

RESEARCH ARTICLE

Chemical Ordering Command Dynamic Reconstruction for Enhanced Water Oxidation

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ABSTRACT

Dynamic surface reconstruction fundamentally dictates the active state of electrocatalysts. However, the lack of mastery over reconstruction kinetics typically imposes a trade-off between high activity and long-term stability. Here, we demonstrate that the degree of chemical ordering (long-range atomic site occupancy) deterministically governs the evolution of alloy surfaces under operating conditions. In this design, the chemical ordering acts as a structural template that commands the reconstruction trajectory. During anodic dealloying, the ordered lattice facilitates a controlled, mild pre-oxidation. This process generates high-valence Fe/Co/Ni sites that trigger a well-balanced, synergistic adsorbate evolution mechanism (AEM)/lattice oxygen mechanism (LOM) dual pathway. Unlike disordered counterparts that suffer from severe deterioration, the thermodynamically stable intermetallic core prevents excessive metal dissolution, reducing elemental leaching by 97.2%, guiding the formation of a homogeneous active reconstruction layer. As a result, the catalyst achieves an overpotential of only 335 mV at 1 A cm⁻² and maintains exceptional stability for over 1000 h. Even under industrial conditions (6 M KOH, 353 K), it reaches 3 A cm⁻² at only 1.50 V. This work establishes chemical ordering as a predictive parameter to govern dynamic reconstruction, offering a robust framework for designing self-adaptive catalysts that harmonize extreme activity with industrial-grade durability.

1 | Introduction

The grand challenge of heterogeneous catalysis lies in the inescapable fact that the catalyst surface under working conditions is rarely the one synthesized in the lab. The dynamic reconstruction of surface atoms, ranging from composition segregation to dealloying and phase transitions, fundamentally dictates the intrinsic active state and long-term fate of catalysts [1–3]. In the context of the oxygen evolution reaction (OER), this phenomenon is particularly pronounced [4–6]. The high anodic potentials and

turing of surface atoms, ranging from composition segregation to dealloying and phase transitions, fundamentally dictates the intrinsic active state and long-term fate of catalysts [1–3]. In the context of the oxygen evolution reaction (OER), this phenomenon is particularly pronounced [4–6]. The high anodic potentials and

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harsh alkaline environments of water electrolysis drive a profound transformation of the precatalyst surface into a disordered (oxy)hydroxide layer [7–9]. Although this reconstructed shell is typically responsible for the observed catalytic activity, the lack of mastery over its pathway remains a critical challenge. This deficiency frequently leads to a catastrophic evolution, characterized by uncontrolled metal leaching and the eventual collapse of structural integrity [10]. Consequently, achieving a synergy between extreme catalytic vigor and industrial-grade durability remains an elusive goal, primarily due to the ambiguous nature of surface restructuring in traditional alloy systems.

In the pursuit of robust materials that are relatively insensitive to over-reconstruction, high-entropy alloys (HEAs) have emerged as a promising frontier. These multicomponent systems are characterized by significant lattice distortion and high structural complexity [11–13], which collectively contribute to the “sluggish diffusion” effect. This intrinsic kinetic barrier may inhibit excessive atomic migration and exchange during electrochemical cycling, thereby minimizing the deviation between the initial surface and the working state [14]. By leveraging the immense chemical space and the inherent structural frustration of HEAs, it is possible to create a stable core that resists the inward propagation of oxidation, maintaining the catalyst’s integrity even under high-current industrial conditions.

Except suppressing over-reconstruction, another formidable obstacle lies in the lack of an effective framework to govern the kinetics and depth of this reconstruction toward the favorable direction. Some notable examples referring to dynamic restructuring for the preparation of high-performance real active phases include pre-cast engineering [15, 16], external field assistance [17], etc. In a sulfate-decorated reconstructed NiFe oxyhydroxides (R-NiFeOOH@SO₄), Fe sites drive conventional adsorbate evolution mechanism, while S dopants activate lattice-oxygen participation, which together enhance the catalytic activity [15]. Other pre-activation strategies, such as premagnetization, can accelerate surface restructuring by promoting the oxidation of Ni²⁺ to Ni³⁺ as primary catalytic sites for the OER [17]. Recent insights suggest that chemical ordering serves as a decisive parameter in commanding the reconstruction trajectory [1]. By providing a fixed structural template and specific atomic motifs, ordered intermetallic phases with higher structural stiffness and lower free energy may effectively “anchor” surface atoms and guide their evolution along a predictable path, thereby avoiding the catastrophic dealloying which is common in disordered systems [18, 19]. Thus, mastering chemical ordering offers a strategic lever to harmonize the often-conflicting requirements of high surface reactivity and bulk structural stability. By introducing chemical ordering into the high-entropy framework, we can theoretically transform the uncontrolled reconstruction into a guided self-adaptation.

Herein, we bridge the gap between high-entropy design and controlled reconstruction by establishing chemical ordering (the long-range atomic site occupancy within the B2 lattice) as a decisive descriptor to govern the surface evolution of a multinary AlCoCrFeNi system. We demonstrate that an enthalpy-driven force can transition the catalyst from a disordered solid solution to a long-range ordered B2 intermetallic phase (Figure 1a). The chemical ordering functions as a structural determinant

that regulates the initial pre-oxidation process to ensure a controlled surface evolution. By precisely directing the restructuring trajectory, the ordered lattice enables a well-balanced, synergistic adsorbate evolution mechanism (AEM)/ lattice oxygen mechanism (LOM) dual-pathway mechanism. Concurrently, the thermodynamically stable intermetallic core serves as a rigid framework that suppresses excessive metal dissolution, leading to a 97.2% reduction in elemental leaching. This synergistic control enables the harmonization of high catalytic activity with exceptional structural durability. Consequently, the catalyst delivers record-breaking activity and maintains industrial-grade durability (>1000 h) even at 1 A cm⁻², reaching 3 A cm⁻² at a cell voltage of just 1.50 V in 6 M KOH at 353 K. This work establishes chemical ordering as a universal design principle to modulate surface reconstruction and reaction pathways, effectively decoupling the trade-off between catalytic activity and structural integrity. Our findings provide a predictive framework for engineering the next generation of self-adaptive energy materials with optimized performance and longevity.

2 | Results and Discussion

2.1 | Electrocatalyst Characterization

We identified the hypoeutectic composition Al_{0.95}CoCrFeNi_{2.15} HEA for our catalyst precursor. The calculated thermodynamic equilibrium pseudo-binary phase diagram of the Al_xCoCrFeNi_{3.1-x} system (Figure 1e) shows a eutectic point at approximately 15.57 at.% Al, aligning with experimental data [20, 21]. Phase and fraction calculations (Figure S1 and details in the Supporting Information) predict a mixed L₁ and BCC microstructure above 1000 K, with decreasing L₁ fraction upon cooling. However, below this threshold, while thermodynamically favored B2 and sigma phases possess significantly lower enthalpies of formation, their precipitation is typically kinetically inhibited during conventional cooling. The alloy was fabricated by copper-mold suction casting (Figures S2 and S3), rapidly quenching the high-temperature melt, to ensure optimal dual-phase ratio. Electron backscatter diffraction (EBSD) phase maps (Figure 1b) confirmed the presence of primary FCC dendrites and eutectic lamellae, with the FCC phase comprising ~79.2% and the BCC phase ~20.8%. Higher magnification analysis of the eutectic region (Figure 1c,d) yielded relative phase fractions of ~65% FCC lamellae and ~35% BCC lamellae. Figure 1f presents the x-ray diffraction (XRD) patterns of the as-cast HEA. The as-cast alloy consists of FCC and BCC phases, with a faint ordered diffraction peak at ~31° indicating a predominantly disordered dual-phase microstructure [22]. The transition from this metastable state to an enthalpy-stabilized ordered configuration was triggered during anodic activation in dilute sulfuric acid. Upon applying a positive potential, we found that the FCC peaks diminished markedly in XRD patterns, while the B2 ordered superlattice peak of (100) intensified. Samples etched for 1800, 3600, and 5400 s were designated as Al0.95–1800, Al0.95–3600, and Al0.95–5400, respectively. To quantify this disorder-to-order evolution, the peak area ratio of S1 to S2 in the XRD patterns was calculated to reflect the degree of structural ordering [23, 24] (Figure 1g), which reached a maximum of 15.50% after 3600 s of etching, signifying the highest degree of atomic ordering of B2 intermetallics in Al0.95–3600 sample.

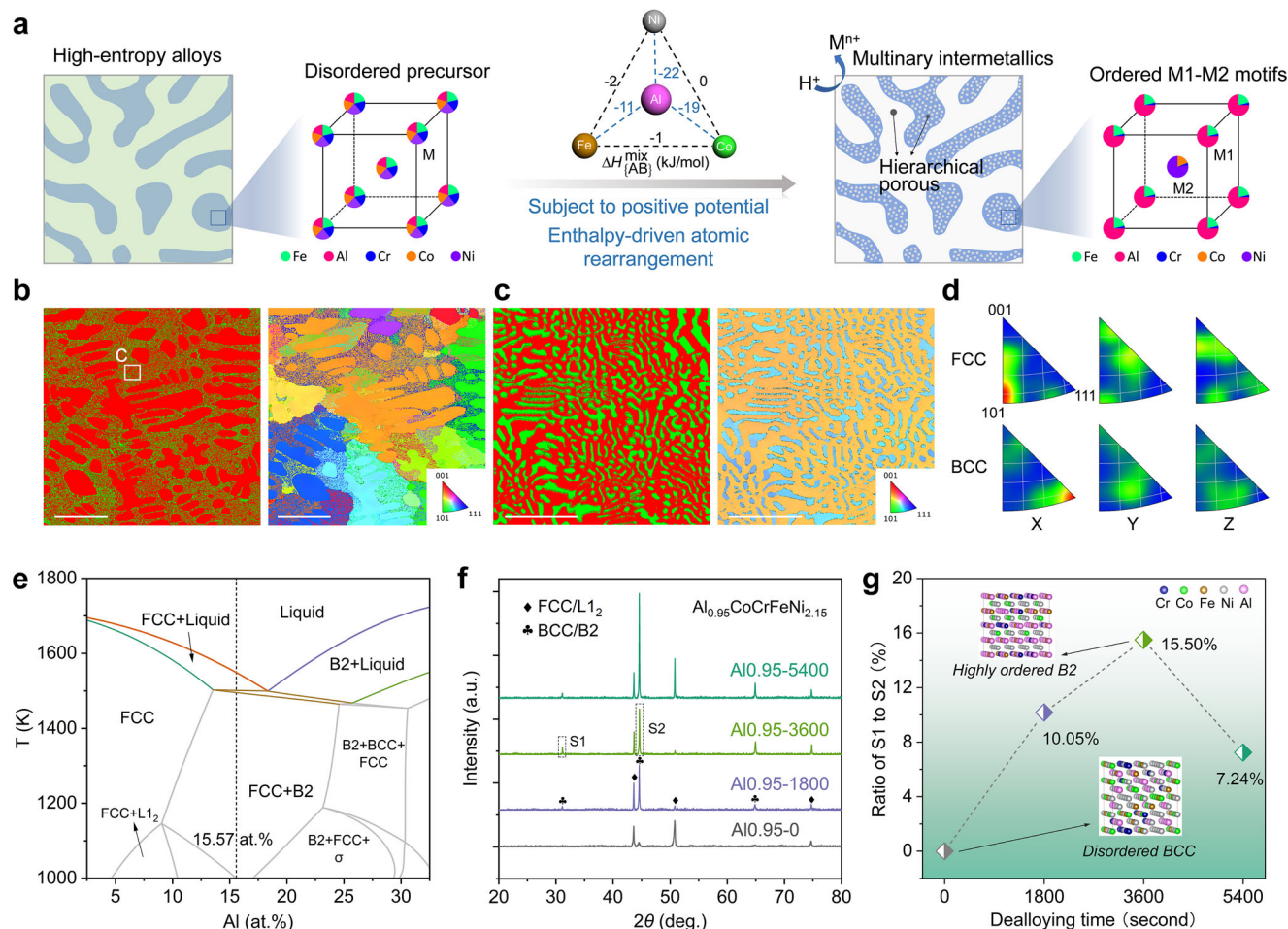


FIGURE 1 | Alloy design and enthalpy-driven disorder-to-order reconstruction in $Al_{0.95}CoCrFeNi_{2.15}$ HEA. (a) Schematic illustration of the one-step anodic activation process: preferential dissolution of FCC phase under positive potential generates hierarchical porous, while simultaneously driving entropy-favored BCC-to-B2 ordering reconstruction in the residual skeleton through atoms' migration. EBSD phase maps and orientation maps of as-cast $Al_{0.95}CoCrFeNi_{2.15}$ HEA showing (b) primary FCC dendrites and (c) eutectic FCC/BCC lamellae, in which red region represents FCC phase, while green region represents BCC phase. (d) IPF images of FCC dendritic phase and BCC eutectic lamella. (e) Calculated pseudo-binary phase diagram of the $Al_xCoCrFeNi_{3.1-x}$ system, the dashed line highlights the hypoeutectic composition. (f) Evolution of XRD patterns during electrochemical dealloying in dilute sulfuric acid solution. (g) Peak area ratio S1/S2 in (f) as a function of dealloying time quantify the ordering degree. Insets are lattice models showing the transition from random BCC (as-cast) to highly ordered B2 structure (optimally activated). Scale bars: 100 μm (b), 10 μm (c).

This phenomenon suggests that the acid and anodic environment provides the necessary chemical potential to overcome kinetic barriers, allowing the system to relax toward its thermodynamic ground state, the long-range ordered B2 intermetallic phase. Element distribution and atomic compositions of two phases in as-cast alloy are shown in Figure S4, Tables S1 and S2, Supporting Information. Phase volume fractions obtained from XRD results, as shown in Figure S5, evolved from 76.6% FCC and 23.4% BCC in the as-cast HEA to 25.2% FCC and 74.8% BCC in $Al_{0.95-3600}$. The atomic composition variations of HEAs are shown in Figures S6 and S7. This enthalpy-governed phase reconfiguration effectively strips away the less stable disordered components while simultaneously locking the remaining atoms into a high-formation-enthalpy B2 lattice, providing the structural foundation for the subsequent active-site formation and exceptional corrosion resistance.

The preferential anodic dissolution of the FCC phase sacrificially generates a trimodal hierarchical pore structure (Figure 2a)

encompassing nanopores (<30 nm), submicropores (300–700 nm), and micropores (5–20 μm). This three-dimensional interconnected architecture minimizes transport dead zones and boosts mass transfer efficiency: micron-scale pores act as primary channels for mass transport, easing macroscopic bubble release; submicron-scale pores enable efficient electrolyte diffusion and replenishment; and nano-scale pores expand the specific surface area, increasing the number of active sites [25–27]. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF STEM) further confirmed the periodically ordered B2-type atomic configuration in $Al_{0.95-3600}$ (Figure 2b). Furthermore, selected area electron diffraction (SAED) pattern in Figure 2b was indexed to [011] axis, exhibiting clear superlattice spots, indicating complete evolution to B2 intermetallics. And the lattice fringe spacings of 2.09 and 2.96 Å could readily be assigned to the (011) and (100) facets, respectively. Fine eutectic lamellas could be observed in Figure S8. To highlight the specific sublattice occupations in the $Al_{0.95-3600}$, atomic-resolution elemental maps of Fe, Co,

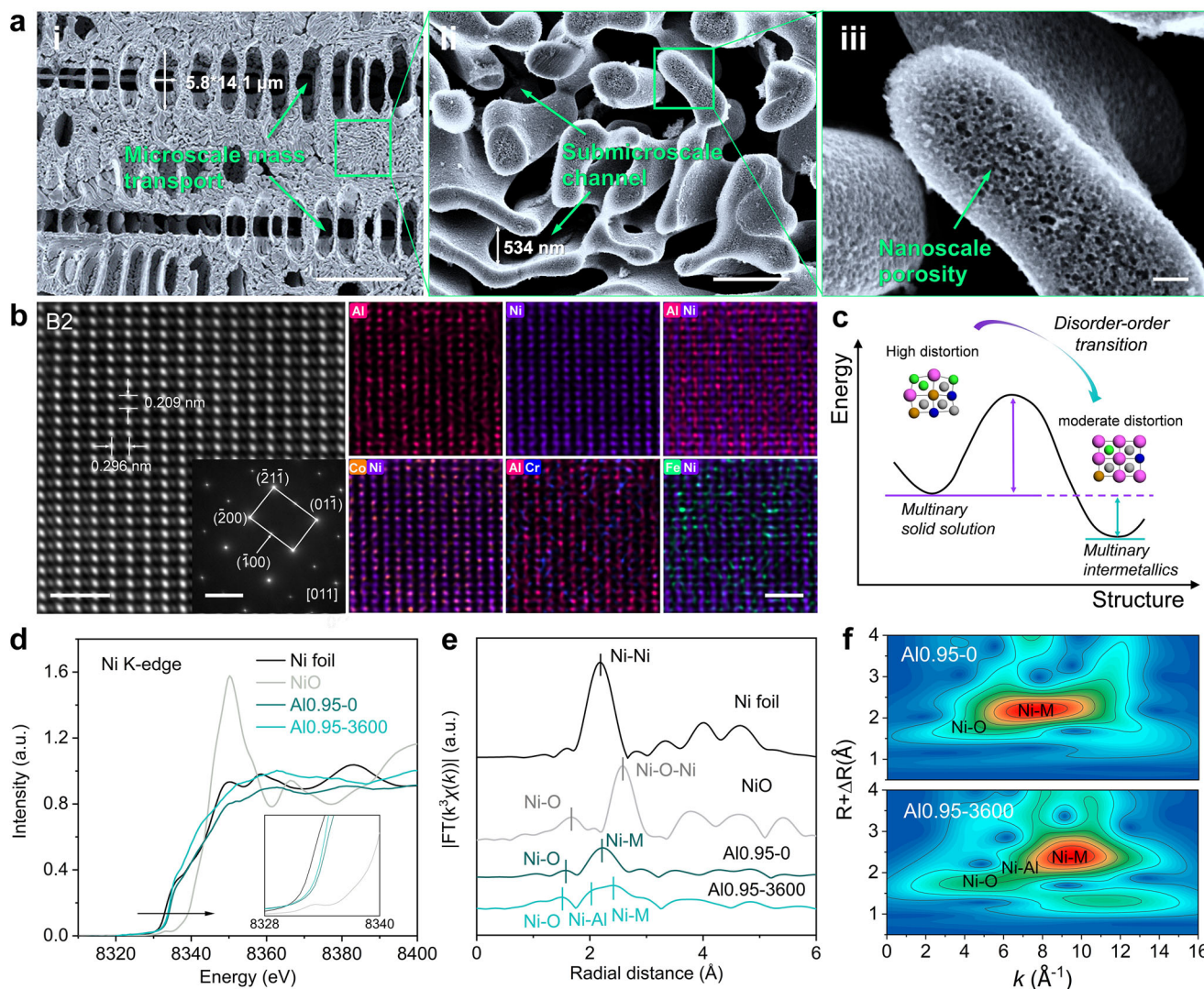


FIGURE 2 | Hierarchical porosity, atomic-scale B2 ordering, and electronic modulation in optimally activated Al_{0.95}-3600. (a) SEM images revealing trimodal pore structure: (i) microscale porosity (5–20 μm), (ii) submicroscale porosity (300–700 nm), and (iii) nanoscale porosity (<30 nm). (b) Aberration-corrected HAADF-STEM image with indexed SAED pattern confirming B2 superlattice; atomic-resolution EDS maps. (c) Schematic illustration of structure and energy route of disorder-to-order transition from multinary solid solution to multinary intermetallics. (d) Ni K-edge XANES spectra and (e) EXAFS spectra of as-cast (Al_{0.95}-0) and activated (Al_{0.95}-3600) samples. Ni foil and NiO were also included for comparison. (f) k^3 -weighted wavelet transform EXAFS contour plot for Al_{0.95}-0, Al_{0.95}-3600. Scale bars: 20 μm (a-i), 1 μm (a-ii), 100 nm (a-iii), 1 nm (b), 5 nm⁻¹ (b).

Ni, Cr, Al are shown in Figure 2b and Figure S9. The Al and Fe atoms occupy the vertices, while the Ni and Co atoms sit on body centers, with Cr distribution relatively random. As schematically depicted in Figure 2c, the thermodynamic-driven energetically favorable disorder-to-order transition results in a high density of M1(vertex)-M2(body-center) motifs [28–30]. Such multicomponent long-range ordering significantly modulates the local electronic structure, thereby profoundly influencing catalytic performance.

To directly probe this electronic modulation, we conducted x-ray photoelectron spectroscopy (XPS) on the as-synthesized and anodically activated states. In Figure S10, anodic polarization dramatically depletes metallic Fe⁰, Co⁰, Ni⁰, Al⁰, and Cr⁰ species while enriching high-valence states (Fe³⁺/Fe²⁺, Co³⁺, Ni³⁺, Al³⁺, Cr³⁺). The weak lattice O signal present in the pristine sample,

arising from unavoidable surface oxidation of oxygen-affine elements Al and Cr, disappears almost entirely after activation, confirming preservation of the metallic character without forming bulk oxides throughout dealloying and reconstruction. Among the elements, Fe, Co, and Ni exhibited the most pronounced charge redistribution. The Fe³⁺/(Fe³⁺+Fe²⁺+Fe⁰) ratio shifts from 40.7% (disordered) to 54.3% (ordered) (Figure S11), indicating higher ratio of high valence Fe³⁺, which are known to help minimize the OER overpotential on transition metal-based catalysts [31–33]. Meanwhile, Fe and Ni experience substantial electron depletion (positive binding-energy shift), whereas Co exhibits a marked negative shift, indicating electron acceptance from neighboring Fe and Ni atoms.

Accordingly, this synergistic multi-element charge transfer is enabled by the ordered heteroatomic motifs. X-ray absorption

spectroscopy (XAS) was subsequently employed to further interrogate the altered *d*-electron configuration and coordination environment induced by the ordering transition. X-ray absorption near-edge structure (XANES) spectra at the Ni *K*-edge (Figure 2d), benchmarked against Ni foil and NiO standards, reveal that the absorption edges of both the pristine (AlO.95–0) and anodically activated (AlO.95–3600) samples are positively shifted relative to metallic Ni foil. This higher oxidation state, consistent with the multi-element charge transfer dynamics highlighted earlier (where Ni donates electrons to Co acceptors), indicates enhanced covalency in Ni–O bonding, which is crucial for weakening the binding of oxygenated intermediates (*OH, *O, *OOH) and thus reducing the OER overpotential [34, 35]. Extended X-ray absorption fine structure (EXAFS) fitting (Figure 2e and Figure S12) further unveils a distinct Ni–Al scattering path (in the *R* space at 2.45 Å) in the ordered AlO.95–3600 sample, absent in the disordered AlO.95–0, signifying increased Ni–Al nearest-neighbor pairing. This structural evolution stems from the disorder-to-order transition, from a random BCC solid solution to an ordered B2 intermetallic phase, wherein Ni preferentially occupies body-centered positions and Al at corners, amplifying heteroatomic motifs as schematically depicted in Figure 2c. Wavelet transforms of the Ni *K*-edge EXAFS (Figure 2f and Figure S13) confirm this enhanced long-range order. Detailed fitting parameters (Table S3) further reveal a reduced total coordination number after dealloying, thereby generating abundant coordinatively unsaturated sites that facilitate initial *OH binding [36–38]. These coordinated motifs, enriched with high-valence metals, generate electron-deficient active centers that align the *d*-band center far from the Fermi level [39], synergistically optimizing OER kinetics, which will be confirmed by later density functional theory calculations.

2.2 | Electrocatalytic Performance

The OER performance of AlO.95–3600 was evaluated in alkaline electrolyte and compared to other samples and the benchmark catalyst (commercial IrO₂) in 1 M KOH. Polarization curves in Figure 3a show that commercial IrO₂ has an overpotential of 305 mV to reach 10 mA cm^{−2}_{geo}. In comparison, the AlO.95–3600 catalyst shows an improved OER activity, where an overpotential of only 220 mV is required to deliver 10 mA cm^{−2}_{geo}. Moreover, to reach the current density of 100 mA cm^{−2}_{geo}, the catalyst achieves a minimum overpotential of 263 mV (~300 mV lower than that of commercial IrO₂). More importantly, AlO.95–3600 sustains exceptional OER activity at industrial-level current densities, achieving 0.5 A cm^{−2}_{geo} and 1.0 A cm^{−2}_{geo} at overpotentials as low as 304 and 335 mV, respectively. As exhibited in Figure 3f, Figure S14, and Table S4, AlO.95–3600 shows competitive OER activity and stability compared with the state-of-the-art multinary transition-metal catalysts for alkaline OER. Moreover, the smallest Tafel slope of 48.3 mV dec^{−1} (Figure 3b) reflects the fast OER kinetics of AlO.95–3600 compared with AlO.95–0 catalyst (50.7 mV dec^{−1}). To elucidate the relationship between the catalytic activity and structure, we further evaluated the intrinsic OER activity of AlO.95–3600 and compared it with the AlO.95–0, AlO.95–1800, and AlO.95–5400 catalysts. It should be noted that AlO.95–5400 had the largest electrochemical specific surface area (ECSA) (Figure 3c and Figures S15, and S16), ca. 3.5 times higher than that of AlO.95–3600. However, the LSV curves normalized by ECSA (Figure S17) verified the highest specific

activity of AlO.95–3600 compared to AlO.95–5400, AlO.95–1800, AlO.95–0, indicating the much higher intrinsic activity of AlO.95–3600 catalyst than that for other counterparts. The difference in intrinsic activity between AlO.95–3600 (ordered) and other counterparts (disordered) suggests that catalytic activity is not only improved by hierarchical porosity but also regulated by ordered atomic coordination. Notably, although AlO.95–5400 exhibits the lowest charge transfer resistance (Figure S18), its OER performance falls short of that achieved by AlO.95–3600. This underscores the pivotal role of long-range atomic ordering in intermetallic catalysts. Furthermore, the performance of the AlO.95–3600 sample was evaluated under industrially relevant conditions (333 K/353 K, 6 M KOH) and benchmarked against a commercial NiFe LDH catalyst. As illustrated in Figure 3d, the AlO.95–3600 material delivered ultralow potentials of 1.39, 1.43, and 1.50 V at current densities of 1, 2, and 3 A cm^{−2}, respectively, at 353 K, substantially outperforming the commercial NiFe LDH.

In addition to activity, the durability of catalysts is another important consideration for oxygen evolution. Figure 3g shows the chronopotentiometric (CP) responses of AlO.95–1800, AlO.95–5400, and AlO.95–3600 catalysts at room temperature. AlO.95–1800 and AlO.95–5400 sustains operation for at least 280 h at 100 mA cm^{−2}, although with noticeable potential fluctuations. Remarkably, AlO.95–3600 exhibits exceptional stability over 1000 h at 100 mA cm^{−2}, with a minimal degradation rate of only 0.02 mV h^{−1}. The durability of AlO.95–3600 was further corroborated by an accelerated aging test, employing commercial Pt/C as the cathode and cycling the cell voltage between 1.0 and 2.1 V at a scan rate of 5 mV s^{−1}. Figure 3e shows there is only slight deterioration after 6700 cycles. Furthermore, the redox peak near 1.52 V in the first LSV curve significantly decreased to 1.49 V after aging test (Figure 3e and Figure S19). The 30 mV negative shift of the Ni²⁺/Ni³⁺ redox peak after prolonged cycling might indicate in situ formation of a highly active γ-Ni(Fe)OOH-like phase, accounting for the sustainable activity [47]. Moreover, elemental dissolution into the electrolyte following 10 days of chronopotentiometric stability testing was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). The results (Figure 3h) indicates that the AlO.95–3600 sample displayed the lowest leaching rates for all elements among the tested samples, underscoring the superior structural stability of the intermetallic compound.

We studied the composition and structure of the AlO.95–3600 catalyst after the stability test to gain deeper insight into its robust durability. Although XRD (Figure S20) shows a moderate attenuation of the B2 superlattice peak at ~31°, the ordered intermetallic framework remains largely intact, confirming the kinetic robustness of the B2 intermetallics against dissolution. SEM images (Figure S21) shows that the original morphology of multinary intermetallics was retained during OER, as well as the hierarchical pore architecture, ensuring sustained mass-transport efficiency without pore collapse or blockage. A thin oxyhydroxide layer is observed on the surface (Figure S22). The HRTEM image shows a coherent mixture of crystalline and amorphous multinary (Ni,Fe,Co,Cr)OOH phases intimately interfaced with the underlying B2 skeleton. EDS analysis reveals an exceptionally low oxygen content within the remaining B2 matrix of the highly ordered AlO.95–3600 sample, whereas the low-ordering

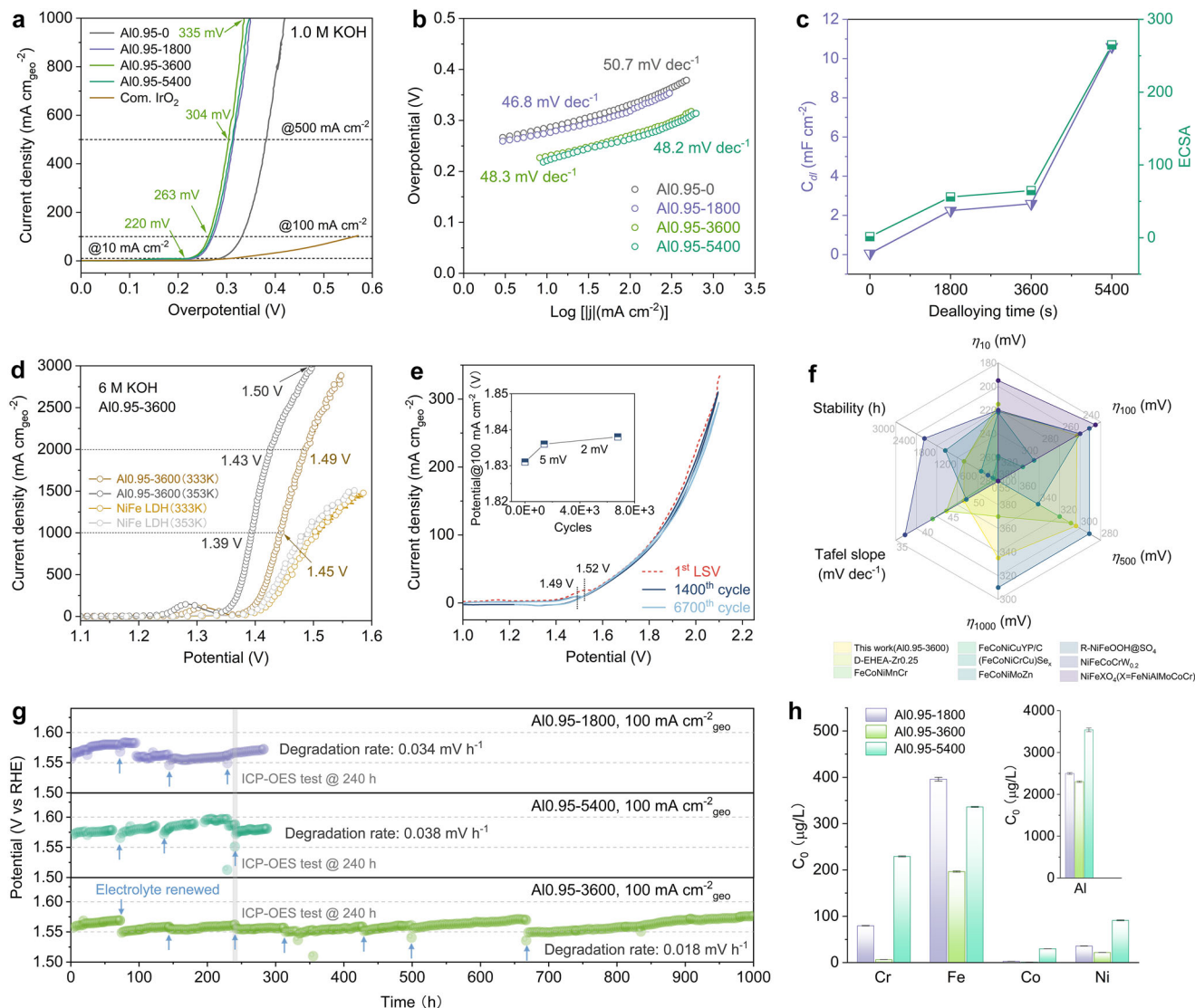


FIGURE 3 | Investigation of OER activity and stability. (a) *iR*-corrected LSV curves for AlO.95-0, AlO.95-1800, AlO.95-3600, AlO.95-5400, and commercial IrO₂ in 1.0 M KOH at ambient temperature. (b) Corresponding Tafel slopes derived from (a). (c) C_{dl} evolution with dealloying time. (d) *iR*-corrected LSV curves for AlO.95-3600 and NiFe LDH in 6.0 M KOH at 333K (60°C) and 353K (80°C). (e) LSV curves of overall water splitting for AlO.95-3600 with commercial Pt/C as cathode without *iR*-correction. CV curves after thousands of accelerated degradation cycles, with the deterioration of potentials at 100 mA cm⁻² as inset. (f) Catalysis performance comparison of AlO.95-3600 and other multi-element catalysts [15, 40–46]. (g) Chronopotentiometry at 100 mA cm⁻² of AlO.95-1800, AlO.95-3600, and AlO.95-5400 without *iR* correction. The gray vertical line denotes the time point for electrolyte sampling in ICP-OES analysis, while the blue arrow indicates the electrolyte replenishment event. (h) ICP-OES analysis of dissolved transition-metal (Al, Co, Cr, Fe, Ni) concentrations in the electrolyte after 10 days' operation.

AlO.95-1800 matrix exhibits massive oxygen intrusion (>10 at.%) (Figures S22 and S23; Table S5 and S6). This indicates that the rigid, periodic network of the ordered B2 lattice serves as a critical kinetic barrier preventing internal over-oxidation and structural collapse. Moreover, the pristine B2 core acts as a structural template that guides a self-limiting surface reconstruction, forming a seamless, coherent interface and a uniform amorphous-nanocrystalline heterogeneous shell (Figure S24). This well-regulated heterostructure effectively accommodates interfacial strain, ensuring long-term mechanical and catalytic stability over 1000 h. In contrast, the disordered core in AlO.95-1800 results in an abrupt interface and a randomly segregated amorphous/crystalline-mixed reconstructed layer (Figure S25). The resulting lattice mismatch and localized stress concentra-

tion lead to rapid structural pulverization and activity decay. Therefore, the catalyst longevity is governed by a synergistic core-shell mechanism, where the robust B2 core secures the inner framework against excessive dissolution while templating a highly active reconstruction layer.

2.3 | Operando Spectroelectrochemical Measurements

We next conducted operando ATR-FTIR and Raman analyses to investigate the OER mechanism used by the different catalysts. To verify the OER pathways, the oxygen intermediate species generated on the electrocatalysts during OER were identified

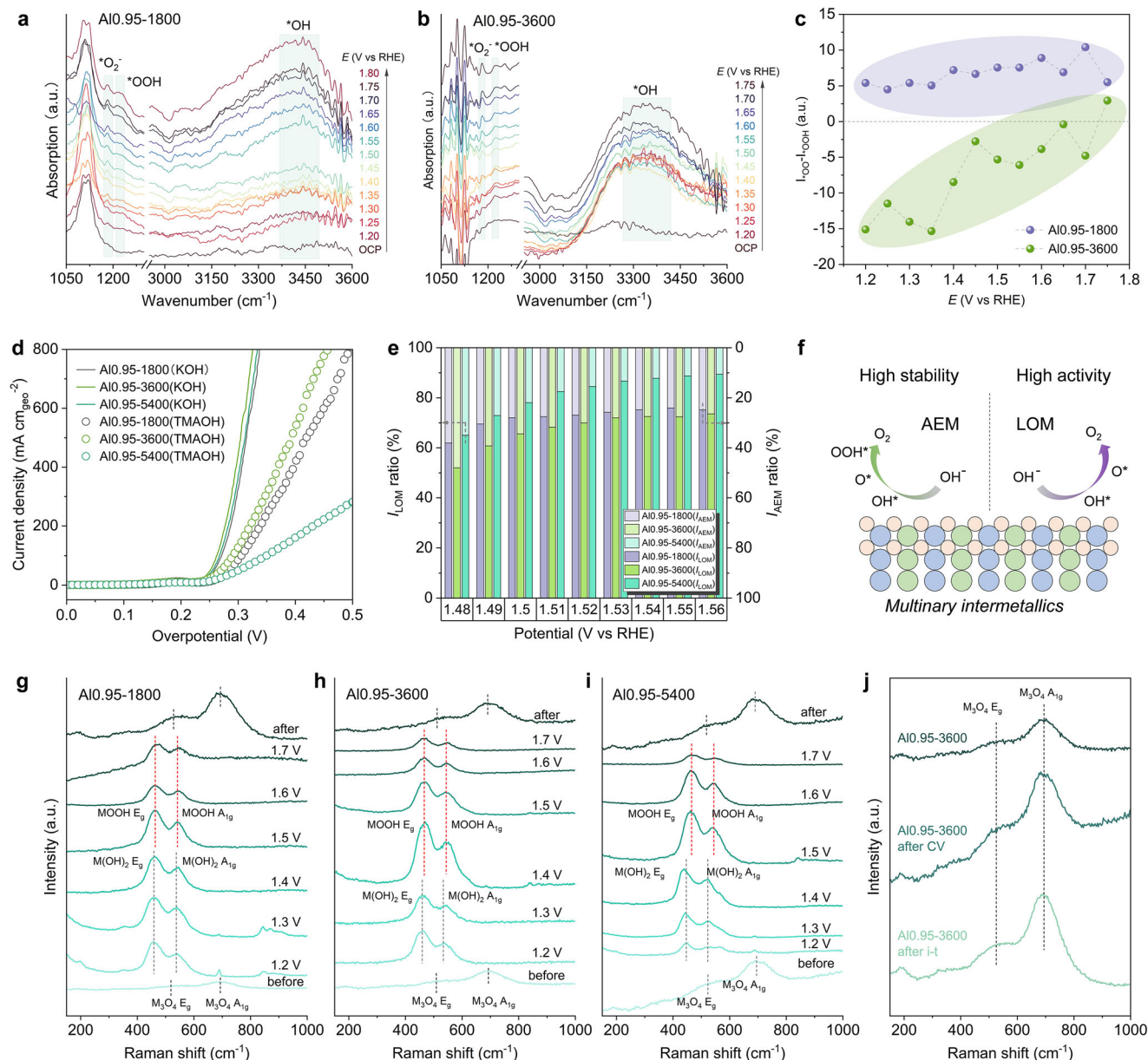


FIGURE 4 | Operando ATR-FTIR and Raman spectroscopy and reaction mechanism insights. Operando ATR-FTIR spectra of (a) Al_{0.95}-1800 and (b) Al_{0.95}-3600 with potentials (vs RHE) applied from 1.20 to 1.75/1.80 V. (c) Detailed comparison of *I*_{OO}-*I*_{OOH} versus applied potential, *I*_{OO} and *I*_{OOH} are the signal intensity obtained from (a) and (b). (d) LSV polarization curves of Al_{0.95}-3600 in 1 M KOH and 1 M TMAOH. (e) Calculated LOM contribution based on the current density reduction ratio from 1.48 to 1.56 V (vs RHE). (f) Schematic illustration of adsorbate evolution and lattice oxygen dual-pathway on the multinary intermetallics surface to balance activity and stability. Operando Raman spectra of (g) Al_{0.95}-1800, (h) Al_{0.95}-3600, and (i) Al_{0.95}-5400 with potentials applied from 1.20 to 1.7 V (versus RHE), before, and after operando Raman test. (j) Raman spectroscopy of Al_{0.95}-3600 in air condition before and after 240-h stability test.

using operando ATR-FTIR analysis. Figure 4a,b shows the operando ATR-FTIR spectra collected from Al_{0.95}-1800 and Al_{0.95}-3600 catalysts as a function of the applied step voltage. Several absorption peaks centered at 1181, 1220, and 3440 cm⁻¹ were observed on Al_{0.95}-1800 as the voltage increased (Figure 4a, Table S7). The absorption peaks centered at 1220 and 3440 cm⁻¹ are assigned to ^{*}OOH and ^{*}OH intermediates formed during the AEM pathway, respectively [48–51]. Similar spectral changes were also observed on Al_{0.95}-3600 (Figure 4b, Table S8). The peak at 1181 cm⁻¹, which is assigned to ^{*}OO [52–55], suggests that the LOM pathway might coexist on these catalysts. We also calculated

the ATR-FTIR wavenumber by the first-principle methods for comparison, which are summarized in Tables S7 and S8. As shown in the tables, the trends of the calculated frequencies for ^{*}OH, ^{*}OOH, and ^{*}OO align well with our experimental peak assignments. We note that the DFT-calculated values are systematically higher than the experimental values. This overestimation is a well-known and common phenomenon in electrochemical modeling. Our DFT calculations are based on static localized surface models (0 K). However, under real operando OER conditions, the surface adsorbed species (^{*}OH and ^{*}OOH) are immersed in the electric double layer (EDL). They

form strong hydrogen bonds with the surrounding interfacial water molecules. Previous studies [56, 57] have shown that the interfacial structure strongly influences the connectivity of the hydrogen-bond network and thereby modulates the hydrogen-bond environment surrounding adsorbed *OH and *OOH. Enhanced hydrogen-bond interactions can weaken and elongate the O–H and O–O bonds, resulting in a red-shift of vibrational frequency by 100–400 cm^{−1} in spectroscopic experiments. For the disordered Al_{0.95}–1800 sample, the DFT-calculated frequency (1009.74 cm^{−1}) is unexpectedly lower than the experimental value (1181 cm^{−1}). This is because the *OO intermediate forms a strongly bound bridging configuration on the disordered BCC surface (inset of Figure 5d). This strong surface pull severely elongates the O–O bond, leading to a much lower calculated frequency at 0 K.

As is well known, LOM processes can contribute partly to high intrinsic OER activity [58, 59]. In view of this, the difference in peak intensities between *OO and *OOH ($\Delta I = I_{*OO} - I_{*OOH}$) was carefully analyzed. As shown in Figure 4c, in the OER potential range, Al_{0.95}–1800 had a relatively steady and high value of ΔI , while for Al_{0.95}–3600 the value gradually increased from a negative value to a positive one at high voltage. This is because for Al_{0.95}–3600, under operando conditions, the lattice oxygen participates in the LOM coupling (*O + O_{Lat} → *O–O_{Lat}) in a smooth manner, which will be proved by DFT results later. Consequently, the *O–O_{Lat} intermediate species exhibit a steady accumulation on the catalytic surface, which is manifested by the gradually increasing $\Delta I = I_{*OO} - I_{*OOH}$ in the FTIR spectra. In the low-ordering sample Al_{0.95}–1800, the chaotic atomic arrangement generates a high density of structural defects and unsaturated oxygen vacancies, which severely destabilizes the lattice oxygen. Upon bias application, a massive amount of lattice oxygen is activated. This uncontrolled flood of lattice oxygen leads to a fast formation of *O–O chemical coupling intermediates via the LOM pathway. Therefore, the ΔI reaches an immediate equilibrium and remains high throughout the entire operando duration. On the other hand, the negatively charged superoxide species (O₂[−]) generated via deprotonation and subsequent O–O coupling during LOM exhibits specific interactions with tetramethylammonium cations (TMA⁺). To probe this, we compared linear sweep voltammetry (LSV) polarization curves in 1 M KOH and tetramethylammonium hydroxide (TMAOH) electrolytes (Figure 4d). The differences in OER activity among the catalysts reflect varying degrees of lattice oxygen activation. This activity decline is ascribed to TMA⁺ attacking O₂[−] species, thereby hindering the O–O coupling critical for the LOM [46, 60, 61]. By quantifying the current density drop from the initial reaction stage to high potentials (1.48–1.56 V) and calculating the LOM contribution based on the reduction ratio (Figure 4e), we found that the Al_{0.95}–3600 sample exhibits a 50%–70% LOM proportion. Lattice oxygen activation is known to enhance catalytic activity; however, the excessively high LOM contributions in Al_{0.95}–1800 and Al_{0.95}–5400 samples likely account for their structural instability and elevated elemental leaching. Consequently, the balanced adsorbate evolution and lattice oxygen dual-pathway in Al_{0.95}–3600 confers both superior activity and stability (Figure 4f).

In situ Raman spectroscopy was employed to monitor the surface reconstruction dynamics of multinary intermetallics electrocatalysts during OER in alkaline media. The pristine samples

exhibited characteristic broad Raman bands (Figure 4g–i), one centered at ~690 cm^{−1} was assigned to the A_{1g} mode, arising from symmetric stretching vibrations of M–O bonds [62, 63], where M primarily denotes Co³⁺ or Ni³⁺; another centered at ~530 cm^{−1}, which is attributed to the E_g modes corresponding to octahedral M–O bending vibrations [62, 63]. The broadening of these bands is indicative of cationic disorder induced by the incorporation of multiple elements (Fe, Cr, Al), which disrupts lattice symmetry and promotes phonon scattering, consistent with high-entropy structures [64, 65]. Upon initiation of OER under anodic polarization, the M–O A_{1g} band rapidly diminished and ultimately vanished, signifying the dissolution-redeposition or oxidative etching of the surface layer. Concomitantly, new sharp peaks emerged at ~457 cm^{−1} (E_g mode) and ~540 cm^{−1} (A_{1g} mode). These spectral signatures are emblematic of the formation of a multiprincipal element oxyhydroxide M(OH)₂, wherein the ~457 and ~540 cm^{−1} bands reflect M–O bending and stretching vibrations.

As the applied potential increased, the initial oxyhydroxide peaks underwent a blue shift to ~468 and ~549 cm^{−1}, respectively. This displacement is ascribed to lattice contraction and enhanced M–O bond stiffness, driven by elevated metal oxidation states, and a structural transition from the M(OH)₂ to a MOOH phase [66–69]. Such evolution underscores the adaptive reconstruction toward a high-valence active surface, facilitating lattice oxygen-participated OER mechanisms and yielding low overpotentials.

Post-OER, upon removal from the electrolyte and ex situ Raman analysis in air, the original spinel bands at ~690 and ~530 cm^{−1} reemerged (Figure 4j), indicating partial reversibility of the surface reconstruction. Comparative analysis across samples with varying structural order, Al_{0.95}–1800, Al_{0.95}–3600, and Al_{0.95}–5400, revealed that the blue shift of oxyhydroxide bands occurs at markedly lower potential in Al_{0.95}–3600, which starts at 1.4 V (vs RHE) for Al_{0.95}–3600, while starting at 100 mV higher (1.5 V vs RHE) for others. This indicates that the active MOOH intermediate phase forms more readily in the ordered B2 intermetallic catalyst at lower potentials than the disordered BCC counterparts. Such enhanced responsiveness is likely due to the superior lattice ordering, which was expected to suppress the Jahn–Teller distortion, enhance crystal-field stabilization, thereby optimizing charge redistribution and OER kinetics [70]. These findings elucidate the role of precatalyst crystallinity in modulating reconstruction thresholds. In summary, the operando spectroelectrochemical measurements revealed an adsorbate evolution and lattice oxygen dual-pathway O₂ evolution process on the Al_{0.95}–3600 catalyst, with long-range ordering promoting the transition into highly active MOOH species, thus resulting in fast OER reaction kinetics and stability, in good agreement with the OER performance determined experimentally.

2.4 | DFT Simulations

To elucidate the atomic-level origin of the superior OER performance and accelerated reconstruction kinetics observed in the highly ordered Al_{0.95}–3600 sample, DFT calculations were performed on the (110) surface of B2-ordered and disordered BCC phases of Al_{0.95}CoCrFeNi_{2.15} HEA. According to the experimental

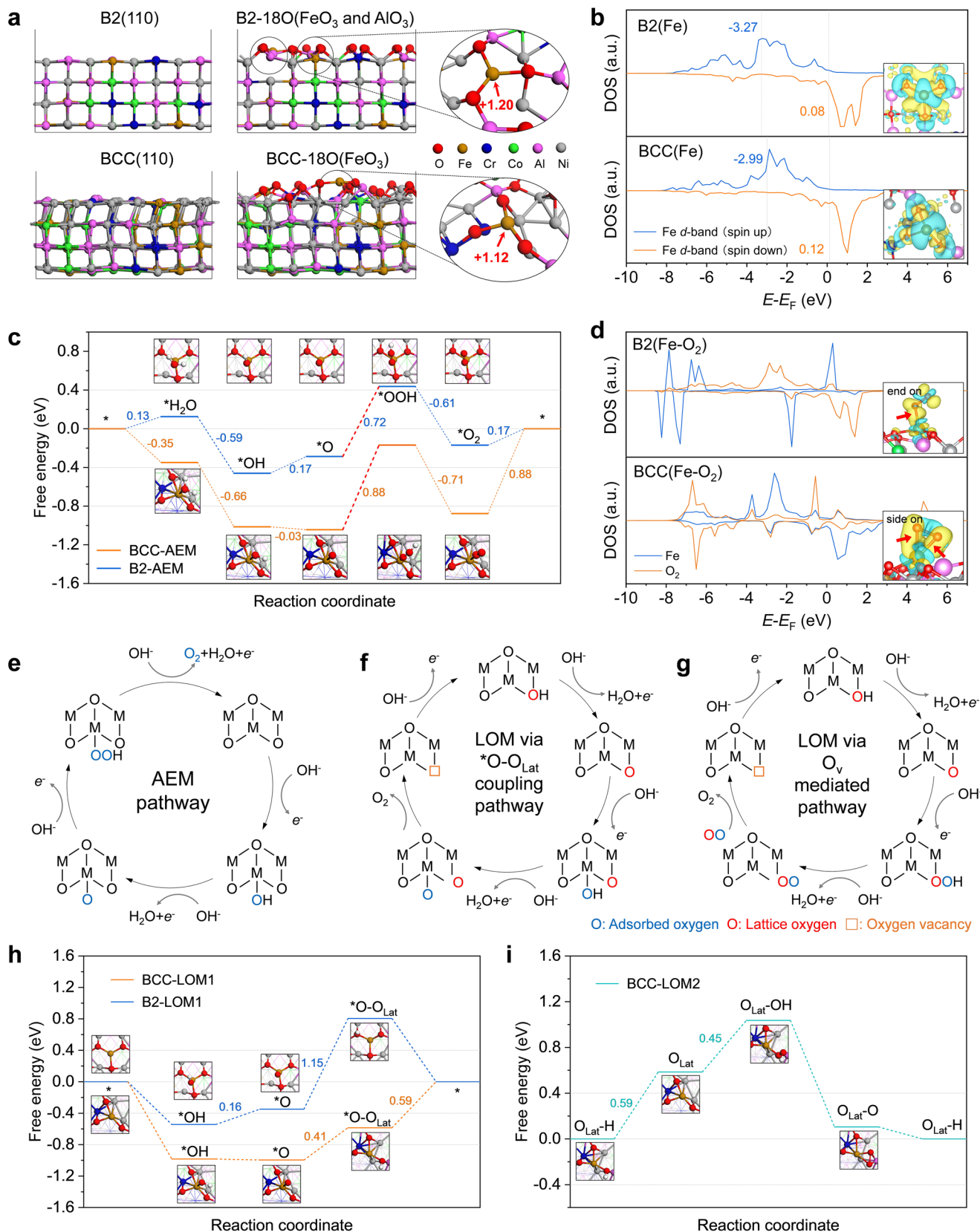


FIGURE 5 | DFT calculations investigating the OER mechanism. (a) Optimized pristine (left) and pre-oxidized (middle) bulk configuration of (110) facets of B2 and BCC phases, with Bader charges of Fe atoms (right). (b) Projected DOS and *d*-band center for the Fe atom in FeO₃ active site. Insets are 3D electron density differences of FeO₃ sites, where blue and yellow represents depletion and accumulation of electrons, respectively. (c) Free energy profiles of OER proceed on the FeO₃ site of B2 (ordered) and BCC (disordered) (110) facets at 1.23 V (vs RHE). The inset shows the relaxed configurations with the adsorption of *H₂O, *OH, *O, *OOH, and *O₂ intermediates at the FeO₃ site. (d) Projected DOS and *d*-band center for the Fe atom in FeO₃ active site after adsorbing *O₂. Insets are 3D electron density differences after *O₂ adsorption onto FeO₃ active site, where blue and yellow represents

results, we constructed B2 supercells with Al/Cr/Fe predominantly at cube corners and Co/Ni at body-center positions, whereas the disordered BCC exhibits random site occupancy (Figure 5a and Figure S26), consistent with the atomic-resolution HAADF-STEM in Figure 2b.

We found that the multinary model inherently possesses exceptionally high surface energies and chemically active surfaces, which spontaneously lower their energy through oxygen chemisorption from ambient air or KOH electrolyte until a thermodynamically stable oxidized termination is achieved. Accordingly, to accurately reflect the real catalytically relevant state prior to OER onset, we constructed (110)-oriented B2 and disordered BCC slabs with 18–20 pre-adsorbed oxygen atoms per supercell (Figure 5a and Figures S27 and S28). Under OER-relevant oxygen chemical potentials, these pre-oxidized surfaces undergo further rapid reconstruction within the topmost two atomic layers, spontaneously forming Fe/Co/Ni-oxy(hydroxide)-like motifs. This computationally predicted transformation is in excellent agreement with operando Raman spectroscopy, which shows the immediate disappearance of the spinel A_{1g} band ($\sim 690\text{ cm}^{-1}$) and the concomitant emergence of oxyhydroxide E_g ($\sim 457\text{ cm}^{-1}$) and A_{1g} ($\sim 540\text{ cm}^{-1}$) vibrations upon anodic polarization, thereby validating the evolution of alloy surface into oxygen-pre-covered catalytic state. Notably, the reconstructed B2 surface retains long-range atomic ordering, while the disordered BCC suffers severe lattice distortion (Figure 5a). Bader charge analysis reveals that Fe in the ordered B2 reconstruction carries +1.20, higher than +1.12 in the disordered case (Figure 5a, right), indicating higher oxidation state in B2 surface, coinciding with EXAFS results, which helps to reduce the propensity for further oxygen adsorption on B2.

Free-energy diagrams of AEM pathway ($U = 1.23\text{ V}$) identify $^*\text{OOH}$ formation as the potential-limiting step on most sites (Fe, Co, Ni, and Cr sites) (Figure 5c–e and Figure S29). Al site is inactive due to a high $^*\text{O}$ formation barrier ($\Delta G_{^*\text{O}} = 2.30\text{ eV}$). The ordered B2 dramatically lowers ΔG_{max} from 0.88 eV (disordered) to 0.72 eV (ordered) on FeO_3 -like sites. Critically, O_2 desorption on B2 is facile ($\Delta G_{^*\text{O}_2} = 0.17\text{ eV}$) versus 0.88 eV on disordered BCC. Projected density of states (PDOS) analyses show that long-range B2 ordering downshifts the Fe 3d-band center (spin-up: -3.27 eV in ordered vs. -2.99 eV in disordered, spin-down: 0.08 in ordered vs. -0.12 eV in disordered) while strengthening Fe–O antibonding states below E_F and weakening adsorbate binding energy per d -band theory (Figure 5b). PDOS of FeO_3 site and adsorbed $^*\text{O}_2$ in B2 and BCC model was also calculated (Figure 5d). On the B2(110)- FeO_3 site, the Fe 3d states exhibit minimal overlap with the O_2 -derived orbitals, resulting in sharply localized $\text{O}_2\ 2\pi^*$ states. This weak hybridization reflects attenuated bonding between active sites and adsorbates, yielding a markedly weakened adsorption strength consistent with the exclusive end-on coordination geometry observed for adsorbed O_2 (Figure 5d, upper inset). In contrast, the disordered BCC(110)- FeO_3 surface displays pronounced Fe 3d- $\text{O}_2\ 2\pi^*$ mixing

centered around -6 eV . Stable side-on configuration was observed in atomic configuration plot (Figure 5d, down inset), which gives rise to excessively strong O_2 binding. Therefore, long-range ordering structure would prevent oxygen trapping and over-oxidation that would otherwise trigger metal dissolution, which is crucial for long-term stability. Overall, the calculations demonstrate that the surface undergoes oxidation reconstruction, and atomic ordering can accelerate formation of high-valence active sites, lowers the thermodynamic barrier for O_2 desorption, and confers exceptional resistance to dissolution.

In addition, we calculated detailed free-energy diagrams for two LOM pathways, including the $^*\text{O}-\text{O}_{\text{Lat}}$ coupling pathway initiated from the FeO_3 site (Figure 5f) and the oxygen vacancy mediated pathway starting from the $\text{FeO}_2(\text{OH})$ oxyhydroxide (Figure 5g). Our results show that while two LOM pathways are operative on the disordered BCC surface, only the $^*\text{O}-\text{O}_{\text{Lat}}$ coupling pathway is feasible on the chemically ordered B2 surface (Figure 5 h,i). This difference can be rationalized by the Gibbs free energies change (ΔG) of hydrogenation on the pre-oxidized surface (Figure S30). At 1.23 V , the formation of $\text{FeO}_2(\text{OH})$ oxyhydroxide is energetically uphill on B2(110)- FeO_3 ($\Delta G = 0.81\text{ eV}$), but significantly downhill on BCC(110)- FeO_3 ($\Delta G = -0.59\text{ eV}$). Consequently, at high overpotentials, the chemically ordered B2 surface retains stable FeO_3 sites, thereby completely blocking the oxygen vacancy-mediated LOM pathway. As a result, the LOM kinetics on the B2 structure are strictly regulated and confined to a single, controllable pathway. As shown in Figure 5h, the rate-determining step of $^*\text{O}-\text{O}_{\text{Lat}}$ coupling LOM pathway on B2(110)- FeO_3 is $^*\text{O} + \text{O}_{\text{Lat}} + \text{OH}^- \rightarrow ^*\text{O}_{\text{Lat}}-\text{H} + \text{O}_2 + e^-$, which exhibits a substantial ΔG of 1.15 eV . This high ΔG means limited lattice oxygen participation during the reaction, thus the lattice is strongly protected against rapid and continuous dissolution. Therefore, this moderate level of LOM provides excellent OER activity, while the structural robustness of the B2 phase prevents severe lattice destruction. In a word, the high-ordering Al_{0.95}–3600 sample achieves much better stability through a well-balanced, synergistic AEM/LOM dual-pathway mechanism. In contrast, the same step proceeds readily on BCC(110)- FeO_3 with a much smaller ΔG of 0.41 eV . It should be noted that both LOM pathways on the BCC surface (Figure 5 h,i) are controlled by the elementary step ($^*\text{O}_{\text{Lat}}-\text{H} + \text{OH}^- \rightarrow ^*\text{O}_{\text{Lat}} + \text{H}_2\text{O} + e^-$) with ΔG of 0.59 eV .

To deeply understand the lattice degradation mechanism, we theoretically evaluated the structural stability loss triggered by the LOM. Generally, the participation of lattice oxygen atoms generates surface oxygen vacancies (V_O), which inevitably disrupts local chemical bonds, decreases the coordination number of neighboring metal sites, and consequently accelerates metal dissolution into the electrolyte. To quantitatively assess this degradation resistance, the oxygen vacancy formation energies (ΔG_{VO}) were calculated for both models (Figure S31). Under standard conditions (0 V), the ordered B2 matrix exhibits a remarkably high ΔG_{VO} of 2.96 eV , which is nearly double that

depletion and accumulation of electrons, respectively. Schematic illustration of (e) the AEM pathway, (f) the $^*\text{O}-\text{O}_{\text{Lat}}$ coupling pathway, and (g) the oxygen vacancy (V_O) mediated pathway. Free energy profiles of (h) the $^*\text{O}-\text{O}_{\text{Lat}}$ coupling pathway (LOM1) proceed on the FeO_3 site of B2 and BCC and (i) the oxygen vacancy mediated pathway (LOM2) proceed on the $\text{FeO}_2(\text{OH})$ site of BCC at 1.23 V (vs RHE).

of the disordered BCC lattice (1.51 eV). More importantly, upon applying an OER potential of 1.23 V vs. RHE, the ΔG_{VO} of the BCC phase drops precipitously to a negative value (−0.95 eV), rendering vacancy formation and subsequent metal dissolution highly spontaneous. In sharp contrast, the ordered B2 structure retains a positive ΔG of 0.50 eV. This prominent energetic contrast demonstrates that the periodic B2 configuration efficiently locks lattice oxygen and suppresses vacancy cascades, thereby shielding adjacent metal sites against severe dissolution.

3 | Conclusion

In summary, we have demonstrated an innovative approach based on chemical ordering to govern the dynamic surface reconstruction of multinary intermetallic electrocatalysts for highly efficient and durable oxygen evolution. By harnessing the high formation enthalpy of the B2-type ordered intermetallic core in $\text{Al}_{0.95}\text{CoCrFeNi}_{2.15}$ HEA, we successfully achieved a controlled and self-adaptive disorder-to-order evolution. This thermodynamic regulation facilitates the precise formation of an active (oxy)hydroxide skin while maintaining a structurally fortified core, effectively balancing the AEM and LOM pathways. Our findings reveal that the explicit M1(vertex)-M2(body-center) heteroatomic motifs within the ordered intermetallic lattice induce pronounced multi-element charge polarization. This unique atomic coordination elevates the oxidation states of Fe/Co/Ni sites and optimizes the *d*-band center, thereby regulating lattice oxygen stability and the reaction pathway. Consequently, the tailored catalyst exhibits record-breaking OER performance, requiring an ultralow overpotential of only 220 mV at 10 mA cm^{-2} and 335 mV at 1 A cm^{-2} in 1 M KOH. Crucially, the enthalpy-stabilized intermetallic core serves as a robust structural anchor, suppressing deleterious elemental leaching compared to disordered counterparts. This exceptional structural integrity translates into superior long-term durability, exceeding 1000 h at 100 mA cm^{-2} , and outstanding performance under industrial conditions (1.50 V at 3 A cm^{-2} in 6 M KOH at 353 K). This chemical ordering command strategy provides a robust and universal framework for the rational design of high-performance electrocatalysts, synergistically optimizing catalytic efficacy and industrial-grade durability for sustainable energy conversion technologies.

Author Contributions

Yiyuan Yang: conceptualization, methodology, investigation, writing – original draft, visualization. **Chengkai Jin:** methodology, writing – original draft. **Zhe Jia:** conceptualization, writing – review and editing, supervision, funding acquisition. **Huahai Chang:** methodology, investigation. **Fan Yu:** investigation. **Shunda Jiang:** investigation. **Gaopeng Zou:** methodology, visualization. **Guoming Yi:** methodology, visualization. **Jifeng Zhou:** methodology, visualization. **Pengcheng Zhao:** investigation. **Lin Zhou:** methodology. **Jixun Zhang:** methodology. **Kai Xu:** writing – review and editing, methodology. **Sida Liu:** writing – review and editing. **Shangqian Zhu:** writing – review and editing. **Xunhua Zhao:** writing – review and editing, funding acquisition, methodology, writing – original draft. **Tao Yang:** writing – review and editing, funding acquisition. **Jian Lu:** writing – review and editing, funding acquisition. **Baolong Shen:** writing – review and editing, supervision, funding acquisition.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: anie73767-sup-0001-SuppMat.docx.