameters (Supplementary Figs. 41-43), further demonstrating the favorable structure and catalytic stabilities for Ni/NiO@La₂O₃/C. Hence, according to these above results of electrocatalytic performances for various Ni-based catalysts, the optimized Ni/NiO@La₂O₃/C is equipped with the best alkaline HER kinetics and durability among all the catalysts investigated, which cannot be afforded by Raney Ni, commercial Pt/C and many other counterparts.

Origin of performance enhancement. In order to explore the origins of HER performance enhancement for Ni/NiO@La₂O₃/C, the electrochemical measurements, XPS, XAS, Raman spectra and electrochemical *in-situ* Raman spectra of different catalysts were applied for collective analyses. Firstly, the highest alkaline HER performance of Ni/NiO@La₂O₃/C can be ascribed to the largest numbers of active sites (ECSA), as revealed by the cyclic voltammetry (CV) curves measured at different scanning speeds and

the calculated double electric layer capacitance (C_{dl}). The C_{dl} value of Ni/NiO@La₂O₃/C is measured to be 50.1 mF cm⁻², much higher than those of Ni/NiO@Sm₂O₃/C (22.3 mF cm⁻²), Ni/NiO/C (6.0 mF cm⁻²), Raney Ni (2.1 mF cm⁻²) and commercial Pt/C (1.7 mF cm⁻²) (Fig. 4a and Supplementary Fig. 44). Simultaneously, the Ohmic semicircle of electrochemical impedance spectroscopy (EIS) for Ni/NiO@La₂O₃/C is the smallest one, and its charge transfer resistance (R_{ct}) is measured to be 10.4 Ω , lower than those of Ni/NiO@Sm₂O₃/C (22.7 Ω), Ni/NiO/C (49.3 Ω), Raney Ni (26.2 Ω) and commercial Pt/C (22.1 Ω), showing its fastest charge conduction rate among all the counterparts investigated (Fig. 4b). Moreover, the XPS results show that the NiO contents are 82.9%, 83.2% and 68.4% for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C, respectively (Fig. 4c). The higher NiO contents on the surfaces of Ni/NiO@La₂O₃/C and Ni/NiO@Sm₂O₃/C versus Ni/NiO/C are beneficial for the improvement of alkaline HER kinetics, which is consistent with the electrochemical measurement result (Fig. 3a-d and Fig. 4c). For those Ni/NiO@La₂O₃/C with different amounts of La₂O₃, the positive shifts of diffraction peaks increase as the La/Ni ratio gradually enhances, which can be attributed to the partial substitution of Ni lattice sites by La (Supplementary Fig. 27). The moderate La₂O₃ and NiO contents (6.7% and 82.9%) on the surface of Ni/NiO@La₂O₃/C achieve the highest alkaline HER performance, rather than the cases of too high and too low La₂O₃ and NiO contents, further revealing the key roles of suitable La₂O₃ and NiO contents effected on the catalytic property of Ni (Fig. 3e, f, Fig. 4d and Supplementary Table 6). Furthermore, the Ni K-edge XANES spectra of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C jointly demonstrate the presence of overall NiO, which is in accordance with the above structure analyses (Fig. 2i and Supplementary Fig. 45a). The Ni K-edge FT-EXAFS spectra of different catalysts exhibit the same R value of Ni-Ni bond for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C (2.49 Å), which is lower than that of Ni foil (2.95 Å). However, the CN of Ni-Ni bond for Ni/NiO@La₂O₃/C (7.4) is different from those of Ni/NiO@Sm₂O₃/C (6.9) and Ni/NiO/C (9.8) (Fig. 2j, Supplementary Fig. 45b and

Supplementary Table 2). This result means that the most suitable contents of NiO and La₂O₃ endow the Ni composition with optimized lattice parameter and coordination environment, achieving the highest alkaline HER performance of Ni/NiO@La₂O₃/C. The Ni K-edge FT-EXAFS spectra in R spaces and corresponding WT analyses further verify the Ni-Ni bond differences among Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C, demonstrating their similar yet distinctive coordination centers (Fig. 2k, l and Supplementary Fig. 46).

In addition, we also measured the Raman spectra of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C and commercial Pt/C in comparison with Vulcan XC-72R C. The Ni/NiO@La₂O₃/C exhibits the largest G peak/D peak intensity (I_G/I_D) ratio of 0.95 among these five samples, revealing the highest degrees of graphitization and conductivity. The lowest electrical resistivity is beneficial to the HER performance improvement for Ni/NiO@La₂O₃/C (Fig. 4e, f). Actually, the OH stretching mode of water molecules on the surface is of great significance for understanding the alkaline HER mechanism catalyzed by Ni/NiO@La₂O₃/C. Accordingly, the *in-situ* Raman spectra of Ni/NiO@La₂O₃/C for alkaline HER catalysis were measured at different voltages with the help of *in-situ* electrolytic cell (Fig. 4g and Supplementary Fig. 47a). The three characteristic peaks in these *in-situ* Raman spectra correspond to the weakly H-bonded water molecules at about 3600 cm⁻¹, the asymmetric H-bonded water molecules at about 3400 cm⁻¹ and the symmetric H-bonded water molecules at about 3200 cm⁻¹. Generally, after the peak fitting at about 3603.8 cm⁻¹, the ratio of weakly H-bonded water molecules displays a tendency of increasing firstly and then reaching to equilibrium (from 4.4% to 8.7%) along with the voltages ranged from 0 V to -0.7 V (Fig. 4h and Supplementary Fig. 47b-h). To be specific, the content of weakly H-bonded water molecules at 0 V is only 4.4%, indicating a low degree of water cleavage in the initial state (Supplementary Fig. 47b). With the voltages changing from 0 V to -0.1 V, -0.2 V, -0.3 V and -0.4 V, the contents of weakly H-bonded water molecules gradually increase until to 8.6% (Supplementary Fig. 47c-

f). When the voltages are exerted to -0.5 V and -0.7 V, the contents of weakly H-bonded water molecules still maintain at around 8.6% (Supplementary Fig. 47g, h). This trend indicates that the surface of Ni/NiO@La₂O₃/C can induce the different degrees of H-bond dissociation after exerting the suitable potentials, forming the more weakly H-bonded water molecules and lowering the overall H-O bond breaking energy barrier. Logically, we can gain the direct relationship among content of NiO, CN of Ni-Ni bond and relative overpotential of alkaline HER for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C, in which the moderate NiO content of 82.9% and Ni-Ni bond CN of 7.4 endow Ni/NiO@La₂O₃/C with the most efficient alkaline HER kinetics (Fig. 4i).

In particular, compared with Ni/NiO/C, the selective introduction of La reshapes the local electronic structure and coordination environment, moderately reduces the CN of Ni-Ni bond and optimizes the adsorption energy of HER intermediates for Ni/NiO@La₂O₃/C. Its characteristic electronic property (contribution from 4f orbital electrons) and lattice distortion effect synergistically result in the rapid charge transfer, accelerating the adsorption and dissociation of water molecules and the desorption cycle of OH* species in alkaline medium. Based on these above experimental results, we can infer the logical alkaline HER mechanism on three parts of Ni/NiO@La₂O₃/C (Fig. 4j). The water molecules can be firstly adsorbed onto the metallic Ni surface, and the intermediate of Ni-H₂O_{ads} is formed. Subsequently, the dual oxides of NiO and La₂O₃ can adsorb the OH* species and promote the Volmer step by breaking the H-OH bond, and thus resulting in the formation of Ni-H_{ads}. The generated Ni-H_{ads} then undergoes the Tafel step and combines with each other to form H₂, which is in line with the above analyses. Thereinto, the La₂O₃ and NiO compositions can act as the electron donors and transfer the electrons to La₂O₃-OH ads and NiO-OH_{ads} adsorbed on the surface to produce the OH-species, collectively enabling the Ni/NiO@La₂O₃/C to achieve the high-performance industrial-scale alkaline HER catalysis. In general, the alkaline HER

mechanism of Ni/NiO@La₂O₃/C is that its three parts of Ni, NiO and La₂O₃ can pertinently promote the Tafel step, Volmer step and Volmer step, respectively.

MEA performance evaluation of Ni/NiO@La₂O₃/C for AEMWE. In order to systematically evaluate the practical AEMWE performance of Ni/NiO@La₂O₃/C, a standardized test platform was built in this study (Supplementary Fig. 48). The used MEA setup contains the AEM, cathode catalyst layer (Ni/NiO@La₂O₃/C), anode catalyst layer (NiFe-LDH@NF), gas diffusion layer (GDL, carbon paper) and bipolar plates (serpentine flow path with groove width of 0.5 mm) (Fig. 5a). As shown in Fig. 5b, the practical cathode and anode catalysts for AEMWE can be uniformly sprayed on the AEM surface, in which the Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C and commercial Pt/C were used as the cathodic catalysts for comparison, respectively, while the NiFe-LDH@NF was always used as the self-supporting anode catalyst layer. The polarization curves of different catalysts were then tested under the standardized test conditions (1 M KOH electrolyte, 60°C, atmospheric pressure). It is found that the MEA with Ni/NiO@La₂O₃/C as HER catalyst reaches the current density of 1 A cm⁻² at the operating voltage of 1.6 V, which is better than those of Ni/NiO@Sm₂O₃/C (1.9 V@1 A cm⁻²), Ni/NiO/C (2.3 V@1 A cm⁻²) and commercial Pt/C (1.7 V@1 A cm⁻²) (Fig. 5c, d). Simultaneously, this MEA only need 1.7 V to achieve the current density of 2 A cm⁻², still much better than those of Ni/NiO@Sm₂O₃/C (2.1 V@2 A cm⁻²), Ni/NiO/C (2.7 V@2 A cm⁻²) and commercial Pt/C (1.9 V@2 A cm⁻²) (Fig. 5c, e). Impressively, the MEA performance of Ni/NiO@La₂O₃/C (1.6 V@1 A cm⁻² and 1.7 V@2 A cm⁻²) for AEMWE not only exceeds that of commercial Pt/C (1.7 V@1 A cm⁻² and 1.9 V@2 A cm⁻²), but also surpasses the 2025 target of U.S. DOE specification (1.8 V@2 A cm⁻²), demonstrating the great potential and practicability for industrialized applications. More importantly, the MEA performance of Ni/NiO@La₂O₃/C for AEMWE has outperformed those of vast majority of non-noble metal-based and even many noble metal-based HER catalysts reported in recent five years (Fig. 5f and Supplementary Table 7). Furthermore, to

evaluate the MEA lifetime of Ni/NiO@La₂O₃/C, the constant current tests at 1 A cm⁻² were performed for these four HER catalysts. As a result, the Ni/NiO@La₂O₃/C can largely maintain its MEA performance for 250 h with only 9.3% voltage decay (decay rate of 76 μ V h⁻¹), slightly better than that of Ni/NiO@Sm₂O₃/C with 11.5% voltage loss after 213 h, but much better than those of Ni/NiO/C (9.8% voltage loss after 164 h) and commercial Pt/C (10.3% voltage loss after 141 h) (Fig. 5g). Consequently, the optimized Ni/NiO@La₂O₃/C can simultaneously achieve the highest alkaline HER and MEA performances among all the catalysts investigated, making it one of the most efficient catalysts ever achieved for those non-noble metal-based HER catalysts reported to date.

Discussion

In this work, we develop a robust method of mass preparation to generally synthesize a new class of hetero-structured Ni/NiO@RE₂O₃/C (RE = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) as the highly efficient alkaline HER catalysts for AEMWE. Particularly, the distinctive heterostructure of representative Ni/NiO@La₂O₃/C is unveiled by the atomic-level structure characterization technique, in which the *fcc*-Ni mainly locates in the interior, the *fcc*-NiO mainly exists in the sub-surface and on the surface, while the *bcc*-La₂O₃ mainly attaches on the local surface. Just due to the coexistence of exposed *bcc*-La₂O₃ and *fcc*-NiO, the intrinsic property of *fcc*-Ni can be largely activated by promoting the Vollmer and Tafel steps. It should be mentioned that the optimized Ni/NiO@La₂O₃/C exhibits a low overpotential of 32 mV at 10 mA cm⁻² and a small Tafel slope of 29.2 mV dec⁻¹ in 1.0 M KOH solution, much better than those of commercial Pt/C (59 mV@10 mA cm⁻², 67.3 mV dec⁻¹), Raney Ni (99 mV@10 mA cm⁻², 139.3 mV dec⁻¹), Ni/NiO/C (216 mV@10 mA cm⁻², 162.8 mV dec⁻¹) and other 15 kinds of Ni/NiO@RE₂O₃/C (45~163 mV@10 mA cm⁻², 57.0~157.4 mV dec⁻¹). The ultrahigh alkaline HER kinetics of Ni/NiO@La₂O₃/C can outperform those of most non-noble metal-based (more than 60 kinds of) catalysts reported in recent five years, making it one of the most efficient HER catalysts reported to

date. More importantly, its MEA can readily realize the industrial-scale current densities of 1 A cm^{-2} and 2 A cm^{-2} at the electrolysis voltages of 1.6 V and 1.7 V for AEMWE, exceeding the U.S. DOE's target in 2025 specifications ($1.8 \text{ V}@2 \text{ A cm}^{-2}$), even better than those of vast majority of non-noble metal-based and many noble metal-based HER catalysts reported in recent five years (total for more than 80 kinds of catalysts). Simultaneously, its MEA exhibits a long-term lifetime with only 19 mV voltage decay at the industrial-scale current density of 1 A cm^{-2} for 250 h, demonstrating a large potential for practical AEMWE application. The experimental results jointly reveal that the dual oxides of NiO and La_2O_3 play the key roles in promoting the inherent HER performance of Ni, which can largely accelerate the rates of electron transfer and OH-species production, and even lower the overall H-O bond breaking energy barrier, enabling the Ni/NiO@ La_2O_3 /C with remarkable alkaline HER and MEA performances for AEMWE. This study highlights a scalable and general production approach to creating the hetero-structured Ni/NiO@ RE_2O_3 /C, representing a key step towards the realization of high-performance industrial-scale AEMWE technology with completely non-noble metal-based HER catalysts.

Methods

Chemicals. Nickle (II) acetylacetonate ($\text{Ni}(\text{acac})_2$, $\geq 99.99\%$) was obtained from Acme Biochemical. Scandium (III) acetate ($\text{Sc}(\text{Ac})_3$, $\geq 99.9\%$), yttrium (III) acetate ($\text{Y}(\text{Ac})_3$, $\geq 99.99\%$), lanthanum (III) acetate ($\text{La}(\text{Ac})_3$, $\geq 99.9\%$), cerium (III) acetate ($\text{Ce}(\text{Ac})_3$, $\geq 99.99\%$), praseodymium (III) acetate ($\text{Pr}(\text{Ac})_3$, $\geq 99.9\%$), neodymium (III) acetate ($\text{Nd}(\text{Ac})_3$, $\geq 99.99\%$), samarium (III) acetate ($\text{Sm}(\text{Ac})_3$, $\geq 99.99\%$), Europium (III) acetate ($\text{Eu}(\text{Ac})_3$, $\geq 99.99\%$), gadolinium (III) acetate ($\text{Gd}(\text{Ac})_3$, $\geq 99.99\%$), terbium (III) acetate ($\text{Tb}(\text{Ac})_3$, $\geq 99.99\%$), dysprosium (III) acetate ($\text{Dy}(\text{Ac})_3$, $\geq 99\%$), holmium (III) acetate ($\text{Ho}(\text{Ac})_3$, $\geq 99.99\%$), Erbium (III) acetate ($\text{Er}(\text{Ac})_3$, $\geq 99.99\%$), thulium (III) acetate ($\text{Tm}(\text{Ac})_3$, $\geq 99.99\%$), ytterbium (III) acetate ($\text{Yb}(\text{Ac})_3$, $\geq 99.99\%$) and lutetium (III) acetate ($\text{Lu}(\text{Ac})_3$, $\geq 99.99\%$) were supplied by Aladdin. Ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\geq 99.9\%$), ammonium

chloride (NH_4F , $\geq 99.5\%$), urea ($\text{CH}_4\text{N}_2\text{O}$, $\geq 99.0\%$) and potassium hydroxide (KOH , $\geq 99.99\%$) were purchased from Macklin. Commercial carbon powder (C, Vulcan XC-72R) was purchased from Cabot. Isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$, analytical reagent, $\geq 99.7\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd. Nafion (5%) and commercial Pt/C (40 wt%, 2-5 nm Pt NPs on Vulcan XC-72R C) were purchased from Suzhou Sinero Technology Co. Ltd. Commercial Raney Ni ($\geq 90.0\%$) was purchased from Anhui Zesheng Technology Co., Ltd. Ethanol (EtOH , analytical reagent, $\geq 99.7\%$) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$) were purchased from Xilong Scientific. The water ($18.0 \text{ M}\Omega \text{ cm}^{-1}$) used in all experiments was prepared by passing through an ultrapure purification system. All the chemicals were used as received without further purification.

Materials synthesis. In a typical synthesis process of 500 g-Ni/NiO@La₂O₃/C, 2.3 kg Ni(acac)₂, 0.13 kg La(Ac)₃ and 0.13 kg Vulcan XC-72R C were added into a beaker (25 L). Then, 5.0 L NH₃·H₂O, 5.0 L H₂O and 5.0 L EtOH were added to the beaker and ultrasonically treated for about 40 min to obtain a uniform mixture. The obtained mixed solution was heated to evaporation at 100 °C and the product was collected. The obtained product was heated to 400 °C with a specific annealing equipment and held for 2 h under the 95% Ar/5% H₂ atmosphere. For the preparation of other 10 g-Ni/NiO@La₂O₃/C with different La₂O₃ contents (3.0%, 6.7%, 9.9% and 18.2%), all conditions are similar to those of 500 g-Ni/NiO@La₂O₃/C except for changing the feeding amounts of La(Ac)₃ to 1.3 g, 2.6 g, 5.2 g and 10.4 g, respectively. For the preparation of other 10 g-Ni/NiO@La₂O₃/C with different NiO contents (67.0%, 73.1%, 82.9%, 86.6% and 91.9%), all conditions are similar to those of 10 g-Ni/NiO@La₂O₃/C (6.7% La₂O₃) except for changing the reaction temperatures to 300 °C, 350 °C, 450 °C and 500 °C, respectively. For the preparation of other 15 kinds of 10 g-Ni/NiO@RE₂O₃/C, all conditions are similar to those of 10 g-Ni/NiO@La₂O₃/C (6.7% La₂O₃, 82.9% NiO) except for changing the precursors of RE elements with corresponding feeding amounts (5.7 g for Sc(Ac)₃, 4.9 g for Y(Ac)₃, 2.8 g for Ce(Ac)₃, 5.4 g for Pr(Ac)₃,

3.6 g for Nd(Ac)₃, 6.0 g for Sm(Ac)₃, 5.0 g for Eu(Ac)₃, 4.5 g for Gd(Ac)₃, 6.9 g for Tb(Ac)₃, 6.1 g for Dy(Ac)₃, 4.9 g for Ho(Ac)₃, 3.9 g for Er(Ac)₃, 9.1 g for Tm(Ac)₃, 7.8 g for Yb(Ac)₃ and 6.8 g for Lu(Ac)₃. The synthesis of referenced 10 g-Ni/NiO/C was conducted under the above identical conditions to 10 g-Ni/NiO@RE₂O₃/C except without the addition of any RE element precursors. To prepare the home-made NiFe-LDH grown on Ni foam (NF), 0.4 g Fe(NO₃)₃·9H₂O, 0.29 g Ni(NO₃)₂·6H₂O, 0.13 g NH₄F and 0.6 g CH₄N₂O were add-ed into a beaker with 40 mL water. The mixture was ultra-sonicated for 10 min, then transferred to a Teflon-lined stainless-steel autoclave with the NF (2 × 2 cm²) and heated at 120 °C for 6 h in an oven. After natural cooling, the product was washed with water for several times, then dried at 80 °C for 1 h in the vacuum atmosphere to obtain the final home-made NiFe-LDH@NF³⁸.

Characterizations. TEM images and TEM-EDS were operated on a JEM-1400 microscope at 100 kV. HAADF-STEM and HRTEM were performed on an FEI Tecnai F30 microscope at 200 kV. AC-HAADF-STEM images were obtained by a JEOL JEM-F200 microscope operated at 200 kV. XRD patterns were collected on the Rigaku Ultima IV powder diffractometer equipped with a Cu radiation source ($\lambda = 0.15406$ nm). SEM-EDS was performed with the ZEISS SUPRA 55 SAPPHIRE field emission SEM. XPS was performed by using a Thermo Scientific ESCALAB 250 XI spectrometer. All XPS data were corrected for charging effects with C1s peak at 284.8 eV as the reference. XAS data were collected at the TPS-44A beamline of the National Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan) using a Si (111) quick-scanning monochromator. All the XAS data were processed according to standard procedures using the Demeter program package (Version 0.9.24).

Electrochemical measurements. The different Ni/NiO@RE₂O₃/C (8 mg) were sonicated in a mixture of 400 μ L isopropyl alcohol and 5 μ L Nafion (5%) for 1 h to obtain the uniform catalyst ink. The working electrode was prepared by dropping the catalyst ink on the glassy carbon (GC) electrode. The electrochemical measurements were conducted on the CHI660E electrochemical station (Chenhua,

Shanghai). In the three-electrode system, a saturated calomel electrode (SCE) and a graphite rod were used as the reference electrode and counter electrode, respectively. The CV and LSV curves of different catalysts were acquired in 1.0 M KOH solutions. All the used potentials were calibrated from the SCE to the reversible hydrogen electrode (RHE). During these measurements, the 95% iR compensation was employed and the scan rate was set to 1 mV s⁻¹. The Tafel slope was derived by plotting the potential (η) against log |j| based on the LSV curve. For the measurements of ECSAs for different catalysts, the CV curves within the non-Faradaic potential windows were recorded at various scanning rates. By utilizing the C_{dl} formula, the ECSAs of different electrocatalysts can be calculated. The EIS was recorded in the frequency range of 0.1 to 106 Hz using a sine wave with an amplitude of ± 5 mV at -0.15 V versus (vs.) RHE, and the Nyquist plots for different catalysts were obtained at -0.15 V vs. RHE in the HER medium.

***In-situ* Raman measurements.** The setup for *in-situ* Raman measurements is a custom-made two-chamber three-electrode electrochemical cell with a quartz window. A gold electrode is used as the working electrode. A Pt wire serves as the counter electrode. A Hg/HgO electrode is used as the reference electrode. A Gamry Reference 600+ potentiostat was used to control the electrode potential. Before the measurements, the gold electrodes were polished with a 0.05 μ m alumina suspension. Then, 5 μ L of Ni/NiO@La₂O₃/C ink is dropped onto the gold electrodes to prepare the Ni/NiO@La₂O₃/C modified gold electrode. The *in-situ* Raman spectroscopy measurements are conducted by using a LabRAM HR Evolution microscope (Horiba Jobin Yvon) equipped with a 532 nm laser, a $\times 50$ objective lens (NA = 0.55) and a CCD detector. The Raman frequency is calibrated by using a silicon wafer before each experiment. The laser intensity is set to 10.0% to prevent changes to the Pt surface due to the irradiation of deposited organic additives. The acquisition time for each spectrum is set to 150 s.

MEA test. When preparing the ink for MEA catalysis, each catalyst and anion exchange resin solution were ultrasonically dispersed in water/isopropanol (v/v = 1/4) for 1 h. The resulting mixture was evenly

sprayed onto a W-25 type AEM (W-25, thickness: 25 μm , dimension: $3.0 \times 3.0 \text{ cm}^2$) by using a manufactured sprayer instrument from Suzhou Sinero (SCP102 model) and controlling the loading amount of 10 mg cm^{-2} for Ni/NiO@La₂O₃/C, Ni/NiO@La₂O₃/C and Ni/NiO/C, while the loading amount of commercial Pt/C was 1 mg cm^{-2} . Subsequently, the AEM coated with the needed cathode catalyst, carbon paper (thickness: 190 μm , dimension: $1.0 \times 1.0 \text{ cm}^2$, Chemours) and home-made NiFe-LDH@NF were assembled into the corresponding MEA for AEMWE. The resulting MEA was placed in a fixture and operated at 60 °C with 1 M KOH fed at a rate of 15 mL min^{-1} , and the polarization curves were measured accordingly.

Data availability

All data supporting the findings of this study are available in the main text or Supplementary Information.

Source data are provided with this study.

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Author contributions

L.B., X.H. and H.G. conceived and supervised this work. L.B. and X.W. designed the experiments and performed the majority of analyses. K.J. and X.H. performed the HRTEM test. H.G. and X.S. conducted the XPS test. X.H., H.G., D.W. and J.M. participated in the related discussions. L.B. and X.W. wrote the paper. All authors commented on this manuscript.

Additional information

Supplementary Information The online version contains supplementary material available at <http://www.nature.com/>.

Competing financial interests

The authors declare no competing financial interests.

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Figures

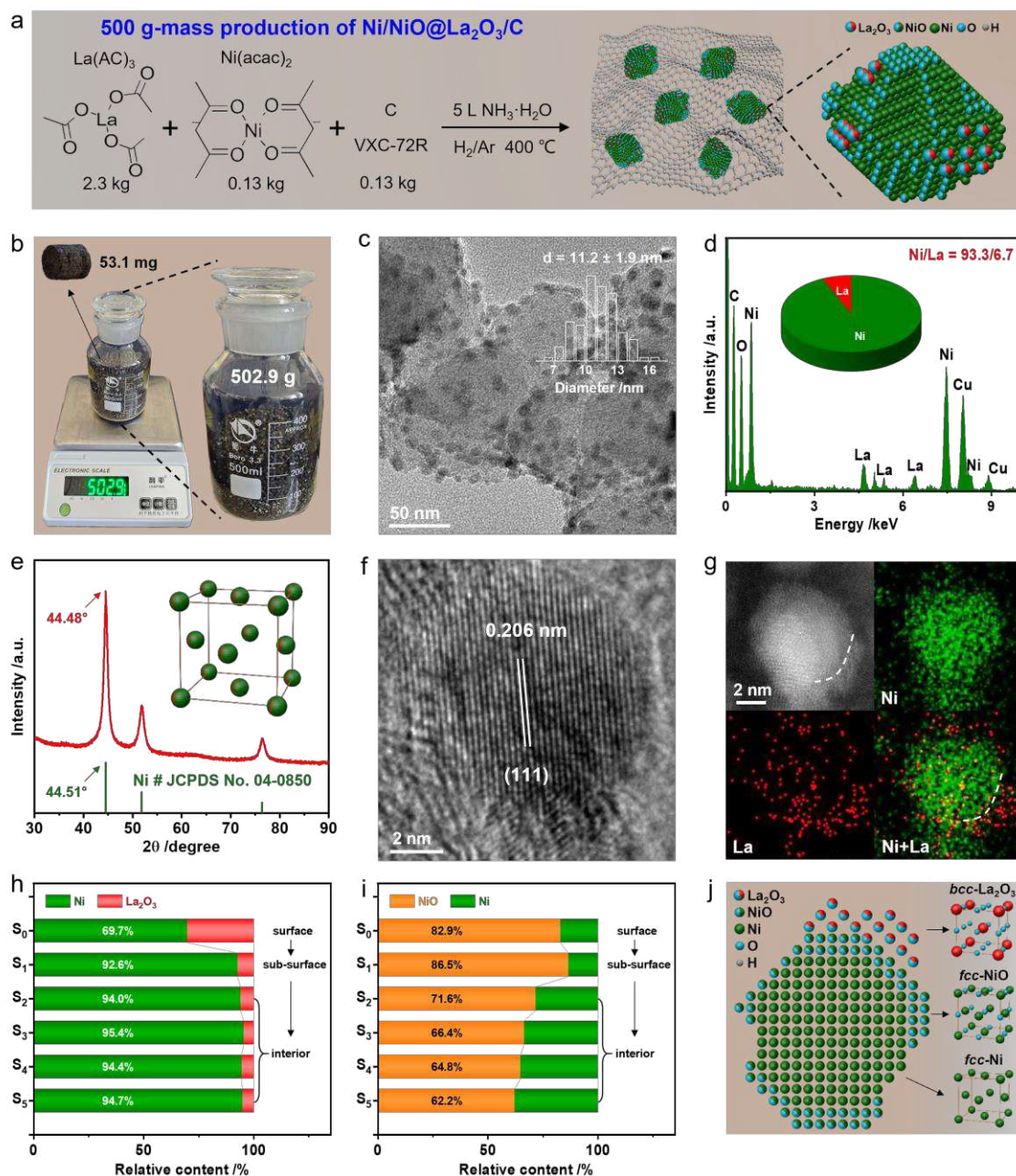


Figure 1. Mass production and structure characterizations of Ni/NiO@La₂O₃/C. **a** Scalable preparation of 500 g-scale and **b** optical photographs of this catalyst and its building block. **c** TEM image with inset of particle size statistics. **d** TEM-EDS with inset of atomic percentages of Ni and La. **e** XRD pattern with inset of crystal structure. **f** HRTEM image. **g** HAADF-STEM image with elemental mappings. The white dotted line shows the boundary of heterostructure interface. **h, i** Composition evolutions of **h** Ni and La₂O₃ and **i** Ni and NiO from surface to interior of Ni/NiO@La₂O₃/C before and after different etching degrees, as revealed by XPS. From S₀ to S₅, the etching degrees are gradually improved. **j** Schematic atom model and corresponding crystal structures of different parts for Ni/NiO@La₂O₃/C.

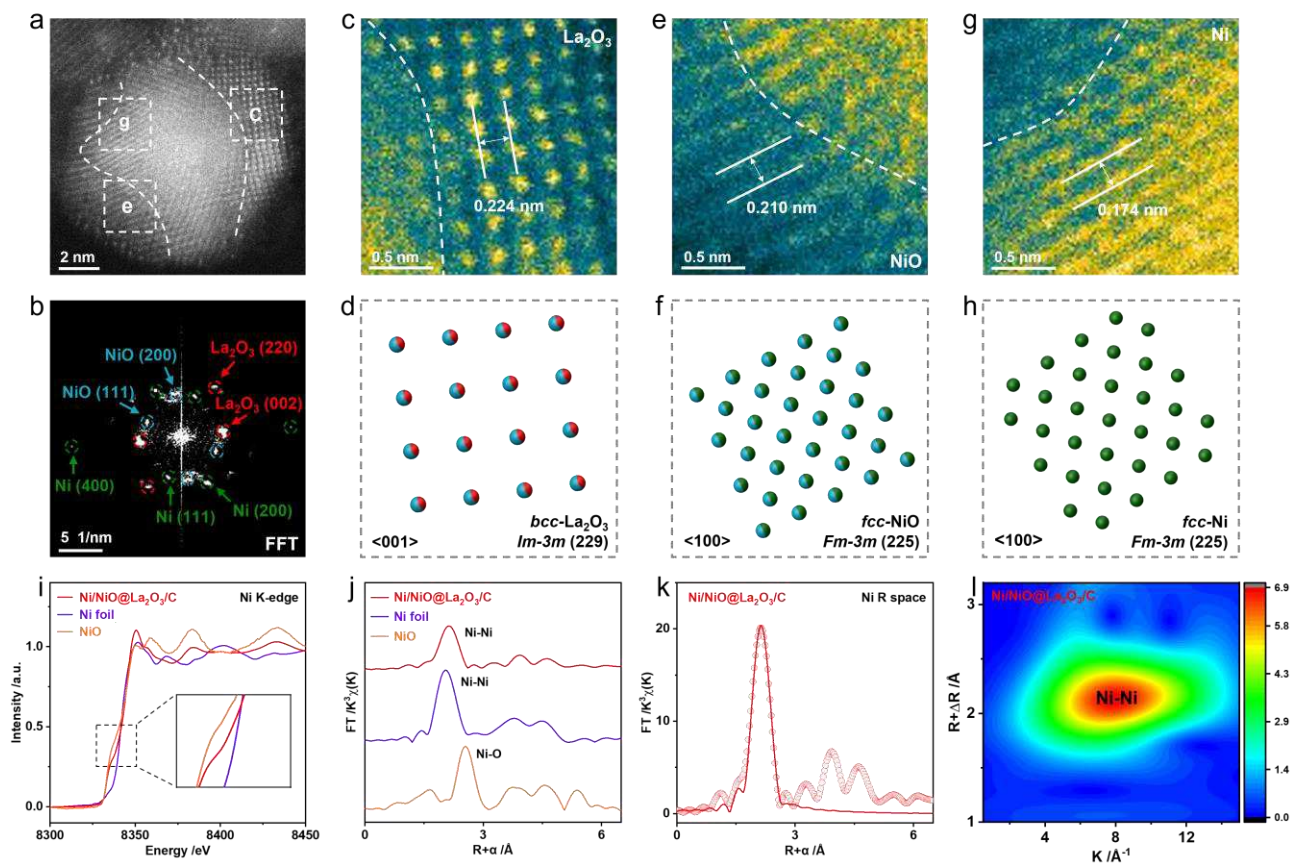


Figure 2. Atomic-level structure analyses of Ni/NiO@La₂O₃/C. **a** AC-HAADF-STEM image and **b** corresponding FFT pattern. The white dotted lines reveal the existence of different lattice boundaries. **c**, **e**, **g** Magnified AC-HAADF-STEM images of selected regions in **a**, clearly showing the atom arrangement states located at different parts. **d**, **f**, **h** Corresponding atomic arrangement models of *bcc*-La₂O₃, *fcc*-NiO and *fcc*-Ni parts from **c**, **e** and **g**, respectively. **i** Ni K-edge XANES profiles and **j** FT-EXAFS spectra in R spaces of Ni/NiO@La₂O₃/C, Ni foil and NiO. **k** Experimental and fit data of Ni K-edge FT-EXAFS spectrum in R space and **l** WT analysis of Ni K-edge FT-EXAFS data for Ni/NiO@La₂O₃/C.

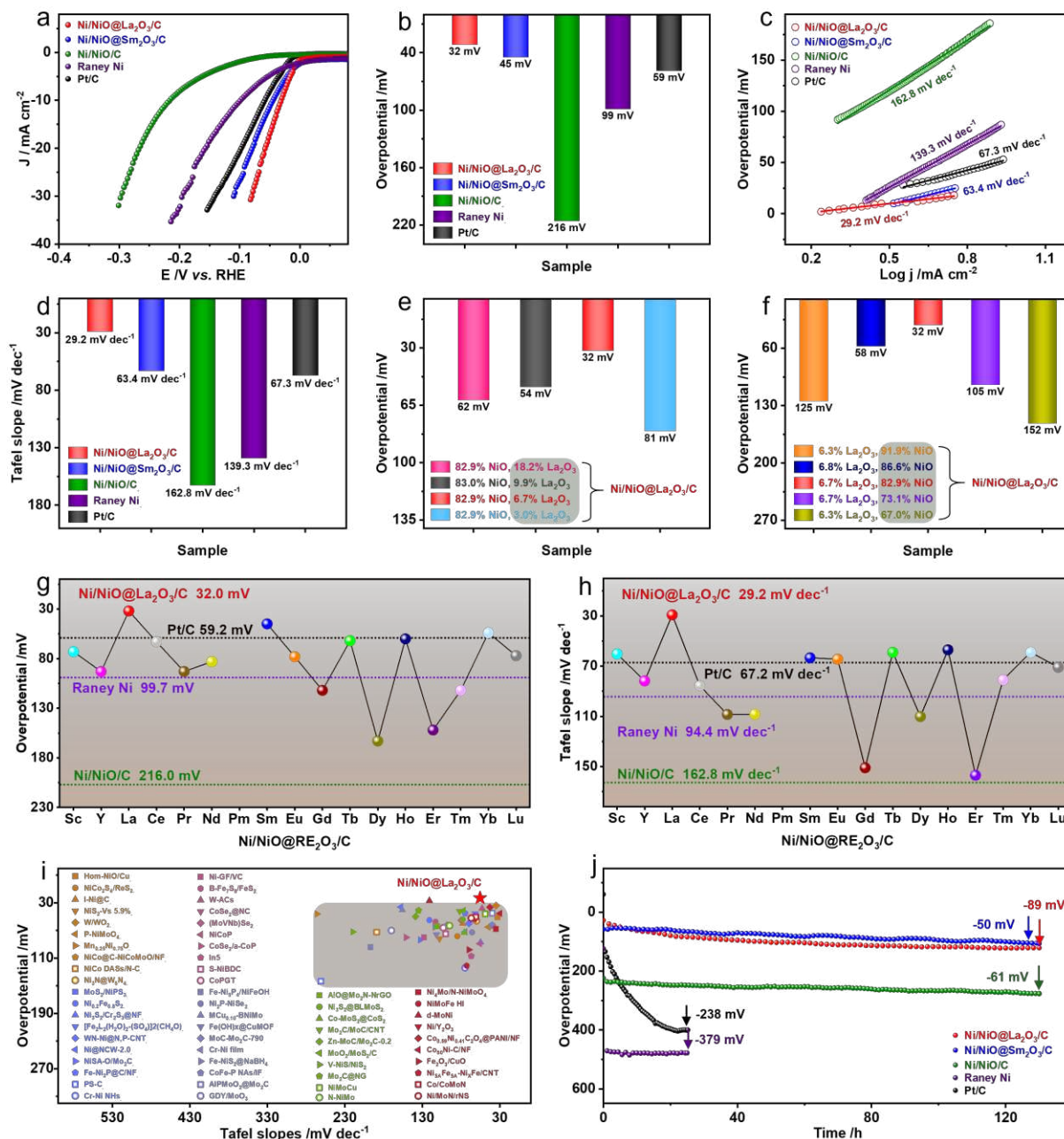


Figure 3. HER performances of Ni/NiO@La₂O₃/C and other counterparts. **a** LSV curves, **b** overpotentials at 10 mA cm⁻² and **c**, **d** Tafel slopes of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C, Raney Ni and Pt/C in 1 M KOH. **e**, **f** Overpotentials of different Ni/NiO@La₂O₃/C at 10 mA cm⁻² with **e** different La₂O₃ contents and **f** different NiO contents, in which the different La₂O₃ and NiO contents were based on the SEM-EDS and XPS measurements, respectively. **g** Overpotentials at 10 mA cm⁻² and **h** Tafel slopes of different Ni/NiO@RE₂O₃/C compared with Ni/NiO/C, Raney Ni and Pt/C. **i** Comparison of overpotentials at 10 mA cm⁻² and Tafel slopes between Ni/NiO@La₂O₃/C and those HER catalysts reported in recent five years. **j** Durability curves of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C, Raney Ni and Pt/C measured at 10 mA cm⁻².

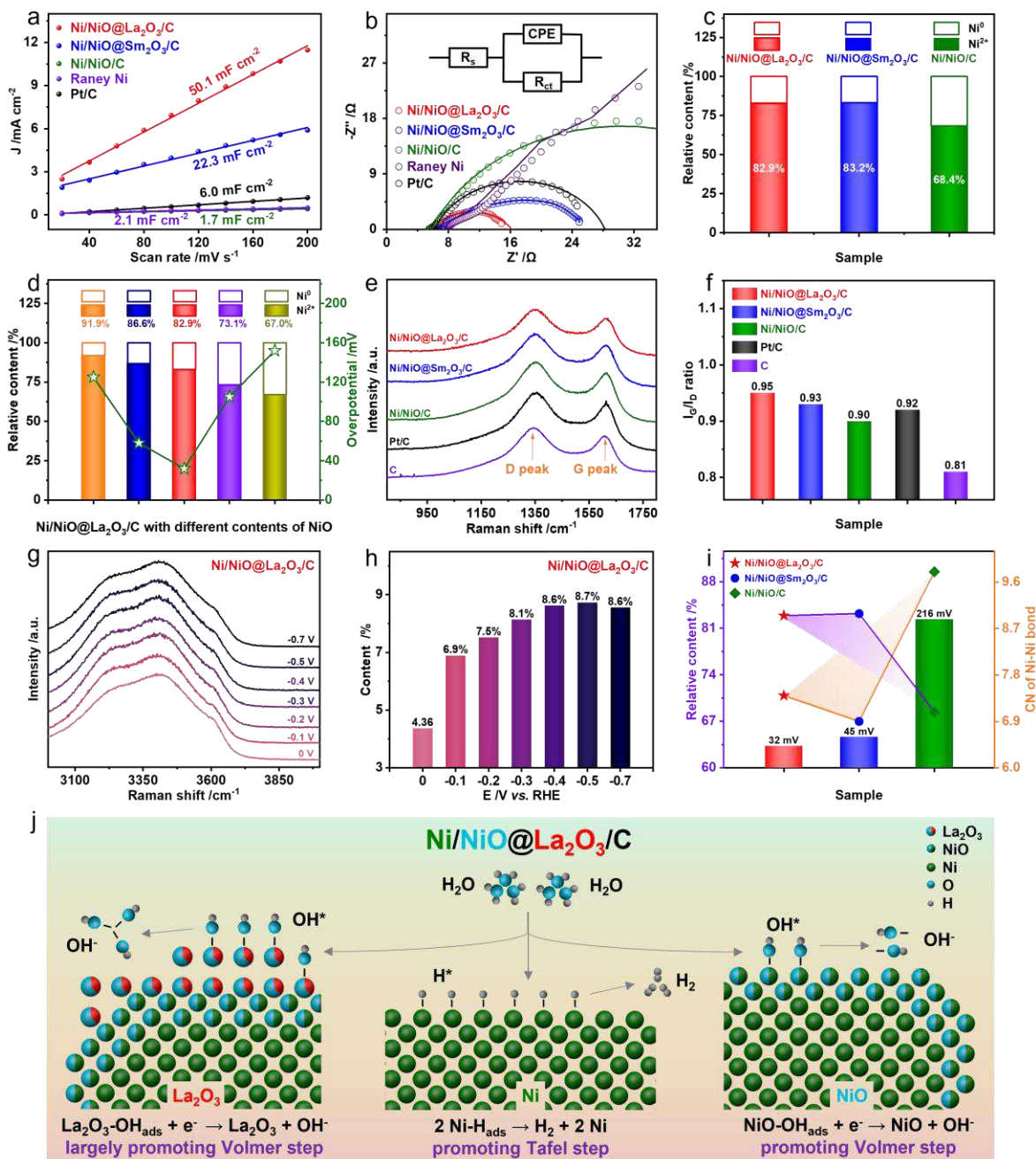


Figure 4. Mechanism investigation. **a** Capacitive currents based on different scan rates and **b** EIS curves of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C, Raney Ni and Pt/C in 1 M KOH. **c** Content analyses of Ni⁰ and Ni²⁺ for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C. **d** Relative contents of Ni⁰ and Ni²⁺ and corresponding overpotentials for different Ni/NiO@La₂O₃/C. **e** Raman spectra and **f** corresponding I_G/I_D ratios for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C and commercial C powder. **g** *In-situ* Raman spectra of Ni/NiO@La₂O₃/C measured at different voltages for alkaline HER catalysis. **h** Content changes of weakly H-bonded water molecules along with different voltages by using Ni/NiO@La₂O₃/C as the HER catalyst. **i** Relationship among Ni⁰/Ni²⁺ ratios, CNs of Ni-Ni bond and overpotentials for Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C and Ni/NiO/C. **j** Schematic illustration of alkaline HER mechanism effected on three parts of Ni/NiO@La₂O₃/C.

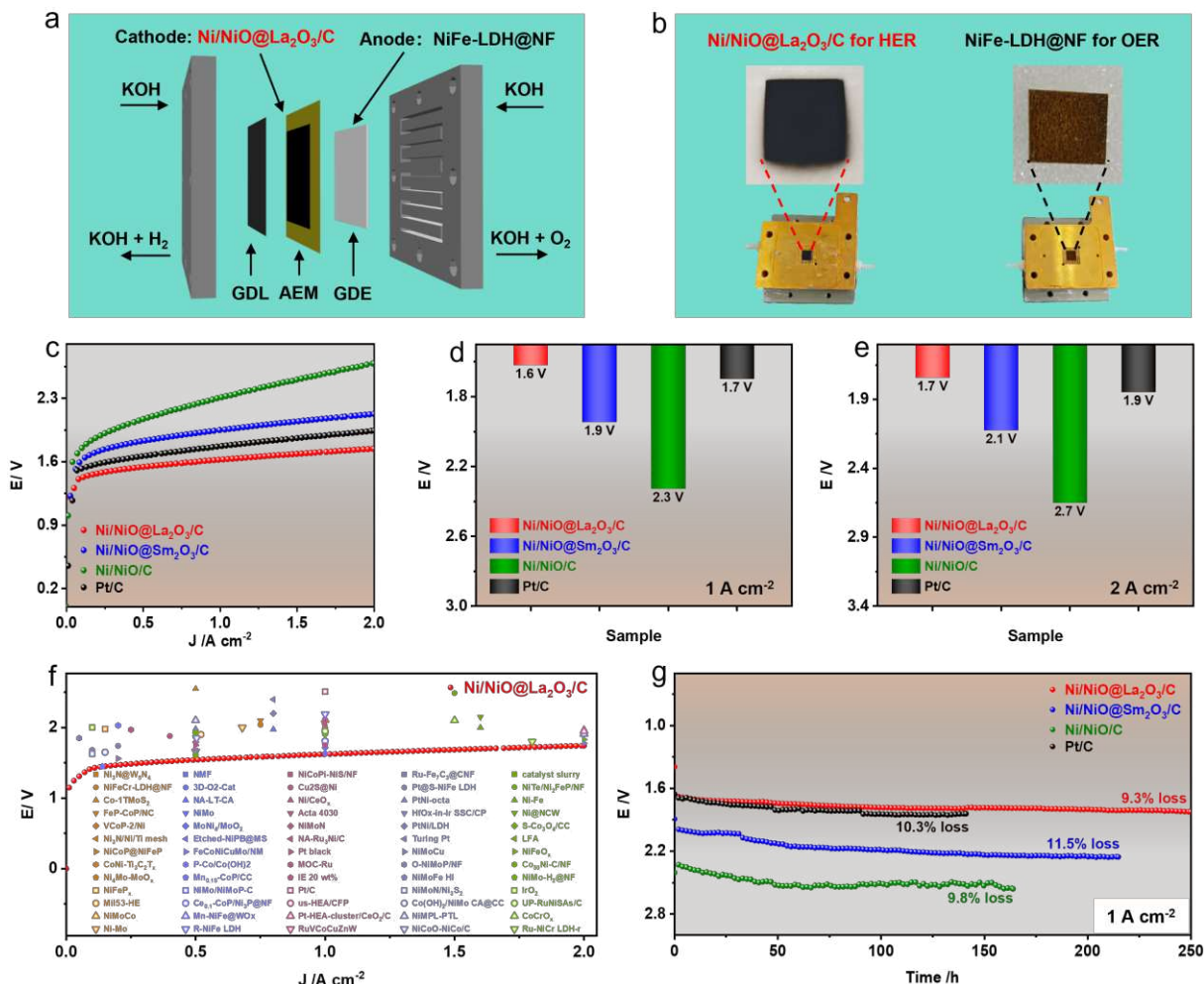


Figure 5. MEA performance evaluation for AEMWE. **a, b** Schematic illustrations of **a** MEA (cathode catalyst || anode anlyst: Ni/NiO@La₂O₃/C || NiFe-LDH@NF) and **b** practical photograph of used cathode and anode for AEMWE. **c** MEA polarization curves of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C and Pt/C and **d, e** corresponding voltages at **d** 1 A cm⁻² and **e** 2 A cm⁻². **f** MEA performance comparison between Ni/NiO@La₂O₃/C and other HER catalysts reported in recent five years. **g** MEA lifetimes of Ni/NiO@La₂O₃/C, Ni/NiO@Sm₂O₃/C, Ni/NiO/C and Pt/C measured at 1 A cm⁻².

Supplementary Files

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