

Component design of Ni-based rock-salt structure oxygen evolution reaction catalyst via cluster plus glue atom model

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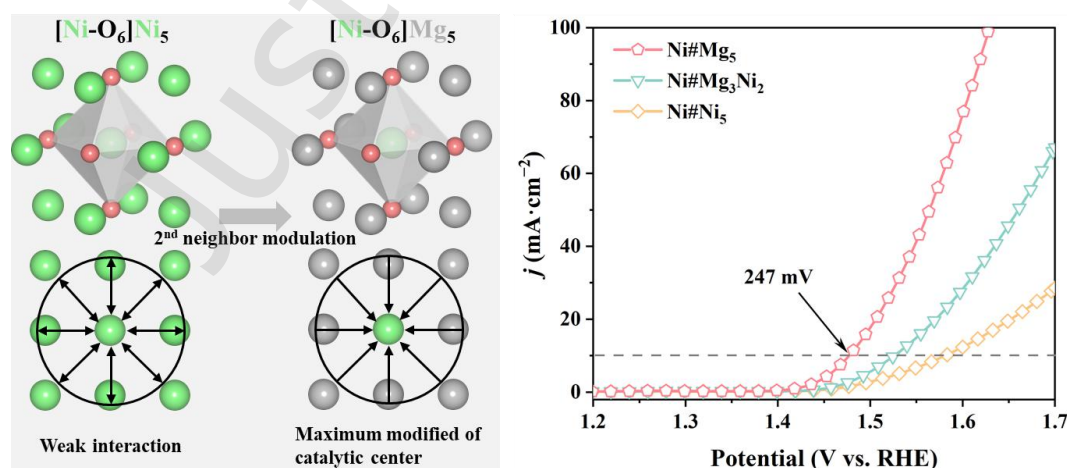
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Graphical Abstract:

A rational component-design strategy for nickel-based rock-salt oxygen evolution reaction (OER) electrocatalysts has been developed using the cluster-plus-glue-atom model. By selectively substituting second-shell nickel glue atoms with magnesium in the $[\text{Ni}-\text{O}_6]\text{Ni}_5$ structural unit, the resulting $\text{Ni}\#\text{Mg}_5$ catalyst preserves the active $\text{Ni}-\text{O}_6$ motif while effectively suppressing detrimental nickel–nickel $d-d$ electronic interactions. Comprehensive structural and spectroscopic analyses confirm homogeneous incorporation of magnesium at glue-atom sites, thereby maintaining the integrity of the rock-salt framework. The $\text{Ni}\#\text{Mg}_5$ catalyst showcases a low overpotential of 247 mV at $10\text{ mA}\cdot\text{cm}^{-2}$ and exhibits outstanding durability over 140 hours. Density functional theory calculations indicate that the $2s$ orbitals of magnesium introduce an electronic shielding effect that narrows the bandwidth of nickel $3d$ states, optimizes the $\text{Ni } 3d-\text{O } 2p$ hybridization, and lowers the free-energy barrier for the formation of the $^*\text{OH}$ intermediate. This study demonstrates orbital shielding as an effective electronic modulation strategy and underscores the predictive capability of the cluster-plus-glue-atom model for the design of high-performance OER electrocatalysts.



Research Article

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ABSTRACT

The development of efficient and durable oxygen evolution reaction (OER) electrocatalysts is crucial for advancing alkaline water electrolysis and enabling sustainable hydrogen production. Nickel-based oxides with rock-salt structures are particularly promising owing to their earth abundance and favorable redox properties. However, strong Ni–Ni *d–d* electronic interactions in NiO frequently result in excessive *O adsorption, sluggish kinetics, and structural instability under OER conditions. Herein, we employ the cluster-plus-glue-atom model to rationally design Ni–Mg rock-salt oxides, with a focus on how Mg substitution at glue-atom sites modulates the electronic structure of the central Ni active site. The resulting Ni#Mg₅ catalyst requires an overpotential of only 247 mV to deliver a current density of 10 mA·cm^{−2} and maintains stable performance over 140 h. Density functional theory (DFT) calculations reveal that Mg atoms at glue-atom sites introduce a distinctive Mg 2s orbital shielding effect. This effect weakens Ni–Ni *d–d* coupling, optimizes Ni

3d–O 2p hybridization, elevates the Ni 3d band center, and reduces the formation energy barrier of the *OH intermediate. This work establishes orbital shielding as a key electronic modulation strategy and highlights the predictive power of the cluster-plus-glue-atom model for the rational design of high-performance Ni-based OER electrocatalysts.

Keywords

oxygen evolution reaction; cluster plus glue atom model; Ni-Mg rock-salt oxide; electronic modulation

1. Introduction

Electrochemical water splitting represents a cornerstone technology for renewable energy storage and sustainable hydrogen production, enabling the conversion of intermittent electricity into storable chemical fuels [1, 2]. In alkaline water electrolysis, the anodic oxygen evolution reaction (OER) constitutes the primary kinetic bottleneck owing to its complex four-electron transfer mechanism, which involves multiple oxygenated intermediates (*OH, *O, *OOH) and imposes substantial overpotential requirements [3]. Transition-metal oxides, particularly nickel-based materials, have attracted extensive research interest owing to their earth abundance, favorable redox properties, and demonstrated activity in alkaline electrolytes [4, 5].

Nickel(II) oxide (NiO), which crystallizes in the rock-salt structure, features Ni²⁺ cations octahedrally coordinated by O²⁻ anions, forming a three-dimensional Ni–O–Ni network [6]. This edge-sharing connectivity gives rise to direct electronic interactions between adjacent Ni 3d orbitals through oxygen-mediated superexchange pathways [7]. Although such Ni–Ni *d–d* coupling can confer metallic-like conductivity under certain conditions, excessive orbital overlap broadens the Ni 3d band and strengthens the adsorption of oxygen intermediates particularly *O thereby elevating the thermodynamic barrier of the rate-determining step and compromising catalytic kinetics [8, 9]. Addressing this fundamental limitation requires strategies that selectively modulate second-shell Ni–Ni interactions while preserving the essential Ni–O coordination environment that defines the

active site. Heteroatom substitution has been extensively pursued to modify the electronic structure of Ni-based oxides [10]. Magnesium, in particular, presents an intriguing alloying element owing to its similar ionic radius to Ni^{2+} , which supports solid-solution formation within the rock-salt lattice, and its closed-shell $2s^2$ electronic configuration, which renders it electronically inert toward OER intermediates [11]. However, conventional doping approaches lack rational guidelines for identifying optimal substitution sites and concentrations, often resulting in random lattice occupation that may disrupt the active site or introduce undesired structural distortions. The absence of a predictive structural framework has hindered the systematic optimization of Ni-based OER electrocatalysts through compositional design.

The cluster-plus-glue-atom model, originally developed for metallic glasses and complex alloy phases, offers a compelling alternative by describing crystalline structures in terms of nearest-neighbor clusters embedded within a matrix of glue atoms [12]. When applied to rock-salt NiO, this framework identifies the fundamental structural unit as $[\text{Ni}-\text{O}_6]$, consisting of a central Ni atom octahedrally coordinated by six oxygen atoms, with five second-nearest-neighbor Ni atoms serving as glue atoms that interconnect adjacent clusters [13, 14]. This formulation, expressed as $[\text{Ni}-\text{O}_6]\text{Ni}_5$, provides a rational basis for targeted substitution: heteroatoms introduced at glue-atom sites can modulate second-shell electronic interactions without disrupting the primary catalytic $[\text{Ni}-\text{O}_6]$ motif.

Here, we employ the cluster-plus-glue-atom model and the sol-gel method to interpret and synthesize Ni-Mg rock-salt oxides, in which MgO and NiO share the same stable rock-salt structure [15]. DFT demonstrated a novel Mg $2s$ orbital shielding effect: when Mg fully occupies the glue atoms, its presence attenuates the direct Ni-Ni d-d interactions, narrows the Ni $3d$ bandwidth, and tunes the adsorption energy into a more favorable range. Moreover, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and X-ray absorption spectroscopy (XAS) demonstrate that the glue Ni atoms are completely substituted by Mg. The synthesized

Ni#Mg5 catalyst exhibits an overpotential of only 247 mV at a current density of 10 mA·cm⁻² and demonstrates stable operation for 140 h. This work provides new insights into the rapid compositional design of Ni-based oxides.

2. Materials and methods

2.1 Preparation of Ni-Mg oxides

The Ni-Mg oxides with different ratios of Ni/Mg were synthesized beginning by dissolving stoichiometric amounts of nickel acetate (97%, Macklin) and magnesium acetate (99%, Macklin) in deionized water to create a clear metallic salt solution. Citric acid is then added to the mixture in a 1:1.5 molar ratio relative to the total metal ions. The citric acid acts as a chelating agent, binding the Ni²⁺ and Mg²⁺ ions to prevent them from precipitating unevenly. The solution is heated at 80°C under constant stirring to evaporate the solvent, gradually increasing the viscosity until a thick, translucent "citrate gel" forms. This gel is then dehydrated further in an oven to produce a foam at 140 °C for 6 h. Finally, this precursor undergoes calcination in a furnace at temperatures between 600°C for 4 h. During this stage, the organic citrate backbone combusts, leaving behind a fine, homogenous Ni-Mg oxide solid solution.

2.2 Material characterization

The morphology, structure, composition, and chemical property of the samples were investigated by SEM (ZEISS SUPRA 55), HR-TEM (JEM-3000F), XRD (Empyrean, operated at 40 kV and 40 mA with Cu K α). Aberration-corrected HAADF-STEM characterization was conducted on a Cs corrected monochromated TEM (Themis Z) instrument at 300 keV. The X-ray photoelectron spectroscopy (XPS) spectra were collected at Thermo Scientific K Alpha with an Al K α monochromatic. The determination of metal concentrations in the samples was carried out using the inductively coupled plasma-optical emission spectrometry (ICP-OES) method with the Thermo Scientific iCAP 7000 Series Spectrometer. X-ray absorption spectroscopy (XAS) at the Ni K-edge was performed at beamline 10C of the Pohang Accelerator Laboratory (PAL) in Korea. The storage

ring was operated at 3.0 GeV, with a ring current of 250 mA. A Si (111) double crystal monochromator was used to eliminate high-order harmonics by reducing the beamline intensity by 20–30%. A reference Fe metal foil spectrum was used to calibrate the spectra of samples, followed by analysis using Athena software in the Demeter package.

2.3 Electrochemical measurements

All oxygen evolution reaction (OER) electrochemical measurements were conducted in a standard three-electrode configuration using a CHI760E. The working electrode consisted of a platinum clip supporting carbon paper (Toray TGP-H-060), the counter electrode was a graphite rod, and the reference electrode was Hg/HgO (1 M KOH). Catalyst inks were prepared by dispersing 5 mg of the as-synthesized material in a mixture of 500 μ L isopropanol, 500 μ L deionized water, and 20 μ L Nafion solution (5 wt%), followed by ultrasonication for 1 h. Subsequently, 100 μ L of the ink was drop-cast onto the carbon paper substrate within a 1×1 cm² geometric area and allowed to dry.

2.4 DFT calculation

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) functional was employed to describe the exchange–correlation interactions. A Γ -centered k-point mesh of $3 \times 3 \times 1$ and a plane-wave basis set with a cutoff energy of 450 eV were used. All structures were fully relaxed until the residual forces on atoms converged to less than 0.02 eV $\text{\AA}^{-1}$. Rock-salt NiO (100) surfaces, with selective substitution of Ni or Mg atoms, were constructed as slab models to investigate the electronic structure and adsorption free energies.

3. Results and discussion

3.1 Composition design based on cluster-plus-glue-atom model

The radial distribution function (RDF) of rock-salt NiO displays two dominant coordination shells corresponding to Ni–O and Ni–Ni interactions (Fig. 1a) [16]. The first intense peak, located at

a shorter interatomic distance, arises from the nearest-neighbor Ni–O coordination within the NiO₆ octahedra, confirming that Ni²⁺ ions are surrounded by six oxygen atoms in an octahedral geometry. The second prominent peak, at a longer distance, originates from Ni–Ni interactions between adjacent octahedra, reflecting the edge-sharing connectivity that defines the rock-salt lattice [17]. Since OER activity predominantly occurs at surface Ni sites, selective modulation of the second coordination shell (Ni–Ni) rather than disruption of the primary Ni–O octahedra offers a rational strategy for optimizing catalytic performance while preserving the overall crystal framework [19].

Fig. 1b schematically illustrates the application of the cluster-plus-glue-atom model to the rock-salt NiO system [13]. In this framework, the fundamental structural unit is the nearest-neighbor [Ni–O₆] cluster, and the surrounding second-nearest-neighbor cation positions are defined as glue-atom sites. Accordingly, pristine NiO is formulated as [Ni–O₆]Ni₅, while Mg substitution at these second-shell cation/glue sites gives [Ni–O₆]Mg₅ (denoted as Ni#Mg₅). This notation is indicated by the symbol "#", which separates the central [Ni–O₆] motif from the surrounding glue atoms. Mg²⁺ therefore substitutes on the rock-salt cation sublattice around the central [Ni–O₆] motif rather than replacing the central octahedral Ni site. Because Mg lacks partially filled d orbitals, such substitution weakens second-shell Ni–Ni electronic interactions while preserving the first-shell Ni–O coordination.

3.2 Material Synthesis and Characterization

X-ray diffraction (XRD) was employed to characterize the crystal structure of the Ni–Mg oxide series. The diffraction patterns exhibit a single-phase rock-salt structure across all compositions (Fig. 2a) [7]. All reflections can be indexed to the cubic $Fm\bar{3}m$ space group characteristic of NiO, confirming that Mg incorporation induces no secondary phases or significant structural distortions beyond shifts in lattice parameters [15]. With increasing Mg substitution, the diffraction peaks shift progressively to lower 2θ values, consistent with lattice expansion arising from the slightly larger ionic radius of Mg²⁺ compared to Ni²⁺. The complete absence of impurity peaks demonstrates that

Mg atoms are incorporated substitutionally into the NiO lattice rather than forming a segregated MgO phase. This structural continuity confirms that glue-atom substitution preserves the overall crystallographic framework while enabling subtle modifications to the local coordination environment, thereby supporting the feasibility of controlled electronic modulation without sacrificing phase stability.

SEM and HAADF-STEM images show that the Ni-Mg oxides consist of uniformly distributed granular nanoparticles with no obvious large agglomerates or phase-separated domains (Fig. 2b,c and Figs. S1,S2). STEM-EDS mapping shows homogeneous distributions of Ni, Mg, and O throughout individual nanoparticles (Fig. 2d and Tab. S1). These results support single-phase and compositionally uniform Ni-Mg oxide formation. Together with the XAS/EXAFS results discussed below, they are consistent with the proposed cluster-plus-glue-atom design, but XRD/SEM/STEM-EDS alone are not used as sole proof of selective second-shell occupation.

Fast Fourier transform (FFT) analysis of the high-resolution HAADF-STEM images displays diffraction spots consistent with the cubic rock-salt structure (Fig. 2e) [10]. The symmetry and spacing of these spots confirm high crystallinity and the absence of detectable structural distortions. No additional diffraction features indicative of impurity phases are present [28]. This crystallographic evidence corroborates the XRD results, demonstrating that Mg substitution does not disrupt long-range structural order. Atomic-resolution HAADF-STEM imaging resolves clear lattice fringes corresponding to the characteristic interplanar spacings of rock-salt NiO (Fig. 2f) [29]. The measured d-spacings align closely with those expected for the (200) or (220) planes, depending on the zone axis, and exhibit a slight expansion relative to pristine NiO, consistent with Mg incorporation. The uniform brightness distribution across the image indicates homogeneous atomic dispersion without clustering of heavier elements [30]. Given that HAADF intensity scales approximately with atomic number (Z-contrast imaging), the subtle contrast variations between Ni and Mg columns confirm that Mg atoms are atomically dispersed within the lattice rather than

segregated into distinct domains [31]. The retention of high crystallinity even after complete glue-atom substitution underscores the structural robustness of the cluster framework and validates the structural model proposed in Fig. 1. Notably, the octahedral coordination geometry remains intact, confirming preservation of the first-shell Ni–O environment despite substitution at glue-atom sites [20]. This retention of the catalytic NiO₆ motif is essential for maintaining the identity and integrity of the active sites [32]. The corresponding intensity profile across atomic columns quantitatively illustrates the periodic lattice arrangement and uniform atomic contrast (Fig. 2g) [33]. The lack of significant intensity fluctuations further rules out phase segregation and reinforces homogeneous Mg incorporation [34]. Overall, the preserved atomic ordering shows that Mg substitution modulates electronic interactions primarily at the second-neighbor level without inducing structural defects or amorphization [35]. This structural integrity is crucial for reliably attributing subsequent electronic-structure changes and catalytic performance improvements to the targeted glue-atom substitution.

3.3 XAS Characterization and Analysis

The Ni K-edge X-ray absorption near-edge structure (XANES) spectra offer direct insight into the electronic state and local coordination symmetry of Ni centers in the Ni–Mg oxide series (Fig. 3a) [36]. All samples display absorption edge positions characteristic of Ni²⁺ in an octahedral environment, confirming that the rock-salt NiO framework is preserved following Mg substitution [37]. Nevertheless, subtle shifts in the edge position and white-line intensity are evident with increasing Mg content. Relative to Ni#Ni5, the Ni#Mg5 sample exhibits a slight shift of the absorption edge to lower energy accompanied by a reduced white-line intensity, suggesting a modest decrease in the effective Ni oxidation state or a redistribution of electronic density around the Ni centers [38]. These results indicate that Mg incorporation modifies the local electronic structure while the main Ni–O coordination feature is largely retained. Linear combination fitting of the XANES spectra provides a quantitative assessment of Ni oxidation-state distribution across the series

(Fig. 3b) [40]. The fits confirm that Ni remains predominantly in the +2 oxidation state in all samples, with only minor variations in average valence upon Mg substitution [41]. No detectable contributions from higher-valent Ni³⁺ or metallic Ni are present, consistent with the Bader charge analysis results.

Wavelet transform (WT) analysis of the k²-weighted EXAFS spectra provides simultaneous resolution in R- and k-space, enabling clear differentiation of scattering contributions from distinct neighboring atoms (Fig. 3c) [22]. In Ni#Ni₅, a prominent intensity maximum at higher k values is observed in the region corresponding to Ni–Ni scattering, indicative of strong second-shell Ni coordination [16]. After Mg incorporation, the second-shell scattering feature shifts toward lower *k* values, consistent with the presence of lighter Mg backscatterers around Ni. Crucially, the persistence of the Ni–O feature demonstrates that the catalytic NiO₆ cluster core remains structurally intact.

Fourier-transformed EXAFS spectra provide quantitative insight into the radial coordination changes across the Ni-Mg oxide series (Fig. 3d, Fig. S3 and Tab. S2). The first-shell Ni-O peak is largely preserved, whereas the second-shell cation-scattering feature decreases and shifts slightly with Mg incorporation. The fitted Ni-Ni coordination number for Ni#Mg₅ is 10.1 (Tab. S2), confirming a physically reasonable average second-shell cation-scattering environment for the rock-salt solid solution. Therefore, the EXAFS results are interpreted as evidence for preservation of the first-shell Ni-O environment and modification of the second-shell cation environment, rather than as a literal integer count of isolated Ni-Ni neighbors. Notably, Ni#Mg₅ is used here to describe a Ni-Mg rock-salt oxide in which local [Ni-O₆]Mg₅-like configurations can form statistically around Ni centers, rather than implying perfectly ordered Mg occupation around every Ni site.

3.4 OER Performance Characterization and Analysis

Linear sweep voltammetry (LSV) curves demonstrate a clear composition-dependent enhancement in oxygen evolution reaction (OER) activity upon Mg substitution (Fig. 4a) [43]. Among the series, Ni#Mg₅ exhibits the lowest overpotential of 247 mV at the benchmark current

density of 10 mA cm^{-2} , representing a substantial decrease of 105 mV relative to pristine Ni#Ni₅ (352 mV) and signifying the most favorable reaction kinetics [1]. Samples with partial Mg substitution display intermediate overpotentials, consistent with a progressive improvement as second-shell Ni–Ni interactions are gradually suppressed. The similar onset potentials across all compositions indicate that the intrinsic redox activation of Ni remains largely unaffected, while the marked reduction in overpotential for Ni#Mg₅ reflects optimized adsorption energetics of OER intermediates. These findings establish that complete glue-atom substitution significantly enhances catalytic efficiency by electronically isolating the active Ni centers [44]. Tafel plots derived from the LSV data (Fig. 4b) provide further insight into reaction kinetics and the rate-determining step. Ni#Mg₅ shows the smallest Tafel slope ($52.22 \text{ mV} \cdot \text{dec}^{-1}$) within the series, indicative of accelerated charge-transfer kinetics and more efficient reaction pathways. A lower Tafel slope is typically associated with improved transformation of intermediates, particularly the *O to *OOH step. In contrast, pristine Ni#Ni₅ exhibits a larger Tafel slope ($71.90 \text{ mV} \cdot \text{dec}^{-1}$), reflecting sluggish kinetics likely due to excessive *O binding strength arising from strong Ni–Ni *d–d* coupling. The systematic decrease in Tafel slope with increasing Mg content supports the hypothesis that weakening second-shell Ni–Ni interactions optimizes the electronic structure of the active site, thereby reducing the kinetic barrier for OER. Mass-normalized activity comparisons (Fig. 4c) further highlight the intrinsic catalytic efficiency per unit mass of Ni. Ni#Mg₅ delivers markedly higher mass activity at both 1.50 V and 1.55 V (vs. RHE) than pristine Ni#Ni₅ and partially substituted samples. This improvement confirms that the enhanced performance originates from intrinsic electronic modulation of the Ni active sites rather than from increased surface area. The monotonic rise in mass activity with Mg content reinforces that glue-site substitution substantially increases the catalytic turnover frequency of individual Ni centers by mitigating detrimental *d–d* electronic interactions.

Nyquist plots show that Ni#Mg₅ has a smaller fitted charge-transfer resistance than Ni#Ni₅ during OER (Fig. 4d and Tab. S3). This R_{ct} value reflects interfacial charge-transfer kinetics and

should not be equated with intrinsic bulk electronic conductivity. The uniformly distributed granular nanoparticles (Fig. 2b,c and Figs. S1,S2) can shorten local transport distances and expose accessible interfacial sites, while Mg-induced electronic modulation optimizes the Ni active sites. Thus, the lower R_{ct} of Ni#Mg₅ is attributed to nanoscale morphology-assisted interfacial kinetics and electronic-structure modulation rather than enhanced metallic conductivity.

Chronopotentiometry shows that Ni#Mg₅ maintains stable operation for 140 h under standard three-electrode alkaline OER conditions (Fig. 4g). Quantitative ICP-OES data for dissolved Ni and Mg have been inserted in Fig. 4g to clarify metal leaching during OER. Post-OER XRD and STEM-EDS characterization (Fig. S5) show retention of the rock-salt diffraction features and homogeneous elemental distribution, and XPS (Fig. S6) indicates that Ni remains predominantly in the Ni²⁺ state after testing. However, these ex situ results cannot fully identify the dynamic active phase under operating conditions; future in situ/operando spectroscopy is still needed to resolve possible surface reconstruction. Accordingly, the stability result is presented as catalyst-level evidence under the tested conditions rather than device-level industrial validation. The benchmarking in Fig. 4h and Tab. S5 is used only for context, and the main significance of Ni#Mg₅ is its Ni-efficient glue-atom composition design, as supported by the low Ni atomic content in Tab. S1.

3.5 DFT calculation and mechanism analysis

The electron localization function (ELF) provides a spatial visualization of electron pairing probability and bonding character (Fig. 5a) [18]. In pristine Ni#Ni₅, pronounced electron delocalization is evident between neighboring Ni atoms, reflecting strong metallic-like Ni–Ni d – d coupling within the second coordination shell. This delocalization broadens the Ni 3*d* band and enhances orbital overlap [42]. In contrast, the ELF map of Ni#Mg₅ reveals a substantial reduction in inter-Ni electron density following glue-atom substitution. Electrons become more localized along the Ni–O bonds and around the Mg sites. Since Mg²⁺ adopts a closed-shell 2*s*² configuration with no partially filled d orbitals, it does not engage in d – d coupling [49]. The resulting suppression of

inter-Ni electron delocalization directly evidences the weakening of Ni–Ni electronic interactions. Accordingly, Fig. 5a offers direct orbital-level insight into the Mg 2s shielding effect, confirming that Mg incorporation electronically isolates the central Ni active site.

Charge density difference plots further quantify the electronic redistribution induced by Mg substitution (Fig. 5b). In pristine Ni#Ni₅, regions of electron accumulation and depletion between neighboring Ni atoms indicate strong orbital overlap and significant electron sharing. Upon Mg substitution in Ni#Mg₅, electron density redistributes predominantly along the Ni–O bonds, with only minimal accumulation around the Mg centers. This pattern implies that Mg functions primarily as an electronically inert spacer rather than an active redox center [50]. Bader charge analysis shows that the charge on the central Ni atom increases modestly from +1.098 |e| to +1.204 |e| between the two configurations, demonstrating that the observed catalytic enhancement does not stem from substantial charge transfer or a change in Ni oxidation state [38]. Instead, the primary effect arises from a modification of the electronic coupling topology. The diminished direct Ni–Ni charge interaction supports the hypothesis that Mg 2s orbitals act as an electronic buffer, spatially disrupting *d*–*d* overlap and thereby stabilizing the electronic structure of the active Ni site.

The projected density of states (PDOS) of Ni#Ni₅ exhibits strong overlap between Ni 3*d* and O 2*p* orbitals near the Fermi level, indicative of pronounced covalent character in the Ni–O bonds (Fig. 5c) [16]. However, the Ni 3*d* band remains relatively broad, reflecting substantial *d*–*d* interactions among neighboring Ni atoms [39]. The elevated density of states near the Fermi level strengthens the adsorption of oxygen intermediates, particularly the *O species. Although moderate adsorption facilitates catalytic turnover, excessive binding elevates the thermodynamic barrier for *OOH formation, thereby hindering overall OER kinetics [3]. Thus, the PDOS of pristine NiO highlights the intrinsic limitation arising from strong Ni–Ni coupling. In Ni#Mg₅, the PDOS reveals a marked narrowing of the Ni 3*d* band relative to Ni#Ni₅ (Fig. 5d) [36]. The *d*-band center shifts slightly downward with respect to the Fermi level, signifying moderated adsorption strength for oxygen

intermediates [19]. Notably, the Mg 2s states lie well below the Fermi level and contribute negligibly within the relevant catalytic energy window, confirming that Mg does not directly participate in the reaction but instead indirectly modulates the electronic environment of the active site. The reduced 3d bandwidth is consistent with the suppression of inter-site Ni–Ni coupling observed in ELF analyses. As a result, the adsorption energies of the OER intermediates are shifted toward a thermodynamically more optimal regime, effectively balancing the adsorption and desorption steps. Accordingly, Fig. 5d provides clear electronic-structure evidence that Mg 2s orbital shielding effectively fine-tunes the *d*-band characteristics of the active Ni center.

To further quantify the effect of Mg substitution on Ni–Ni bonding interactions, crystal orbital Hamilton population (COHP) analysis was performed for the *d*-*d* interactions between the central Ni atom and its neighboring Ni (or Mg-substituted) sites (Fig. 5e, f). For pristine Ni₅, the -COHP curve displays pronounced bonding states below the Fermi level and corresponding antibonding states above it, indicative of strong Ni 3d–Ni 3d orbital overlap characteristic of the edge-sharing network in rock-salt NiO. The integrated COHP (ICOHP) value, which serves as a measure of bond strength, reveals substantial *d*-*d* bonding character that contributes to the broadening of the Ni 3d band and excessive stabilization of adsorbates. In contrast, upon complete substitution of glue-atom Ni with Mg in NiMg₅, the -COHP intensity associated with Ni–Ni interactions is markedly diminished. Since Mg lacks partially filled d orbitals, the primary Ni–Ni *d*-*d* coupling pathways are disrupted, resulting in a significantly reduced ICOHP value. This quantitative bonding analysis corroborates the ELF and PDOS findings, confirming that Mg atoms at glue sites act as electronic insulators that physically and electronically separate the active Ni centers, thereby attenuating detrimental *d*-*d* interactions.

In Fig. 5g and Fig. S7, the Gibbs free-energy profiles indicate that the largest uphill step in our model is the initial *OH formation. For Ni₅, this step requires 1.643 eV, whereas NiMg₅ lowers it to 1.507 eV through modulation of the Ni *d*-band center and Ni 3d–O 2p interaction. We

acknowledge that the *O-to-*OOH step is often rate-limiting on Ni-based oxides; in the present surface model this step is not the maximum barrier, but it remains an important kinetic step and the DFT results are therefore used mainly for relative comparison between Ni#Ni₅ and Ni#Mg₅. The enhanced structural stability imparted by Mg substitution was further assessed through calculations of Ni vacancy formation energy (Fig. 5h). For Ni#Ni₅, the vacancy formation energy is 5.78 eV, whereas Ni#Mg₅ increases this value to 6.05 eV, indicating a higher energetic cost for Ni loss when the active Ni site is surrounded by Mg in the second coordination shell.

4. Conclusions

In conclusion, this work presents a rational component-design strategy for Ni-based rock-salt oxygen evolution reaction (OER) electrocatalysts by applying the cluster-plus-glue-atom model, with a particular focus on regulating second-shell electronic interactions. Selective substitution of glue-site Ni atoms with Mg preserves the integrity of the primary [Ni–O₆] catalytic cluster while effectively suppressing Ni–Ni *d–d* coupling. Comprehensive structural characterizations confirm homogeneous incorporation of Mg at second-shell positions without disrupting the overall rock-salt framework. Electrochemical evaluations demonstrate that the fully substituted Ni#Mg₅ catalyst achieves a substantially reduced overpotential of 247 mV at 10 mA·cm⁻², a smaller Tafel slope, lower charge-transfer resistance, and superior long-term durability relative to pristine NiO. Density functional theory calculations reveal that Mg 2*s* orbitals, positioned well below the Fermi level, function as electronic shielding centers that attenuate Ni–Ni orbital overlap, narrow the Ni 3*d* bandwidth, and optimize Ni 3*d*–O 2*p* hybridization. This orbital-level decoupling moderates the adsorption strength of oxygen intermediates, lowers the free-energy barrier for the rate-determining *OH formation step, and balances the overall reaction energetics. These results establish the suppression of transition-metal *d–d* coupling as a fundamental mechanism for OER performance optimization and underscore the predictive power and generalizability of the cluster-plus-glue-atom model as a robust framework for the rational design of advanced transition-metal oxide

electrocatalysts.

Declaration of Competing Interest

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

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References

- 1 Suen, N.-T.& Hung, S.-F.& Quan, Q. et al., Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives, *Chem. Soc. Rev.* 46 (2017) 337-365. [10.1039/c6cs00328a](https://doi.org/10.1039/c6cs00328a).
- 2 Zhou, T.& Lv, T.& Xiao, B. et al., Cu and Pd dual-single-atoms anchored titanium dioxide for remarkable photocatalytic H₂ evolution efficiency, *Chem. Eng. J.* 478 (2023) 147372. <https://doi.org/10.1016/j.cej.2023.147372>.
- 3 Man, I. C.& Su, H. Y.& Calle - Vallejo, F. et al., Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces, *ChemCatChem* 3 (2011) 1159-1165. [10.1002/cctc.201000397](https://doi.org/10.1002/cctc.201000397).
- 4 Han, L.& Dong, S.& Wang, E., Transition-Metal (Co, Ni, and Fe)-Based Electrocatalysts for the Water Oxidation Reaction, *Adv. Mater.* 28 (2016) 9266-9291. [10.1002/adma.201602270](https://doi.org/10.1002/adma.201602270).
- 5 Burke, M. S.& Enman, L. J.& Batchellor, A. S. et al., Oxygen Evolution Reaction Electrocatalysis on Transition Metal Oxides and (O_{xy})hydroxides: Activity Trends and Design Principles, *Chem. Mater.* 27 (2015) 7549-7558. [10.1021/acs.chemmater.5b03148](https://doi.org/10.1021/acs.chemmater.5b03148).
- 6 He, T.& Zhang, C.& Will, G. et al., Cobalt porphyrin supported on graphene/Ni (111) surface:

Enhanced oxygen evolution/reduction reaction and the role of electron coupling, *Catal. Today* 351 (2020) 113-118. <https://doi.org/10.1016/j.cattod.2018.10.056>.

- 7 Parmaliana, A.& Arena, F.& Frusteri, F. et al., Temperature-programmed reduction study of NiO–MgO interactions in magnesia-supported Ni catalysts and NiO–MgO physical mixture, *J. Chem. Soc., Faraday Trans. 86* (1990) 2663-2669. [10.1039/ft9908602663](https://doi.org/10.1039/ft9908602663).
- 8 Dickens, C. F.& Nørskov, J. K., A Theoretical Investigation into the Role of Surface Defects for Oxygen Evolution on RuO₂, *J. Phys. Chem. C* 121 (2017) 18516-18524. [10.1021/acs.jpcc.7b03481](https://doi.org/10.1021/acs.jpcc.7b03481).
- 9 Su, W.& Zhang, X.& Zhang, J. et al., Strengthening d-p orbital hybridization by fluorine modification for efficient oxygen evolution reaction, *Science China Materials* (2026). [10.1007/s40843-026-4054-x](https://doi.org/10.1007/s40843-026-4054-x).
- 10 Rücker, K. K.& Taffa, D. H.& Bisen, O. et al., Influence of Co and Mn Doping on the Surface Reconstruction of Faceted NiO(111) Nanosheets after the Oxygen Evolution Reaction, *J. Phys. Chem. C* 129 (2025) 9341-9355. [10.1021/acs.jpcc.5c00493](https://doi.org/10.1021/acs.jpcc.5c00493).
- 11 Oliveira Filho, R. M.& Alves, R. F.& Raimundo, R. A. et al., Structural, magnetic and electrocatalytic properties of rock salt oxide nanofibers (Ni_{0.2}Mg_{0.2}Zn_{0.2}Cu_{0.2-x}Co_{0.2+x})O produced by air-heated solution blow spinning (A-HSBS) for oxygen evolution reaction, *Appl. Surf. Sci.* 682 (2025). [10.1016/j.apsusc.2024.161593](https://doi.org/10.1016/j.apsusc.2024.161593).
- 12 Dong, C.& Wang, Q.& Qiang, J. B. et al., From clusters to phase diagrams: composition rules of quasicrystals and bulk metallic glasses, *J. Phys. D: Appl. Phys.* 40 (2007) R273. [10.1088/0022-3727/40/15/R01](https://doi.org/10.1088/0022-3727/40/15/R01).
- 13 Ma, Y.& Dong, D.& Wu, A. et al., Composition Formulas of Inorganic Compounds in Terms of Cluster Plus Glue Atom Model, *Inorg. Chem.* 57 (2018) 710-717. [10.1021/acs.inorgchem.7b02549](https://doi.org/10.1021/acs.inorgchem.7b02549).
- 14 Yu, Y.& Liu, S.& Ren, Y. et al., Composition-constrained rocksalt structure high entropy oxides with non-equimolar cations: Design and synthesis based on cluster-plus-glue-atom model, *Ceram. Int.* 48 (2022) 25647-25650. [10.1016/j.ceramint.2022.05.265](https://doi.org/10.1016/j.ceramint.2022.05.265).
- 15 Veselov, G. B.& Karnaukhov, T. M.& Stoyanovskii, V. O. et al., Preparation of the Nanostructured Ni-Mg-O Oxide System by a Sol–Gel Technique at Varied pH, *Nanomaterials* 12 (2022). [10.3390/nano12060952](https://doi.org/10.3390/nano12060952).

- 16 Tkalych, A. J.& Zhuang, H. L.& Carter, E. A., A Density Functional +U Assessment of Oxygen Evolution Reaction Mechanisms on β -NiOOH, ACS Catal. 7 (2017) 5329-5339. [10.1021/acscatal.7b00999](https://doi.org/10.1021/acscatal.7b00999).
- 17 Dionigi, F.& Strasser, P., NiFe-Based (O_{xy})hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes, Adv. Energy Mater. 6 (2016). [10.1002/aenm.201600621](https://doi.org/10.1002/aenm.201600621).
- 18 García-Mota, M.& Bajdich, M.& Viswanathan, V. et al., Importance of Correlation in Determining Electrocatalytic Oxygen Evolution Activity on Cobalt Oxides, J. Phys. Chem. C 116 (2012) 21077-21082. [10.1021/jp306303y](https://doi.org/10.1021/jp306303y).
- 19 Stevens, M. B.& Trang, C. D. M.& Enman, L. J. et al., Reactive Fe-Sites in Ni/Fe (O_{xy})hydroxide Are Responsible for Exceptional Oxygen Electrocatalysis Activity, J. Am. Chem. Soc. 139 (2017) 11361-11364. [10.1021/jacs.7b07117](https://doi.org/10.1021/jacs.7b07117).
- 20 Fabbri, E.& Habereder, A.& Waltar, K. et al., Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction, Catal. Sci. Technol. 4 (2014) 3800-3821. [10.1039/c4cy00669k](https://doi.org/10.1039/c4cy00669k).
- 21 Kitchin, J. R.& Nørskov, J. K.& Barteau, M. A. et al., Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals, The Journal of Chemical Physics 120 (2004) 10240-10246. [10.1063/1.1737365](https://doi.org/10.1063/1.1737365).
- 22 Bergmann, A.& Martinez-Moreno, E.& Teschner, D. et al., Reversible amorphization and the catalytically active state of crystalline Co₃O₄ during oxygen evolution, Nat. Commun. 6 (2015). [10.1038/ncomms9625](https://doi.org/10.1038/ncomms9625).
- 23 Jamil, H.& Batool, S. S.& Imran, Z. et al., Electrospun titanium dioxide nanofiber humidity sensors with high sensitivity, Ceram. Int. 38 (2012) 2437-2441. [10.1016/j.ceramint.2011.11.010](https://doi.org/10.1016/j.ceramint.2011.11.010).
- 24 Dutkiewicz, J.& Ozga, P.& Maziarz, W. et al., Microstructure and properties of bulk copper matrix composites strengthened with various kinds of graphene nanoplatelets, Materials Science and Engineering: A 628 (2015) 124-134. [10.1016/j.msea.2015.01.018](https://doi.org/10.1016/j.msea.2015.01.018).
- 25 Choi, C.& Seo, S.-D.& Shim, H.-W. et al., Facile synthesis and electroactivity of 3-D hierarchically superstructured cobalt orthophosphate for lithium-ion batteries, J. Alloys Compd. 652 (2015) 100-105. [10.1016/j.jallcom.2015.08.203](https://doi.org/10.1016/j.jallcom.2015.08.203).

- 26 Lee, S.& Dursun, S.& Duran, C. et al., Thermoelectric power factor enhancement of textured ferroelectric $\text{SrxBa}_{1-x}\text{Nb}_2\text{O}_{6-\delta}$ ceramics, *J. Mater. Res.* 26 (2011) 26-30. [10.1557/jmr.2010.78](#).
- 27 Zhang, W.& Zhao, Z.& Shen, L. et al., Surface modification of ion-exchanged float aluminosilicate glass during deposition of amorphous alumina coatings by e-beam evaporation, *Journal of Non-Crystalline Solids* 447 (2016) 80-84. [10.1016/j.jnoncrysol.2016.05.034](#).
- 28 Tomasetta, I.& Barletta, D.& Poletto, M., The High Temperature Annular Shear Cell: A modified ring shear tester to measure the flow properties of powders at high temperature, *Adv. Powder Technol.* 24 (2013) 609-617. [10.1016/j.appt.2012.11.007](#).
- 29 Gellman, A. J., Oligomer desorption during heterogeneous catalytic synthesis of polymers, *Catal. Today* 105 (2005) 144-151. [10.1016/j.cattod.2005.04.011](#).
- 30 Dulles, F. J.& Bartell, L. S., Monte Carlo Study of Small Benzene Clusters. 1. Structure and Internal Motions, *The Journal of Physical Chemistry* 99 (2002) 17100-17106. [10.1021/j100047a010](#).
- 31 Lu, Y.& You, W.& Cai, C. et al., Insights into the micro magnetic loss mechanism of microwave absorption by off-axis electron holography, *J. Magn. Magn. Mater.* 475 (2019) 24-29. [10.1016/j.jmmm.2018.11.045](#).
- 32 Bediako, D. K.& Lassalle-Kaiser, B.& Surendranath, Y. et al., Structure–Activity Correlations in a Nickel–Borate Oxygen Evolution Catalyst, *J. Am. Chem. Soc.* 134 (2012) 6801-6809. [10.1021/ja301018q](#).
- 33 Huang, Z.& Zhang, M.& Cheng, J. et al., Silver decorated alpha-manganese oxide nanostructured electrocatalyst for rechargeable lithium–oxygen battery, *Catal. Commun.* 61 (2015) 44-47. [10.1016/j.catcom.2014.12.009](#).
- 34 Yan, J.& Yao, J.& Zhang, Z. et al., 3D hierarchical porous ZnFe_2O_4 nano/micro structure as a high-performance anode material for lithium-ion batteries, *Mater. Lett.* 245 (2019) 122-125. [10.1016/j.matlet.2019.02.113](#).
- 35 Cui, G.& Li, Y.& Wu, D. et al., Study on the characteristics and predictive model of autoignition induced by shock wave from high-pressure hydrogen leakage, *Int. J. Hydrogen Energy* 79 (2024) 1165-1179. [10.1016/j.ijhydene.2024.07.123](#).
- 36 Görlin, M.& Ferreira de Araújo, J.& Schmies, H. et al., Tracking Catalyst Redox States and Reaction Dynamics in Ni–Fe Oxyhydroxide Oxygen Evolution Reaction Electrocatalysts: The

- Role of Catalyst Support and Electrolyte pH, *J. Am. Chem. Soc.* 139 (2017) 2070-2082. [10.1021/jacs.6b12250](https://doi.org/10.1021/jacs.6b12250).
- 37 Friebel, D.& Louie, M. W.& Bajdich, M. et al., Identification of Highly Active Fe Sites in (Ni,Fe)OOH for Electrocatalytic Water Splitting, *J. Am. Chem. Soc.* 137 (2015) 1305-1313. [10.1021/ja511559d](https://doi.org/10.1021/ja511559d).
- 38 Görlin, M.& Chernev, P.& Ferreira de Araújo, J. et al., Oxygen Evolution Reaction Dynamics, Faradaic Charge Efficiency, and the Active Metal Redox States of Ni–Fe Oxide Water Splitting Electrocatalysts, *J. Am. Chem. Soc.* 138 (2016) 5603-5614. [10.1021/jacs.6b00332](https://doi.org/10.1021/jacs.6b00332).
- 39 Li, Y.-F.& Selloni, A., Mechanism and Activity of Water Oxidation on Selected Surfaces of Pure and Fe-Doped NiO_x, *ACS Catal.* 4 (2014) 1148-1153. [10.1021/cs401245q](https://doi.org/10.1021/cs401245q).
- 40 Wang, Z.& Yang, L.& Wang, S. et al., Measurement and separation of cathodic mass transport resistance in high temperature proton exchange membrane fuel cell, *Progress in Natural Science: Materials International* 30 (2020) 868-875. [10.1016/j.pnsc.2020.10.002](https://doi.org/10.1016/j.pnsc.2020.10.002).
- 41 Zhou, F.& Liu, Y.& Wang, Z. et al., A new type of halogen bond involving multivalent astatine: an ab initio study, *Phys. Chem. Chem. Phys.* 21 (2019) 15310-15318. [10.1039/c9cp02406a](https://doi.org/10.1039/c9cp02406a).
- 42 Nørskov, J. K.& Rossmeisl, J.& Logadottir, A. et al., Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode, *The Journal of Physical Chemistry B* 108 (2004) 17886-17892. [10.1021/jp047349j](https://doi.org/10.1021/jp047349j).
- 43 Song, F.& Hu, X., Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis, *Nat. Commun.* 5 (2014). [10.1038/ncomms5477](https://doi.org/10.1038/ncomms5477).
- 44 Fabbri, E.& Nachttegaal, M.& Binninger, T. et al., Dynamic surface self-reconstruction is the key of highly active perovskite nano-electrocatalysts for water splitting, *Nat. Mater.* 16 (2017) 925-931. [10.1038/nmat4938](https://doi.org/10.1038/nmat4938).
- 45 Lyons, M. E. G.& Floquet, S., Mechanism of oxygen reactions at porous oxide electrodes. Part 2—Oxygen evolution at RuO₂, IrO₂ and Ir_xRu_{1-x}O₂ electrodes in aqueous acid and alkaline solution, *Phys. Chem. Chem. Phys.* 13 (2011). [10.1039/c0cp02875d](https://doi.org/10.1039/c0cp02875d).
- 46 Bo, S.& Zhou, W.& Che, Y. et al., Spatial heteroatom modulates electron itinerancy of spinel lattice for accelerated oxygen catalysis, *Science China Materials* 68 (2025) 4481-4490. [10.1007/s40843-025-3527-x](https://doi.org/10.1007/s40843-025-3527-x).
- 47 da Silva, G. C.& Igel, C. S.& Cherevko, S., Setting the Record Straight: A Systematic Study on

Fe and Ni Dissolution in NiFe-Based Oxygen Evolution Reaction Catalysts, ACS Catal. 16 (2026) 8633-8641. [10.1021/acscatal.6c01228](https://doi.org/10.1021/acscatal.6c01228).

- 48 Tang, J.& Fang, Z.& Huang, Y. C. et al., Bulk and Surface Dual-Modification for Stabilizing RuO₂ Anode in 2 A cm⁻² PEMWE Operation, Adv. Mater. 38 (2026) e21819. [10.1002/adma.202521819](https://doi.org/10.1002/adma.202521819).
- 49 Greeley, J.& Stephens, I. E. L.& Bondarenko, A. S. et al., Alloys of platinum and early transition metals as oxygen reduction electrocatalysts, Nat. Chem. 1 (2009) 552-556. [10.1038/nchem.367](https://doi.org/10.1038/nchem.367).
- 50 Sun, H.& Chen, M.& Xiao, B. et al., Interface Engineering Induced Electron Redistribution at PtNs/NiTe-Ns Interfaces for Promoting pH-Universal and Chloride-Tolerant Hydrogen Evolution Reaction, Small 19 (2023) 2303974. <https://doi.org/10.1002/sml.202303974>.
- 51 Qiu, L.& Dong, A.& Yan, P. et al., Distinctive Plasma Engineering Ensuring Deep Reconstruction of Heterostructured Ni₂P/Fe₂P Into Metal Oxyhydroxides With Activated Lattice Oxygen for Water Oxidation at Industrial Current Density, Adv. Funct. Mater. 36 (2026) e08353. <https://doi.org/10.1002/adfm.202508353>.

Fig. 1

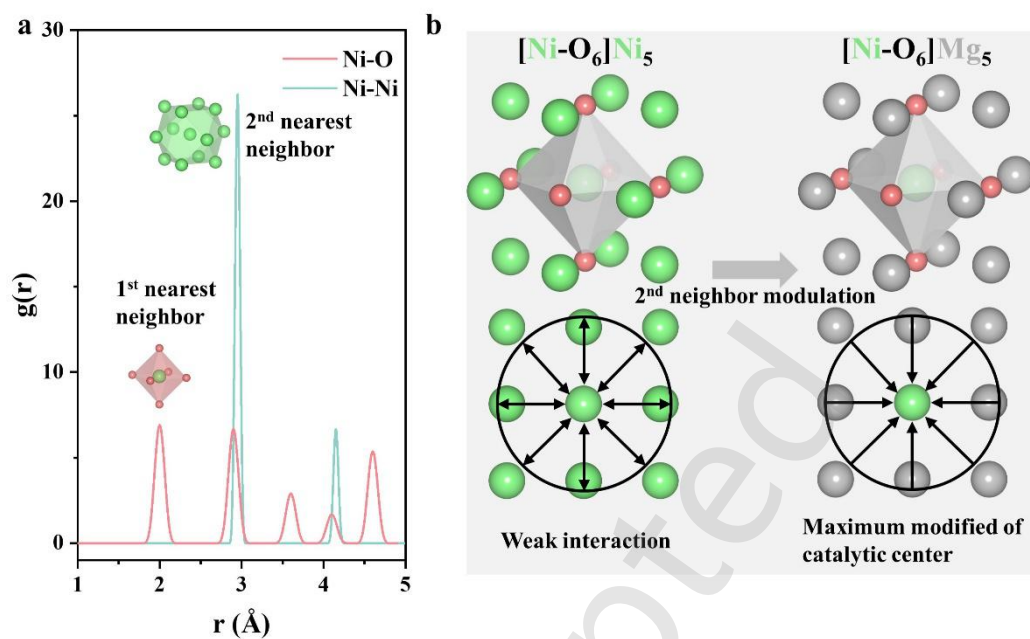


Fig. 1 (a) RDF of Ni-O and Ni-Ni in NiO. (b) Schematic illustration of composition design of rock-salt oxide catalysis based on cluster-plus-glue-atom model.

Fig. 2

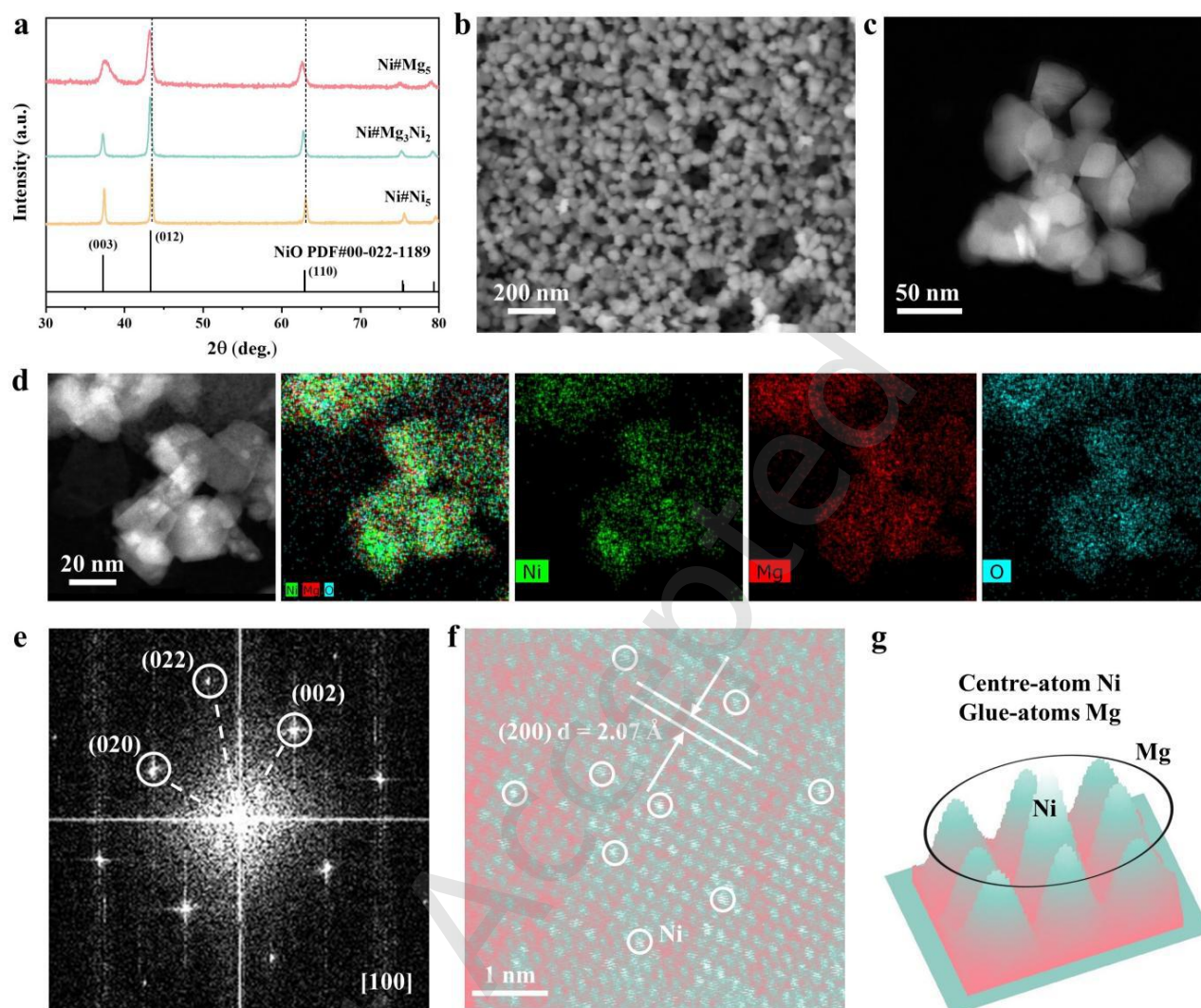


Fig. 2 (a) XRD patterns of Ni-Mg oxides. (b) SEM (c) HAADF-STEM images (d) STEM-EDS of $\text{Ni}\#\text{Mg}_5$. (e) FFT image (f) atomic resolution HAADF-STEM image and (g) surface plot of $\text{Ni}\#\text{Mg}_5$.

Fig. 3

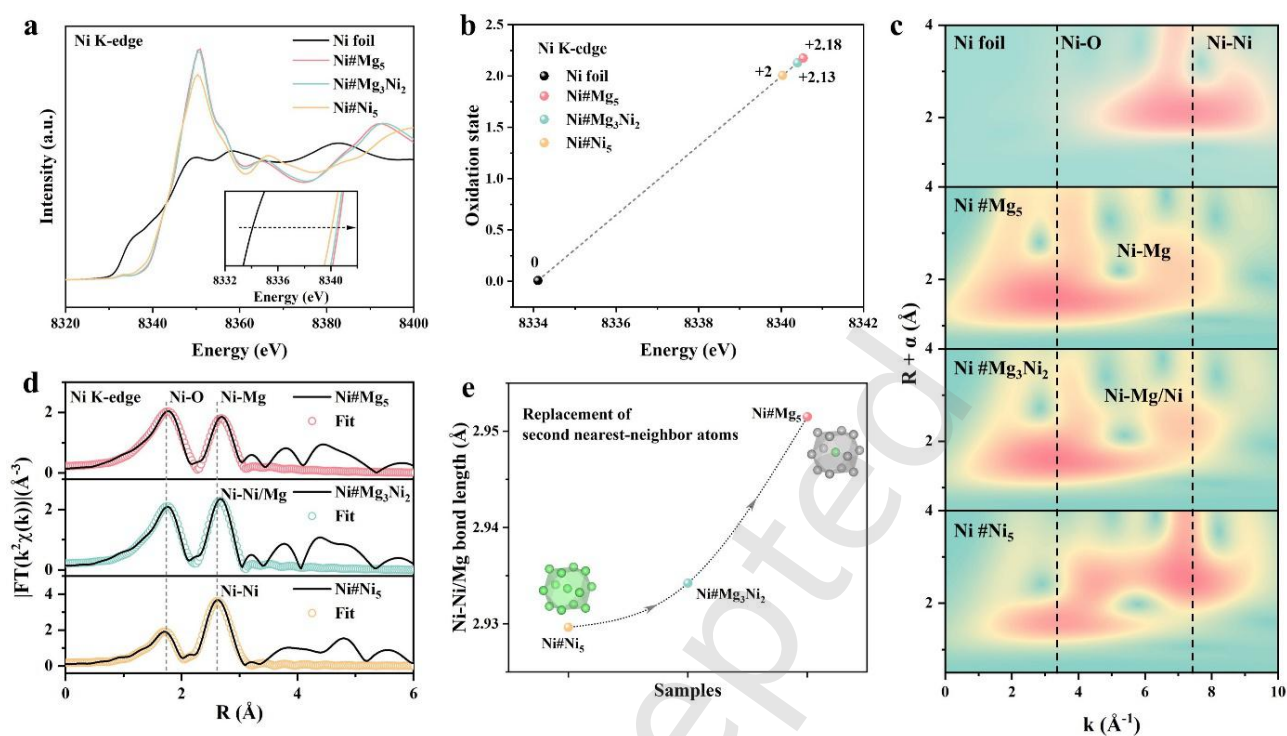


Fig.3 (a) Ni K-edge XANES spectra, (b) Oxidation state fitting from Ni K-edge XANES spectra (c) Wavelet transforms for the k²-weighted EXAFS for Ni-Mg oxides. (d) Fourier transform spectra of k²-weight Ni K-edge EXAFS spectra, and (e) Ni-Ni/Mg bond length of Ni-Mg oxides.

Fig. 4

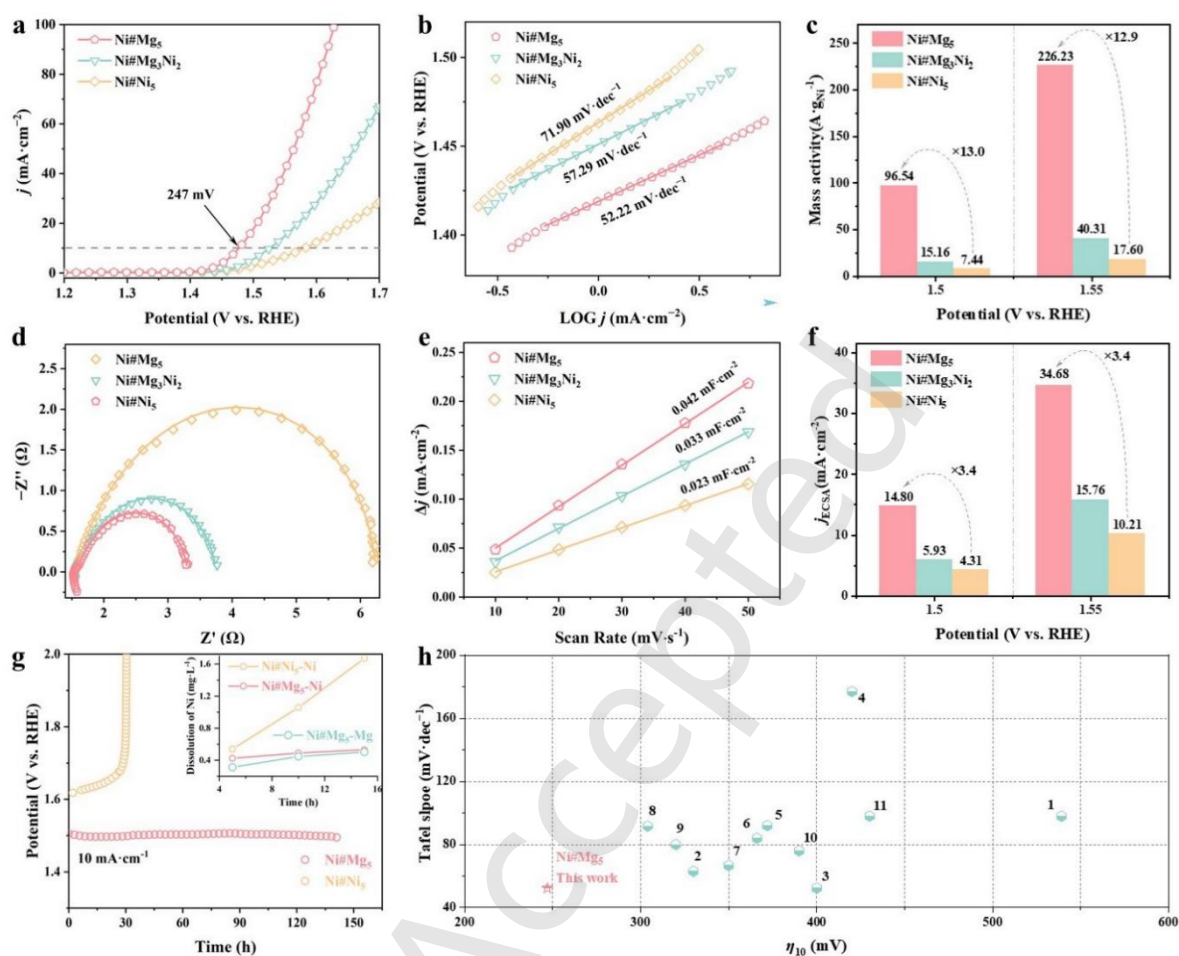


Fig. 4 Electrocatalytic OER performance evaluation for Ni-Mg oxides in 1 M KOH. (a) LSV polarization curves, (b) Tafel plot. (c) Ni mass activities of Ni-Mg oxides at potentials at 1.50 and 1.55 V (vs RHE). (d) Nyquist plots of EIS and fitting result. (e) Electrical double-layer capacitor. (f) ECSA normalized activities of Ni-Mg oxides at potentials at 1.50 and 1.55 V (vs RHE). (g) Chronopotentiometric curve of Ni#Mg₅ (Inset: The amount of Ni and Mg dissolved). (h) Comparison of the OER activity for various reported Ni based electrocatalysts.

Fig. 5

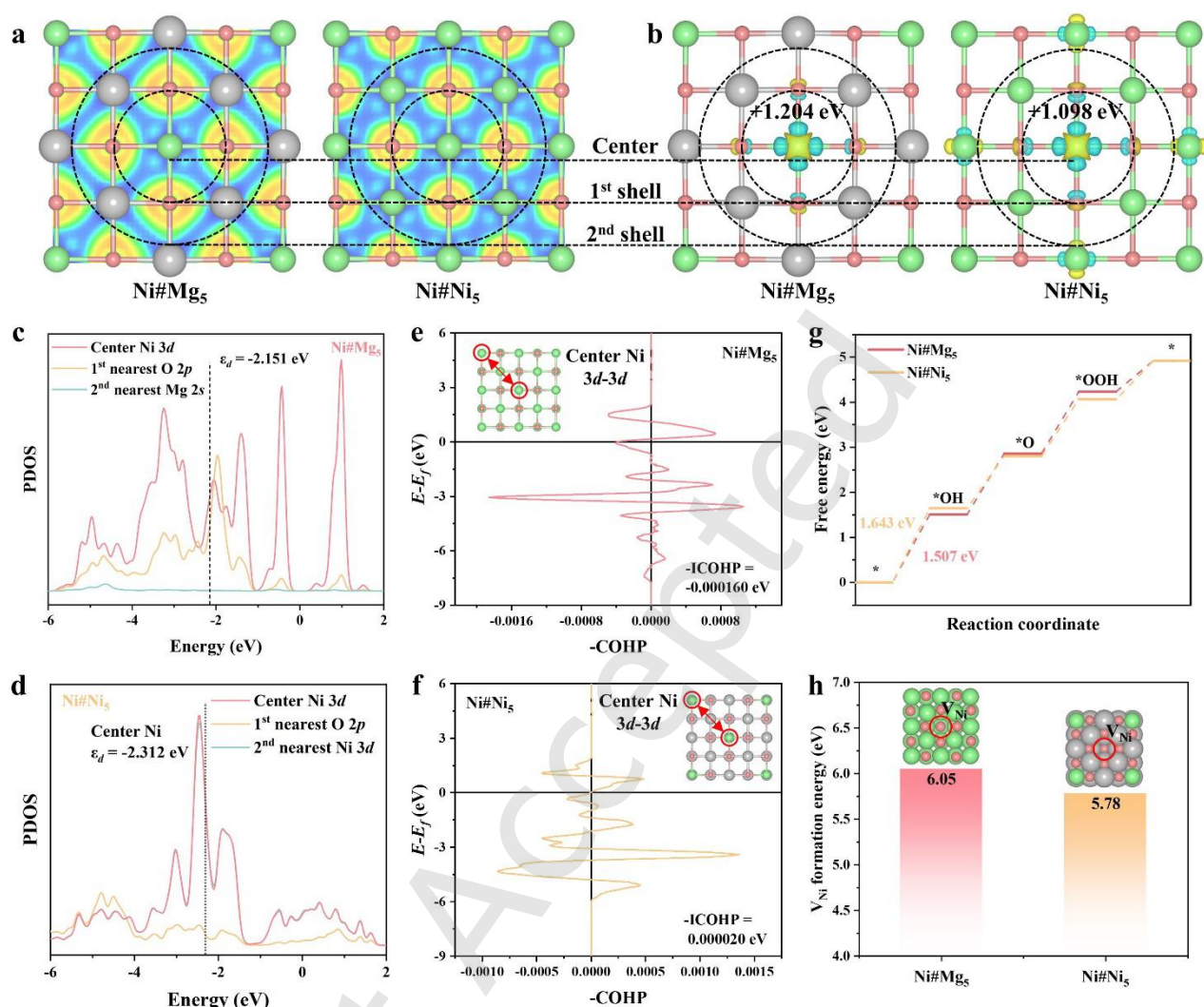


Fig. 5 (a) Electron location function (b) Charge density difference and bader charge calculation of Ni#Mg₅ and Ni#Ni₅. (c, d) PDOS of Ni 3d, O 2p and Mg 2s for Ni#Mg₅ and Ni#Ni₅. (e, f) COHP of center Ni 3d-3d for Ni#Mg₅ and Ni#Ni₅. (g) Gibbs free energy diagrams on Ni site at U = 0 V Ni#Mg₅ and Ni#Ni₅. (h) Ni vacancy formation energy of Ni#Mg₅ and Ni#Ni₅.