NanoNEXT

Review Article

DOI: 10.54392/nnxt2631

High-Entropy Oxides for Energy Storage and Electrocatalysis: Defect Chemistry, Entropy Stabilization, and Structure–Performance Design Rules

I. Pradeep [a], S. Balaprabhakaran [b, *]

[a] Department of Physics, Nehru Institute of Technology, Coimbatore-641105, Tamil Nadu, India.
[b] Department of Science and Humanities (Physics), KGiSL Institute of Technology, Coimbatore-641035, Tamil Nadu, India.
* Corresponding author Email: balaprbhakaran.s@kgkite.ac.in
DOI: https://doi.org/10.54392/nnxt2631
Received: 30-04-2026; Revised: 18-07-2026; Accepted: 29-07-2026; Published: 08-08-2026

Abstract: High-entropy oxides (HEOs) are an important class of compositionally complex oxide materials for energy storage and electrocatalysis. Their significance does not arise solely from the presence of five or more cations; multication disorder also influences phase stability, defect chemistry, oxygen-vacancy formation, local lattice strain, redox activity, and surface reconstruction. Since the first experimental demonstration of entropy-stabilized rocksalt (MgCoNiCuZn)O, the field has expanded to include rocksalt, spinel, perovskite, fluorite, pyrochlore, layered, and mixed-anion oxide frameworks. These structures are now being explored for solid electrolytes, supercapacitors, oxygen evolution, oxygen reduction, hydrogen evolution, lithium-ion and sodium-ion batteries, and bifunctional water-splitting systems. This review examines the thermodynamic basis of HEO formation, the role of crystal structure in compositional design, the impact of synthesis techniques on phase purity and defect populations, and the mechanistic links between local disorder and electrochemical function. Particular attention is given to oxygen vacancies, mixed-valence cations, short-range ordering, operando surface reconstruction, and descriptor-based catalyst design. The review also assesses how density functional theory, CALPHAD, machine learning, active learning, and inverse design are accelerating HEO development. One key conclusion is that future progress will depend more on designing the right type of disorder for a specific function than on simply adding more components. Standardized terminology, reproducible synthesis protocols, improved local and operando characterization, morphology-matched benchmarking, open datasets, and device-level validation are all required for the field to advance reliably.

Keywords: Defect Chemistry, Electrocatalysis, Entropy Stabilization, Ion Transport, Oxygen Vacancies, Surface Reconstruction.

1. Introduction

High-entropy materials emerged from the development of multi-principal-element alloys, in which several principal elements are combined to form compositionally complex solid solutions rather than alloys dominated by a single principal element. Their common thermodynamic foundation is the Gibbs free energy of mixing, where configurational entropy can lower the free energy of a disordered phase at elevated temperatures [1]. This concept has since been extended to ceramics, including carbides, nitrides, borides, silicides, and oxides, where entropy operates together with strong ionic or covalent bonding, charge neutrality, ionic-size differences, coordination preferences, and crystal-chemical constraints [2]. High-entropy oxides (HEOs) have become one of the most significant classes of high-entropy ceramics because the oxygen sublattice provides a stable lattice framework, while the cation sublattice accommodates broad compositional diversity. The field was experimentally established with entropy-stabilized rocksalt oxides such as (MgCoNiCuZn)O, which form a single-phase structure at high temperature and reversibly decompose at lower temperature [3]. HEOs became especially important for electrochemistry after rocksalt-type HEOs were shown to function as lithium-ion battery anodes with improved reversibility and cycling stability relative to selected binary oxides [4]. Since then, HEO research has expanded to rocksalt, spinel, perovskite, fluorite, pyrochlore, layered, oxyfluoride, and mixed-anion frameworks. Current studies focus on applications in lithium-ion and sodium-ion batteries, solid electrolytes, supercapacitors, oxygen evolution, oxygen reduction, hydrogen evolution, and bifunctional water-splitting reactions. The central question is no longer whether multication oxides can be synthesized, but how this intrinsic disorder influences phase stability, defect chemistry,

ion mobility, redox processes, and electrochemical performance.

The high-entropy concept cannot be transferred directly from metallic alloys to oxides. In metallic alloys, atoms often share a common metallic lattice, and phase formation is commonly discussed in terms of atomic-size difference, mixing enthalpy, electronegativity difference, and valence-electron concentration. In oxides, the anion sublattice imposes stronger structural and electronic constraints. Charge neutrality, coordination geometry, site preference, crystal-field effects, and local metal–oxygen bonding are among the requirements that cations must satisfy. Fluorite and pyrochlore systems are strongly influenced by oxygen-vacancy ordering and migration; spinels contain both tetrahedral and octahedral sites; perovskites separate A-site and B-site chemistry; and rocksalt oxides require cations compatible with octahedral coordination. This distinction is crucial because a multication oxide is not automatically entropy-stabilized simply because it contains five or more elements. Without direct evidence of entropy stabilization, a material may appear single-phase by X-ray diffraction yet be kinetically retained, enthalpy-stabilized, locally segregated, or merely compositionally complex [5]. Likewise, electrochemical benefits may arise from conventional substitution chemistry, particle size, surface area, nanostructuring, oxygen vacancies, mixed valence, or synthesis-induced microstructure rather than from configurational entropy itself. Therefore, entropy-stabilized oxides, high-entropy oxides, and the broader class of compositionally complex oxides must be distinguished carefully in HEO research. Defect chemistry is especially important because of the oxygen sublattice. Oxygen vacancies, oxygen non-stoichiometry, and mixed cation valence directly influence electronic conductivity, ionic transport, catalytic adsorption, surface redox activity, and electrochemical degradation. In HEOs, defect formation occurs across many local cation environments rather than at a single fixed site type. This can generate broad distributions of oxygen-vacancy formation energies, migration barriers, and adsorption strengths, but it can also promote vacancy trapping, blocked percolation, unstable reconstruction, or cation segregation. Consequently, the functional significance of HEOs lies in controlled disorder tailored to a specific electrochemical role rather than in maximum disorder alone.

Energy storage and electrocatalysis are particularly suited to HEO design since they both depend on connected material characteristics. A battery electrode needs to have a combination of redox capacity, ion transport, electronic conductivity, structural reversibility, and interfacial stability. A solid electrolyte must provide rapid ion mobility while maintaining chemical and mechanical compatibility. Accessible redox-active sites, electrolyte contact, and cycling stability are necessary for a supercapacitor electrode. Favourable intermediate adsorption, quick charge transfer, and resistance to dissolution, passivation, or uncontrolled reconstruction are all requirements for an electrocatalyst. Within a single oxide framework, HEOs provide a way to adjust these linked properties. Multication disorder can disperse redox activity, inhibit harmful phase transitions, buffer conversion events, and alter ion-migration landscapes in battery electrodes [4, 6]. When migration paths stay connected, high-entropy design in solid electrolytes can decrease deep trapping and expand mobile-ion site-energy distributions [7, 8]. Multication surfaces increase the likelihood of creating near-optimal active sites in electrocatalysis by offering a variety of local adsorption conditions for oxygenated or hydrogenated intermediates [8–10]. However, these benefits are subject to certain conditions. Performance may suffer if disorder inhibits ion transport, lowers conductivity, encourages dissolution, or produces unstable surface phases. The most significant electrocatalytic example is OER, where the real active phase is frequently not the pure oxide. Under anodic conditions, several transition-metal oxides reassemble into highly oxidized or oxyhydroxide-like surface layers. Instead of acting as an unaltered active catalyst in this situation, the HEO bulk may serve as a cation reservoir, structural scaffold, or defect regulator. Operating-state characterization is therefore crucial for mechanism assignment. Similar care must be used when studying batteries, as high capacity or extended cycling may be more indicative of half-cell conditions, electrode composition, or morphology than of intrinsic high-entropy chemistry.

High-entropy oxides, high-entropy energy materials, and their electrochemical applications have been covered in several reviews [11-13]. Although these reviews have helped define the field, the next stage requires a more mechanism-centered and evidence-ranked assessment. HEOs are still frequently compared with binary or ternary oxides synthesized, processed, or tested under different conditions [14-16]. This makes it difficult to determine whether enhanced performance arises from configurational entropy, local lattice distortion, oxygen vacancies, mixed-valence chemistry, surface reconstruction, nanostructuring, or

simply differences in testing protocol. Three gaps are particularly important. First, nomenclature remains inconsistent. Entropy-stabilized oxides, high-entropy oxides, and compositionally complex oxides are often used interchangeably even though they require different levels of evidence [17, 18]. Second, average structure is often overinterpreted. While X-ray diffraction can verify a dominant crystallographic phase, it cannot demonstrate operating-surface stability, short-range ordering, oxygen-vacancy distribution, or local cation heterogeneity [19, 20]. Third, inconsistent phase labels, incomplete synthesis information, unbalanced datasets, and the scarcity of negative results continue to limit computational and data-driven design. Machine learning, CALPHAD, DFT, cluster expansion, and active learning can accelerate HEO discovery only when they are linked to reliable experimental metadata and mechanism-based validation. For this reason, an evidence hierarchy is used throughout this review. Entropy stabilization is supported more strongly by direct thermodynamic evidence than by element count alone. Reversible phase formation, calorimetry, high-temperature diffraction, and validated thermodynamic modeling provide stronger evidence than nominal composition alone. Likewise, pair distribution function analysis, X-ray absorption spectroscopy, neutron diffraction, and STEM-based mapping are more reliable probes of local cation disorder than laboratory XRD by itself. Because the active surface may differ from the pristine bulk oxide, operando or post-test spectroscopy is also essential for electrocatalytic mechanism assignment. Unless morphology, surface area, mass loading, and testing procedures are matched, electrochemical comparisons should be interpreted cautiously.

High-entropy oxides for batteries, solid electrolytes, supercapacitors, and electrocatalysis are the main topics of this review. Studies that link electrochemical performance to phase stability, local structure, oxygen vacancies, mixed-valence chemistry, ion transport, surface reconstruction, or data-driven design are given priority in the discussion. Primary experimental and computational research are employed for mechanistic interpretation, while general review papers are used for field positioning. Cataloguing every HEO composition that has been reported is not the goal. Rather, the review poses four recurrent questions: whether the stated behaviour is primarily defect-driven, morphology- or surface-area-driven, operating-state reconstruction-controlled, or truly entropy-assisted. In order to advance the field from composition discovery to function-specific disorder engineering, the manuscript establishes the characterization, benchmarking, data-quality, and device-validation criteria as well as structure-defect-performance design rules for HEOs.

2. Conceptual Foundations of High-Entropy Oxides

2.1 Configurational Entropy and Phase Stabilization

The Gibbs free energy of mixing, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, is commonly used to describe the thermodynamic basis of high-entropy oxides. In this expression, ΔH_{mix} represents the enthalpic contribution from interactions between unlike cations, whereas configurational entropy on the entropy-bearing sublattice dominates ΔS_{mix}. For an ideal random solid solution with n components on a single equivalent crystallographic sublattice, the configurational entropy is $\Delta S_{conf} = -R\Sigma x_i \ln x_i$. Under equimolar conditions, this becomes $R\ln n$. Accordingly, a five-component equimolar system gives $\Delta S_{conf} = 1.61R$, which is often used as a practical threshold for high-entropy classification [12]. This is a useful first approximation, but it is not a complete thermodynamic description. It assumes ideal random mixing, equivalent sites, no short-range ordering, no site preference, and no charge ordering. Real oxides rarely satisfy all of these conditions. Spinels contain tetrahedral and octahedral cation sites, perovskites contain chemically distinct A and B sites, and pyrochlores or fluorites may exhibit coupled cation and oxygen-vacancy disorder. Entropy must therefore be evaluated on the actual entropy-bearing sublattice rather than inferred from the nominal number of elements alone. As Sconfig increases, the distribution of polar dipoles becomes more disordered, as illustrated in Figure 1.

The rocksalt (MgCoNiCuZn)O system remains the benchmark example because its reversible high-temperature single-phase formation and low-temperature decomposition provided direct evidence for entropy stabilization [3]. This example also defines an important limitation: entropy stabilization is a temperature-dependent thermodynamic condition, not a permanent label for every five-cation oxide. A material may appear single phase after quenching because it is kinetically retained, because favourable enthalpy supports mixing, or because secondary phases are below the detection limit of laboratory XRD.

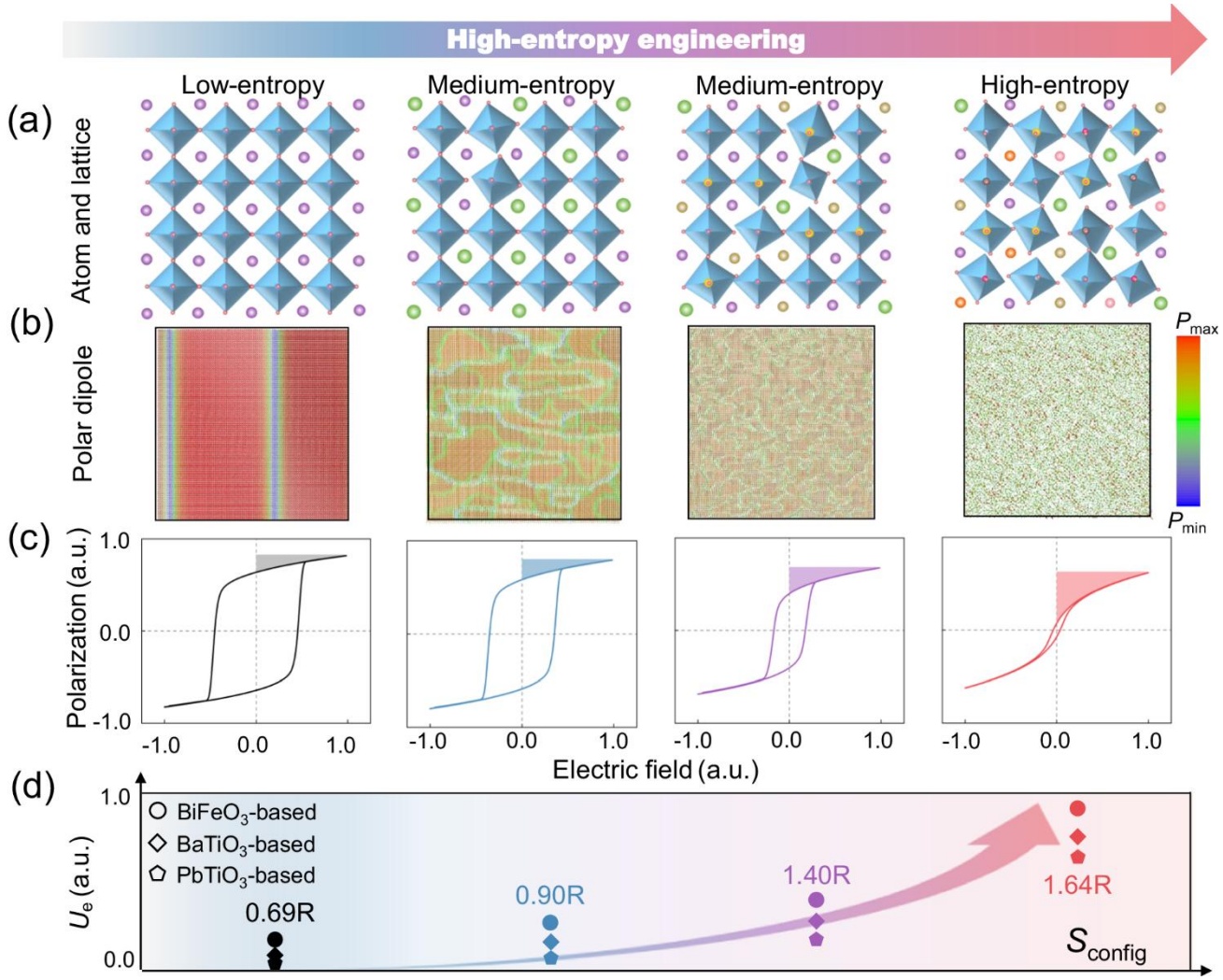

Figure 1. Phase-field simulations of the effect of configurational entropy (Sconfig) on energy-storage performance [21]. a Schematics of atomic disorder and lattice changes in perovskite structures from low entropy to high entropy. b Corresponding polarization distributions in BiFeO3-based dielectrics with different Sconfig. c Normalized P–E loops under the same applied electric field, where the shaded areas represent the dischargeable energy density Ue. d Normalized Ue of BFO-, BTO-, and PTO-based dielectrics at Sconfig values of 0.69R, 0.90R, 1.40R, and 1.64R.

A defensible claim of entropy stabilization should therefore be supported by reversible phase behaviour, calorimetry, high-temperature diffraction, thermodynamic modeling, or local structural evidence [5, 13].

2.2 High-entropy, entropy-stabilized, and compositionally complex oxides

Reliable interpretation still depends heavily on terminology. The most stringent category, entropy-stabilized oxides, should be used only when configurational entropy is shown to stabilize the single-phase structure, ideally through reversible temperature-dependent phase behaviour. A single-phase or predominantly single-phase oxide that approaches or exceeds the high-entropy threshold, typically ΔS_conf > 1.5R for an equimolar five-component sublattice, is referred to as a high-entropy oxide. Multicomponent oxides with substantial compositional complexity, but without rigorous entropy criteria or direct evidence of entropy stabilization, fall into the broader category of compositionally complex oxides [5, 15]. Because performance claims depend on mechanism, this distinction is important. Improved capacity, conductivity, or catalytic activity may be mistakenly attributed to entropy if a four-cation or partially ordered oxide is labeled as a HEO. Instead, conventional substitution, local strain, oxygen vacancies, nanostructuring, surface area, or electrode formulation may be the true cause. If single-phase formation is primarily kinetic or enthalpic, even a five-

cation oxide may not be entropy-stabilized. In this review, single-phase or mostly single-phase multicomponent oxides with high configurational entropy on a defined sublattice are referred to as HEOs. Systems with direct thermodynamic evidence are referred to as entropy-stabilized oxides. When multication chemistry is important but strict entropy proof is absent, the term "compositionally complex oxide" is used. This terminology separates configurational entropy from other performance-controlling factors such as lattice distortion, mixed valence, oxygen vacancies, local ordering, morphology, and surface reconstruction [16, 17].

2.3 Lattice Distortion, Local Disorder, and the Limits of Classical "High-Entropy Effects"

Four effects—high configurational entropy, lattice distortion, the cocktail effect, and sluggish diffusion—are frequently used to frame the conceptual language of high-entropy materials. These ideas are useful starting points, but in oxides they must be interpreted carefully. Oxides are governed by metal–oxygen bonding, charge neutrality, oxygen stoichiometry, cation coordination, and surface redox chemistry. As a result, the four-effect framework should not replace mechanism-based analysis. For HEOs, lattice distortion is among the most physically meaningful of these effects. When cations with different ionic radii, valence states, and bonding preferences occupy the same sublattice, the surrounding oxygen polyhedra become locally distorted. As a result, the local structure can exhibit a broad distribution of metal–oxygen bond lengths and bond angles even when the average crystal structure remains highly symmetric. This local distortion can influence electronic bandwidth, polaron hopping, ion-migration barriers, oxygen-vacancy formation energies, and catalytic intermediate adsorption energies [18, 19].

The cocktail effect is the least precise of these concepts. It is often invoked when a property of a HEO exceeds the weighted average of its component oxides. However, the term remains descriptive rather than mechanistic unless the roles of individual cations, defects, surface area, morphology, and operating-state reconstruction are clearly distinguished. For example, Ni–Fe active sites, Co-assisted conductivity, Cr-induced stability, oxygen-vacancy formation, or reconstruction into oxyhydroxide-like layers may all contribute to enhanced OER activity in electrocatalysis. Rather than grouping these contributions under a vague synergistic label, they should be assigned to specific cation functions and active states [20]. The sluggish-diffusion concept also requires qualification. Disorder in oxides may suppress segregation and slow cation diffusion, but it may also facilitate mobile-ion transport if it broadens site-energy distributions and creates connected migration pathways. For Li^+, Na^+, O^{2-}, or H^+ transport, the key question is not whether diffusion is slow, but whether the local energy landscape permits percolated and accessible migration. HEO transport should therefore be analyzed in terms of the mobile species, defect concentration, site-energy distribution, and migration-network connectivity rather than by directly importing alloy-derived terminology.

2.4 Thermodynamic and Kinetic Control of Phase Formation

Both thermodynamics and kinetics influence the formation of the HEO phase. Binary oxides, ternary oxides, ordered compounds, defect-rich phases, and nanoscale segregated regions all compete thermodynamically with the disordered phase. Modest changes in cation ratio, oxygen partial pressure, synthesis temperature, dwell time, heating rate, cooling rate, or precursor chemistry can shift the product from single-phase to partially segregated or multiphase because the free-energy difference between a single-phase HEO and competing phase assemblages may be small [13].

Kinetic factors are equally important. Atomic-scale mixing at high temperatures requires sufficient cation diffusion. Although the high-temperature disordered phase may not be the equilibrium room-temperature state, it can be retained metastably during cooling or quenching. Even when diffraction shows a single average pattern, inadequate heat treatment can leave the product spatially heterogeneous. Excessive treatment, by contrast, may lead to the loss of volatile species such as Li, Na, Zn, or Cu, grain coarsening, reduced surface area, or the formation of secondary phases. Thus, synthesis history is part of the material identity. Two HEOs with the same nominal formula but different processing histories may differ in local cation distribution, oxygen-vacancy concentration, surface segregation, grain size, and electrochemical behaviour [22–24]. Figure 2 illustrates how Mn- and Fe-containing rocksalt compositions evolve with temperature [23].

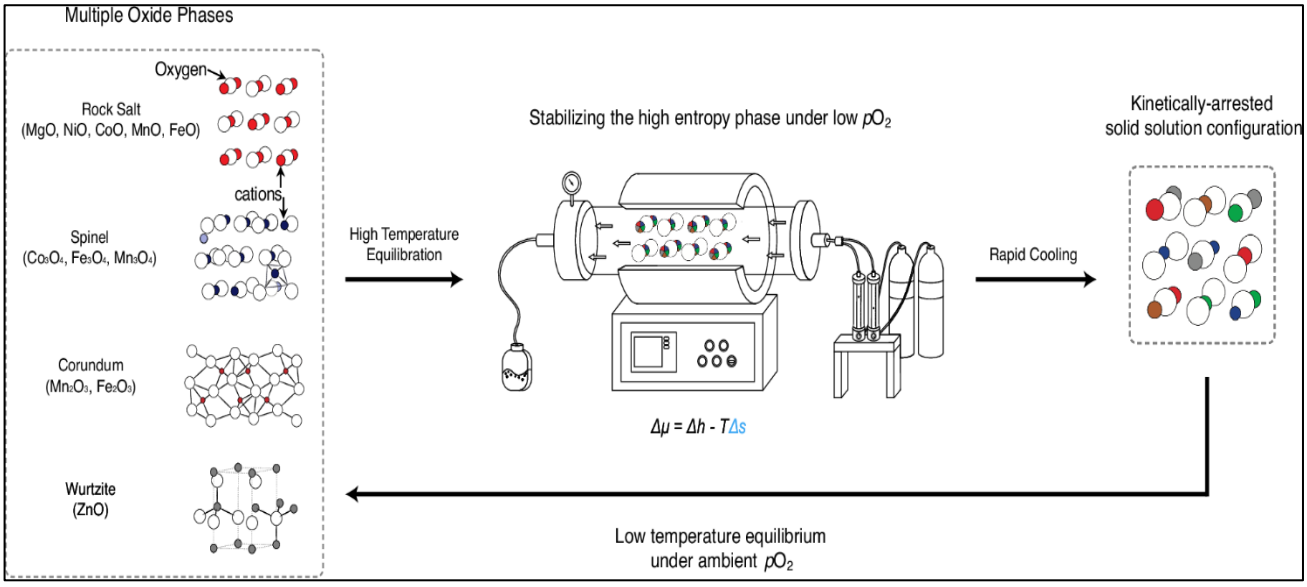

Figure 2. Evolution of Mn- and Fe-containing rocksalt compositions with temperature [23].

2.5 Conceptual Design Principles

These conceptual foundations lead to several design principles. First, configurational entropy should be treated as one design variable rather than as the sole explanation for performance. Entropy may assist phase formation, but electrochemical function is often expressed through redox-active cations, defect chemistry, transport pathways, local disorder, morphology, and operating surfaces. Second, the entropy-bearing sublattice must be defined precisely. The ideal RLNN expression alone cannot be used to evaluate a five-cation oxide with non-equivalent sites. Third, average and local structure must be distinguished. A single XRD phase cannot prove random cation distribution, the absence of clustering, or a uniform oxygen-vacancy distribution. Fourth, disorder should be function-specific. Multication disorder can stabilize the conversion matrix and disperse reaction strain in a conversion-type battery anode. In a layered cathode, disorder may suppress structural transitions but become harmful if it blocks alkali-ion diffusion. In a solid electrolyte, disorder is beneficial only when it creates connected, moderate-energy migration pathways. In an OER catalyst, bulk disorder is useful mainly when it produces a stable and active reconstructed surface. Finally, increasing the number of elements should not be treated as a goal in itself. Carefully designed medium-entropy or compositionally complex oxides may outperform poorly designed five- or six-component systems if they provide the right cation roles, defect landscape, and surface chemistry. Future HEO design should therefore move from element-count maximization to function-specific disorder engineering.

3. Crystal Structures and Composition–Defect Design

3.1 Structure Selection as the First Design Decision

The functional behaviour of high-entropy oxides is determined not only by the number of cations, but also by the oxide framework in which those cations are placed. Rocksalt, spinel, perovskite, fluorite, pyrochlore, layered, and mixed-anion structures impose different constraints on ionic radius, valence compatibility, coordination preference, oxygen stoichiometry, and defect mobility. The first design decision in HEO research is therefore not simply which five or more elements to mix, but which crystallographic framework can translate multication disorder into a useful electrochemical function. Three questions are useful when comparing HEO structures. First, which sublattice bears the entropy? Second, which transport process or defect governs performance? Third, does disorder help or hinder the intended function? Because disorder in rocksalt oxides is typically concentrated on a single octahedral cation sublattice, the structure is well suited for studying cation-disordered cathodes, entropy stabilization, and conversion-type lithium storage. In spinels, cation inversion and site preference become crucial because disorder is distributed across tetrahedral and octahedral sites. In perovskites, A-site and B-site disorder have distinct effects: B-site disorder directly

influences redox chemistry, electronic structure, and catalytic activity, whereas A-site disorder mainly affects lattice tolerance, segregation, and oxygen-vacancy formation. Fluorite and pyrochlore HEOs are especially relevant when the main design goal is disorder tolerance, vacancy mobility, or oxygen-vacancy generation. Layered HEOs are particularly relevant to alkali-ion battery cathodes, where disorder in the transition-metal slab may suppress phase transitions, but excessive cation migration can block Li^+ or Na^+ transport. This structure-specific perspective avoids a common overgeneralization in the HEO literature. The entropy, defect chemistry, and electrochemical behaviour of five-cation rocksalt, spinel, perovskite, and layered oxides are not directly comparable. Their performance depends on whether disorder is created on the appropriate sublattice and whether it supports the rate-limiting functional process.

3.2 Comparative Design Logic across Major HEO Frameworks

Rocksalt HEOs remain the benchmark structure because the prototype (MgCoNiCuZn)O provided direct evidence for entropy-stabilized oxide formation through reversible high-temperature phase behaviour [3]. Structurally, these materials are relatively simple because they contain a single cation sublattice, but their electrochemical behaviour is complex. In lithium-ion battery anodes, redox-active cations such as Co, Ni, Cu, Fe, or Mn can contribute to conversion reactions, whereas less active cations such as Mg or Zn can help maintain the reaction matrix and reduce particle aggregation during cycling [4, 25]. In cation-disordered rocksalt cathodes, however, the key requirement is different: disorder is beneficial only when Li-rich percolation pathways remain connected. Thus, the same rocksalt disorder that stabilizes a conversion-type anode can reduce rate capability in a cathode if it blocks Li migration [26]. Spinel HEOs are structurally more complex because tetrahedral and octahedral sites are not equivalent. Their value lies in their ability to distribute catalytic, conductive, and stabilizing roles across different cations. Fe and Ni often contribute directly to active oxyhydroxide-like surface formation, while Co, Mn, Cr, and other cations can tune conductivity, oxygen-vacancy generation, and durability for alkaline OER [8, 20]. Even so, spinel HEOs should not be treated as completely random multication oxides. Cation site preference, partial inversion, and short-range ordering can lower the effective configurational entropy, although they may also improve function if active cations occupy favorable sites [27, 28]. The design goal is therefore useful site distribution rather than maximum randomness. Perovskite HEOs offer broader compositional tunability, but they also impose stricter crystal-chemical constraints. B-site disorder more directly regulates oxygen-vacancy chemistry, transition-metal redox, and electrocatalytic activity, while A-site disorder can improve tolerance to lattice strain and may suppress harmful surface segregation in Sr-containing cathodes [29, 30]. Although dual-site disorder expands the design space, it also increases the risk of uncontrolled oxygen non-stoichiometry and secondary-phase formation. Perovskite HEOs are therefore attractive for OER, oxygen exchange, and SOFC-related applications, but they require careful control of tolerance factor, charge balance, B-site redox continuity, and oxygen-vacancy concentration.

Fluorite and pyrochlore HEOs are best understood in terms of vacancy behaviour and oxygen-sublattice disorder. Aliovalent cation mixing can diversify local migration environments and increase the concentration of oxygen vacancies in fluorite-type systems such as multication ceria- or zirconia-based oxides [31]. However, higher oxide-ion conductivity does not necessarily follow from a higher vacancy concentration. Vacancies must remain mobile and connected rather than becoming trapped in strongly binding local cation environments. Pyrochlore HEOs add another layer of complexity because they combine ordered fluorite-derived frameworks with local cation and anion disorder. Local site-disorder studies show that strong local distortion can coexist with average structural order in pyrochlore HEOs [32], which is important for ionic transport, high-temperature stability, and radiation tolerance. Layered and mixed-anion HEOs are especially relevant to alkali-ion battery cathodes. Multication disorder in the transition-metal slab of layered sodium oxides may improve cycling stability and suppress cooperative P2–O2 and related structural transitions [33]. However, disorder becomes detrimental if transition metals migrate into alkali layers or block diffusion pathways. Mixed-anion and oxyfluoride HEOs further broaden the design space because anion substitution can tune redox voltage, ion migration, and metal–anion covalency. Because multiphase mixtures, amorphous surface layers, and local segregation can be mistaken for single-phase high-entropy materials, these systems require particularly rigorous structural verification.

3.3 Composition-Selection Rules for Function-Specific HEOs

The target electrochemical problem should be the first consideration when choosing a composition. Redox-active and structurally stabilizing cations should be balanced in the composition if the goal is to stabilize conversion-type lithium storage. Disorder should prevent harmful phase transitions while maintaining Na-ion transport if the goal is a layered sodium cathode.

Table 1. Structural families of high-entropy oxides and function-relevant defect variables.

Structural family	Representative HEO system	Entropy-bearing sublattice	Function-relevant defect variables	Primary design value and caution	Ref.
Rocksalt	(MgCoNiCuZn)O; Li-containing rocksalt variants	Single octahedral cation sublattice	Cation disorder; local lattice distortion; oxygen/cation vacancies; Li-percolation topology	Strong model for entropy stabilization and conversion-type LIB anodes. Do not infer local randomness from cubic XRD alone.	[3,4,26,34]
Spinel	$(FeCoNiCrMn)_3O_4$ and multication AB_2O_4 variants	Tetrahedral and octahedral cation sites	Cation inversion; mixed valence; site preference; surface reconstruction; oxygen vacancies	Useful for OER/ORR and pseudocapacitive systems. Effective entropy may be reducedd by non-random site occupancy.	[8,20,27,28]
Perovskite	$La(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O_3$; A-site/B-site variants	A site, B site, or both	Tolerance factor; B-site redox flexibility; oxygen vacancies; A-site segregation	Strong platform for OER, SOFC cathodes, and oxygen exchange. Stability depends on charge balance, segregation control, and oxygen non-stoichiometry.	[29,30,35]
Fluorite	(Ce, Zr, Hf, Y, Gd)O_{2-d} and related compositions	Cation sublattice coupled with oxygen-vacancy disorder	Vacancy concentration; vacancy trapping; migration barrier distribution; cation-vacancy association	Relevant to oxide-ion conductors and SOFC-related materials. High vacancy concentration is beneficial only when migration pathways remain connected.	[31,36]
Pyrochlore	Nd2M2O7-type HEOs; rare-earth zirconate/hafnate variants	A site, B site, or both	Ordered vacancy sublattice; local disorder; cation-size variance; vacancy ordering	Useful for disorder tolerance, thermal stability, and possible oxygen-exchange systems. Electrochemical benchmarking remains less mature.	[31,32,36]
Layered oxides	$Na_{0.67}(MnCoNiCuFe)O_2$; high-entropy layered cathodes	Transition-metal layer	Transition-metal disorder; stacking-transition suppression; alkali-ion diffusion; TM migration	Promising for SIB/LIB cathodes. Disorder should stabilize the slab without blocking alkali-ion pathways.	[26,33,37,38]

If the target is an OER catalyst, the selected cations should generate a stable reconstructed active surface while maintaining electronic conductivity and limiting dissolution. If the target is an oxide-ion conductor, vacancy concentration must be balanced against vacancy trapping and loss of percolation. Configurational entropy, ionic-radius variance, valence compatibility, electronegativity difference, tolerance factor, octahedral factor, oxygen-vacancy formation energy, cation site preference, and projected decomposition energy are among the variables that can guide composition selection. Although these descriptors are useful for screening, they are not sufficient on their own. High calculated configurational entropy cannot compensate for incompatible cation coordination, severe charge imbalance, unstable oxygen stoichiometry, or blocked ion-transport pathways. Likewise, a nominally single-phase XRD pattern cannot prove local compositional homogeneity or entropy stabilization. A sequential design strategy is therefore the most defensible approach. First, choose the structural family according to the intended function. Second, identify the entropy-bearing sublattice. Third, select cations according to their functional roles, such as redox center, structural stabilizer, vacancy former, electronic modifier, segregation suppressor, or surface-reconstruction regulator. Fourth, choose a synthesis pathway that can deliver the required phase, defect state, morphology, and local homogeneity. Finally, verify whether the observed performance truly reflects the intended structure–defect design rather than uncontrolled morphology or testing conditions. Table 1 summarizes the structural families of HEOs and their function-relevant defect characteristics.

4. Synthesis, Characterization, and Benchmarking Strategy

4.1 Processing as a Functional Design Variable

In HEO research, synthesis should be regarded as a functional design variable rather than as a routine preparatory step. Because many HEOs lie close to phase-stability boundaries, slight changes in precursor chemistry, mixing route, calcination atmosphere, dwell time, heating rate, cooling rate, and post-treatment can alter phase assemblage, local homogeneity, oxygen stoichiometry, particle size, surface area, and electrochemical performance. Two samples with the same nominal composition may therefore behave differently if their thermal and chemical histories differ. The targeted application should guide the choice of synthesis pathway. Bulk thermodynamic studies and solid electrolytes often require well-crystallized, dense, and chemically homogeneous ceramics. Electrocatalysts and supercapacitor electrodes require high surface area, controlled surface defects, electrolyte accessibility, and stable working surfaces. Battery electrodes require phase stability, controlled particle size, electronic connectivity, and resistance to repeated structural change. No single synthesis route is universally superior. The appropriate route is the one that delivers the required combination of phase purity, local disorder, defect population, morphology, and scalability.

4.2 Comparative Assessment of Synthesis Routes

Solid-state synthesis is the most reliable route for producing HEOs because it provides the high thermal energy required for cation interdiffusion and entropy-assisted phase formation. It is simple, scalable, and well suited to phase-stability studies, bulk ceramics, and dense electrolyte pellets. Its main disadvantages are slow diffusion, long firing times, coarse particles, low surface area, and possible volatilization of Li, Na, Zn, Cu, or other mobile species. Solid-state synthesis is therefore less suitable when high catalytic surface area or nanoscale morphology is needed, although it remains valuable for thermodynamic studies and ceramic applications [39]. Solution-based routes such as sol-gel and Pechini methods improve precursor-level cation mixing and can lower calcination temperature or particle size [40, 41]. These routes are attractive for battery and catalytic powders because higher surface area and shorter diffusion lengths can improve electrochemical kinetics. However, solution chemistry also introduces risks. Differences in precursor solubility, hydrolysis rate, ligand binding, pH sensitivity, and decomposition behaviour can generate local heterogeneity before calcination. Residual carbon, incomplete precursor decomposition, and locally reducing conditions can also alter oxygen-vacancy concentration and cation valence state. Solution-derived HEOs therefore require careful validation of composition, phase purity, residual impurities, and oxidation state. Figure 3 compares solid-state and mechanochemical synthesis routes.

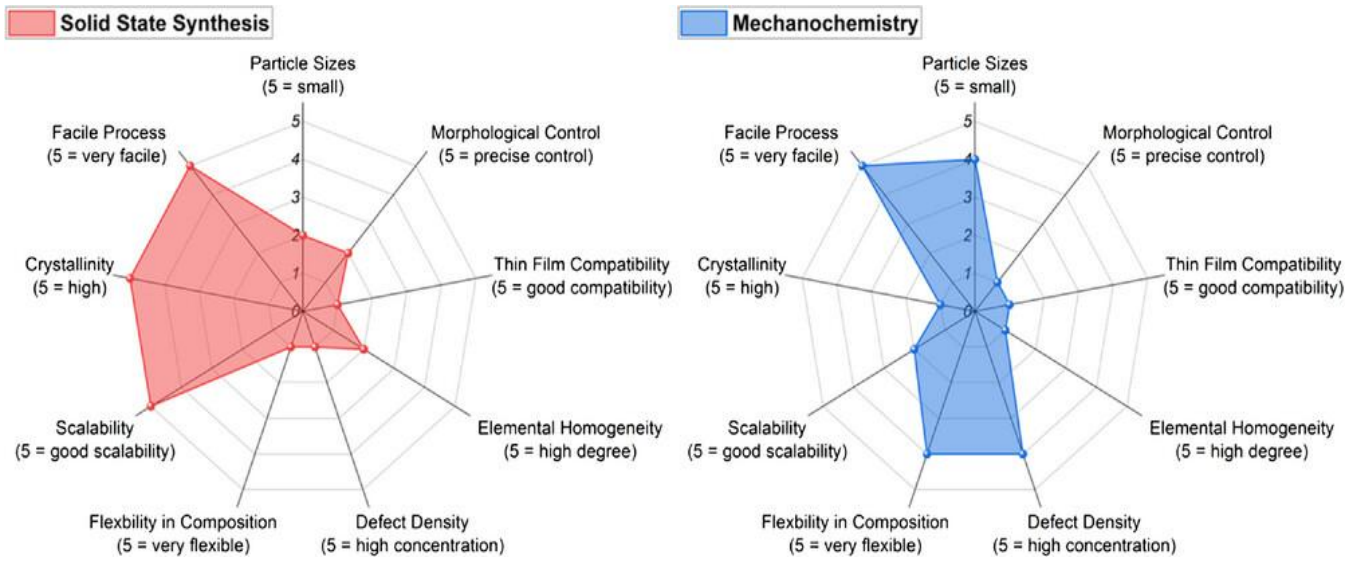

Figure 3. Radar charts for solid-state and mechanochemical synthesis methods [42].

Rapid thermal techniques such as flame spray pyrolysis, combustion synthesis, rapid Joule heating, and photoflash synthesis are attractive because they can generate high temperatures on short time scales while suppressing grain growth [24, 43, 44]. These routes are particularly appealing for rapid composition screening and nanoparticle catalyst synthesis. Their advantages include high surface area, metastable or kinetically retained compositions, and access to fine particles. Their main limitation is that diffraction-level phase purity does not necessarily guarantee local equilibration. Products formed under millisecond heating conditions should therefore be validated by elemental mapping, local-structure probes, and surface-sensitive analysis before strong claims of homogeneous HEO synthesis are made. Mechanochemical synthesis is another route to highly mixed and defect-rich precursor states [45]. It can introduce nanocrystallinity, lower synthesis temperature, and generate grain boundaries or defects that may improve electrode kinetics. It is also solvent-free and relatively scalable. Its limitations include broad particle-size distributions, incomplete crystallization, contamination from the milling media, and limited control of oxygen stoichiometry. Accordingly, milling time, speed, ball-to-powder ratio, vial and ball material, atmosphere, post-annealing conditions, and contamination analysis should all be reported in mechanochemical HEO studies.

The role of thin-film synthesis is distinct. Molecular beam epitaxy, sputtering, pulsed laser deposition, and related methods can produce compositionally controlled films with defined strain, thickness, orientation, and interfacial structure [46]. These films are useful as model systems for separating the effects of strain, surface orientation, interfaces, and local disorder. However, they are generally not scalable for large-area electrocatalysts, supercapacitors, or powder-based battery electrodes. Unless the target device is itself a thin-film architecture, thin films should therefore be regarded primarily as mechanistic platforms. Nanostructuring and template-based routes are useful when performance is dominated by surface processes. Mesoporous particles, hollow structures, electrospun fibers, nanosheets, and hierarchical architectures can all improve electrolyte access, shorten ion-diffusion distances, and expose more active sites [47]. Nevertheless, low-entropy oxides can also benefit from these features. For that reason, nanostructured HEOs must be compared with morphology-matched lower-entropy counterparts. Otherwise, improved performance may reflect porosity or surface area rather than high-entropy chemistry.

4.3 Minimum Characterization Required for Reliable Claims

Characterization should be matched directly to the claim being made. If the claim is single-phase HEO formation, XRD should be supported by measured composition and, where possible, local elemental mapping. If the claim is entropy stabilization, reversible temperature-dependent phase behaviour, calorimetry, high-temperature diffraction, or thermodynamic modeling is required. If the claim concerns oxygen-vacancy engineering, XPS alone is insufficient because it is surface-sensitive and strongly affected by hydroxylation or adsorbates; bulk- or defect-sensitive methods such as neutron diffraction, controlled-atmosphere thermogravimetry, X-ray absorption

spectroscopy, EPR, Raman spectroscopy, conductivity analysis, or validated computation should be used. If the claim involves short-range ordering or local disorder, average diffraction is not enough; pair distribution function analysis, XAS, neutron scattering, atomic-resolution STEM, EDS/EELS mapping, or atom probe tomography should be considered according to the material system. If the claim concerns electrocatalytic activity, the working surface must be examined because the pristine HEO may reconstruct into oxyhydroxide, hydroxide, reduced-oxide, or mixed surface layers during operation. If the claim is battery-cycle stability, post-cycling structural and morphological analysis should be included to identify conversion products, phase retention, SEI evolution, cracking, or impedance growth. Characterization should not be decorative. Each technique should test a specific mechanism such as phase formation, local homogeneity, oxygen stoichiometry, redox state, ion transport, surface reconstruction, or degradation. This strengthens the manuscript and avoids listing characterization methods without explaining their mechanistic relevance.

4.4 Benchmarking Risks Created by Synthesis and Morphology

One major problem with HEO literature is that synthesis, morphology, and testing conditions are often mixed together. A nanostructured HEO may outperform a bulk binary oxide due to its smaller particles, larger surface area, enhanced porosity, or stronger electrode contact. A defect-rich HEO may show increased electrocatalytic activity due to the existence of additional oxygen vacancies rather than being entropy-stabilized. A solution-derived HEO may outperform a solid-state analogue because of morphology rather than intrinsic composition. Therefore, synthesis-route comparisons are meaningful only when morphology, surface area, electrode loading, electrolyte, and testing protocol are controlled. For battery electrodes, benchmarking should include active-material loading, binder and conductive carbon fraction, electrolyte, voltage window, current density, areal capacity, Coulombic efficiency, cycle life, rate capability, and post-cycling analysis. For solid electrolytes, density, bulk and grain-boundary conductivity, activation energy, transference number, electrochemical stability window, and electrode compatibility should be reported. For supercapacitors, gravimetric capacitance should be supported by areal capacitance, mass loading, potential window, current density or scan rate, energy density, power density, and cycling retention. For electrocatalysts, overpotential, Tafel slope, iR correction, catalyst loading, surface-area normalization, Faradaic efficiency, stability testing, and post-test surface analysis are essential. Future synthesis studies should therefore move beyond proving that a HEO can be made. The stronger question is which synthesis route produces the defect structure, local homogeneity, morphology, and operating surface required for a particular function. A comparative synthesis study is valuable only when the same composition is prepared through different routes and then evaluated under identical structural, surface, and electrochemical protocols. Table 2 summarizes synthesis routes, characterization needs, and benchmarking risks for HEO research.

5. Defect Chemistry and Operating-State Structure

5.1 Defect Chemistry as the Functional Core of HEOs

Defect chemistry is the primary link between high-entropy oxide composition and electrochemical function. Although HEOs are frequently introduced via configurational entropy and phase stabilization, their behaviour in batteries, solid electrolytes, supercapacitors, and electrocatalysts is typically governed by oxygen vacancies, cation vacancies, mixed-valence states, antisite defects, local lattice distortion, short-range ordering, grain-boundary defects, and reconstructed surface species. These flaws influence electronic conductivity, ion migration, surface redox activity, catalytic adsorption, electrode stability, and degradation pathways. HEOs should not be seen only as single-phase multication oxides. They should be thought of as defect-coupled oxide frameworks, with configurational disorder influencing the likelihood, energy, mobility, and spatial distribution of functional defects. This link differs from binary and ternary oxides. A simple oxide's oxygen vacancy or aliovalent substitution is often charge-compensated by a small number of adjacent cation species. In a HEO, the same defect may be surrounded by many chemically diverse cations with varying ionic size, electronegativity, valence flexibility, and metal-oxygen bond strength. Defect generation thus happens over a range of local coordination settings rather than at a single fixed crystallographic location.

Table 2. Synthesis routes, characterization needs and benchmarking risks

Synthesis route	Typical product/use	Defect and microstructure tendency	Minimum characterization needs	Main benchmarking risk	Refs.
Solid-state reaction	Bulk HEO ceramics; thermodynamic studies; dense electrolytes	Good crystallinity; coarse grains; possible volatilization of Li/Na/Zn/Cu; lower surface area	XRD/Rietveld; measured composition; phase fraction; cooling rate and atmosphere; density for electrolytes	Poor comparison with nanostructured catalysts because surface area and morphology differ strongly	[3,39,48]
Sol-gel/Pechini	Nanopowders for batteries, supercapacitors, and catalysts	Improved cation mixing; smaller particles; possible residual carbon and valence changes	Precursor chemistry; pH/ligand ratio; calcination profile; XRD; SEM/TEM; XPS/XAS where needed	Performance may reflect smaller particle size rather than entropy-driven chemistry	[40,41,48]
Flame spray/spray pyrolysis	Continuous nanoparticle production for catalysts and battery powders	Rapid quenching; high surface area; possible non-equilibrium defects and compositional gradients	Precursor volatility; residence time; elemental mapping; BET area; surface chemistry	Activity/capacity can be dominated by high surface area and defect-rich surfaces	[43, 48]
Combustion synthesis	Porous powders for electrocatalysis and pseudocapacitance	High porosity; broad particle size; defect-rich and sometimes incompletely crystallized products	Fuel/oxidizer ratio; ignition condition; post-calcination; XRD; Raman/XPS; BET	Porosity and residual phases may falsely appear as intrinsic HEO advantage	[48]
Rapid Joule/photoflash synthesis	Metastable or ultrafine HEO nanoparticles; rapid screening	Kinetic trapping; suppressed grain growth; potentially high local homogeneity if validated	Peak-temperature estimate; pulse duration; atmosphere; HAADF-STEM/EDS; local probes	Diffraction-single-phase product may still be locally non-equilibrated	[24,44]
Mechanochemical synthesis	Nanocrystalline or defective HEO powders and oxyfluorides	High defect density; grain boundaries; possible contamination; incomplete crystallization before annealing	Milling medium; speed/time; ball-to-powder ratio; contamination check; annealing profile	Defect-enhanced performance may be confused with entropy effect	[42,45]
Thin-film deposition	Model HEO systems with controlled strain, orientation, and interfaces	Epitaxial/textured films; strain-modulated oxygen vacancies and electronic structure	Substrate; oxygen pressure; thickness; growth temperature; XRD/reciprocal-space mapping; STEM	Mechanistic value is high, but direct scalability to powder electrodes is limited	[46,49]
Nanostructure/template routes	Fibres, nanosheets, hollow/mesoporous structures for catalysis and supercapacitors	High surface area; exposed sites; under-coordinated atoms; surface hydroxylation	Morphology controls; BET/ECSA; loading; XPS/Raman; post-test characterization	Morphology-matched low-entropy controls are mandatory to isolate HEO chemistry	[36,47,48,50]

This results in a wide range of oxygen-vacancy formation energies, local redox potentials, migration barriers, and adsorption energies. Such heterogeneity is advantageous when it enhances the likelihood of favourable active sites or transport paths, but it can be detrimental when it results in deep traps, unstable surfaces, or permanent local segregation. The main design principle is not to maximize disorder or defect concentration. The goal is to generate useful disorder in which the kind, concentration, mobility, and location of faults correspond to the desired function. A battery anode may benefit from flaws that increase reaction reversibility and spread conversion strain. Immobile vacancy clusters are not sufficient for a solid electrolyte; instead, mobile and coupled defect routes are required. Oxygen vacancies and mixed valence may benefit an OER catalyst if they allow for controlled surface reconstruction and stable charge transfer. Defect chemistry must be optimized as a function-specific variable.

5.2 Oxygen Vacancies and Mixed-Valence States

Oxygen vacancies are among the most important defect features in HEO electrochemistry. Their concentration and distribution are influenced by cation selection, synthesis temperature, oxygen partial pressure, cooling rate, post-treatment, and electrochemical operating conditions. When an oxide ion is removed, excess electronic charge remains and must be compensated by neighboring cation reduction, electron delocalization, or changes in local bonding. In transition-metal HEOs containing Co, Fe, Mn, Ni, and Cu, this compensation can be distributed across several redox-active cations. Such distributed compensation may reduce the energetic penalty for vacancy formation relative to simpler oxides in which charge compensation is more localized [51]. The functional consequences of oxygen vacancies depend strongly on the application. In electrocatalysis, vacancies can modify metal–oxygen covalency, create undercoordinated surface sites, tune adsorption energies, and facilitate surface reconstruction. In solid electrolytes and oxygen-exchange materials, vacancies are essential for oxide-ion transport, but only when they remain mobile and percolated. In battery electrodes, vacancies can improve Li/Na reaction kinetics and electronic conductivity, but excessive vacancy concentrations may destabilize the lattice, promote parasitic side reactions, or drive irreversible phase transitions. An optimal vacancy population is therefore more important than simply maximizing vacancy concentration.

Rather than treating oxygen-vacancy behaviour in HEOs as a single fixed formation energy, it should be described as a distribution of site-dependent energetics. High-throughput computations show that vacancy formation energies in oxides can vary strongly with local chemical environment, and configurational complexity broadens this energetic landscape [52]. Such distributions may be advantageous for catalysis because they increase the likelihood of forming highly active local sites. For ionic conductors, however, the same distribution can be detrimental if it creates vacancy traps or breaks migration connectivity. Oxygen-vacancy design must therefore consider not only vacancy concentration, but also cation–vacancy association, charge compensation, spatial distribution, and mobility under operating conditions. Oxygen vacancies are closely linked to mixed-valence cations. Redox-active cations provide charge flexibility and can support reversible electrochemical processes. In HEO catalysts, mixed valence may improve intermediate adsorption and charge transfer. In battery electrodes, multication redox can distribute electrochemical reactions across several species and reduce local stress concentrations. However, mixed valence can also worsen instability if it promotes cation dissolution, oxygen loss, or uncontrolled surface reconstruction. Mixed valence should therefore be treated as a controlled redox resource rather than as a universal benefit of high entropy.

5.3 Local Disorder and Short-Range Ordering

Many HEO studies assume that cations are randomly distributed over equivalent crystallographic sites, yet real HEOs often show local disorder, preferred cation pairings, site-selective occupation, and short-range ordering. This distinction matters because electrochemical behaviour is governed more strongly by local bonding than by average symmetry alone. X-ray diffraction may show a single average phase even when the material contains nanoscale cation fluctuations, local bond-length variations, or partially ordered cation environments. Local structural studies of entropy-stabilized rocksalt oxides and related HEOs show that the average lattice can mask substantial local distortion [18, 53]. Short-range ordering is not necessarily detrimental. Although it lowers the effective configurational entropy relative to an ideal random

solution, it can improve performance when favorable cations are concentrated at functional sites. In spinel HEOs, for example, tetrahedral and octahedral site preferences can influence defect chemistry, conductivity, magnetic behaviour, and catalytic activity [27]. In rocksalt anodes, a more homogeneous local cation distribution can support more uniform lithiation and better cycling stability, whereas severe clustering may create uneven reaction fronts or local mechanical weakness [19]. In layered cathodes, transition-metal disorder may suppress harmful structural transitions, whereas migration into alkali-ion layers can block diffusion channels. Local ordering should therefore be judged by its functional consequences rather than by entropy loss alone. In structure–performance analysis, the nominal composition, average crystal structure, and local chemical environment must be distinguished. The nominal formula defines the intended cation ratio, the average structure identifies the predominant crystallographic framework, and the local environment governs adsorption energies, migration barriers, redox distributions, vacancy formation, and reconstruction pathways. Because this is the level at which entropy, defect chemistry, and electrochemical response interact, local structure deserves particular emphasis in mechanism-centered HEO analysis.

5.4 Surface Reconstruction and Active Operating States

Surface reconstruction is one of the most important processes in HEO electrocatalysis. Under electrochemical operation, especially during OER, the near-surface region of an oxide catalyst may change in oxidation state, composition, coordination, crystallinity, and defect concentration. The pristine HEO surface is therefore not always the active phase; the active state may instead be a cation-enriched surface, a hydroxylated oxide, a reduced oxide, an oxyhydroxide-like layer, or another reconstructed surface state. HEO electrocatalysts should consequently be interpreted as operating-state materials rather than as static bulk compositions. The parent HEO remains important because it governs which cations migrate, which dissolve, which oxidation states are stabilized, and which reconstructed surface layer forms. In Ni-, Fe-, and Co-containing systems, OER activation can generate NiOOH-, FeOOH-, CoOOH-, or mixed oxyhydroxide-like environments [54]. A multication oxide may therefore function as a precursor and reservoir for the active surface. Stabilizing cations such as Cr, Ti, Mn, or rare-earth elements may not always be the primary active sites, but they can strongly influence the reconstructed layer through mechanical stabilization, electronic tuning, dissolution resistance, or oxygen-vacancy generation. This perspective changes the design objective. The most effective OER-active HEO may not be the one that preserves its pristine surface, but the one that reconstructs in a controlled manner into a conductive, stable, and active layer while maintaining a robust underlying framework. Similarly, oxide surfaces may partially reduce and form metal/oxide interfaces during HER, while ORR and Zn–air operation can expose the surface to repeated oxidation, reduction, hydroxylation, and peroxide attack. The active structure should therefore be identified under operating conditions rather than inferred solely from the as-synthesized material.

5.5 Operando Evidence and Mechanism Validation

Operando and in situ evidence are highly valuable because HEOs can evolve dynamically during electrochemical operation. Although ex situ characterization before and after testing is useful, it may miss potential-dependent surface reconstruction, intermediate phases, reversible structural changes, and transient valence states. Operando XAS has shown that lithiation and delithiation in rocksalt HEO anodes involve multication redox and local coordination changes, supporting the view that charge storage is distributed across multiple cation environments [55]. Operando synchrotron transmission X-ray microscopy has also been used to track particle-level reaction evolution in HEO anodes, providing stronger mechanistic evidence than capacity retention alone [56]. For electrocatalysts, operando Raman spectroscopy, XAS, and post-test surface analysis can determine whether OER activity originates from the pristine HEO, a reconstructed oxyhydroxide layer, or a dissolved/redeposited surface phase. Multi-element XAS is particularly valuable because each cation in a HEO may play a different role. Some cations participate directly in redox cycling, some stabilize the structure, some dissolve, and others tune electronic conductivity or defect concentration. Without this element-specific evidence, it is difficult to assign catalytic activity to the correct active species. Figure 4 shows the atomic-scale structural and electronic analyses of multilevel-disordered MnNiCoFe-CeO2.

5.6 Defect-Centred Design Rules

Several design rules emerge from current understanding of HEO defect chemistry.

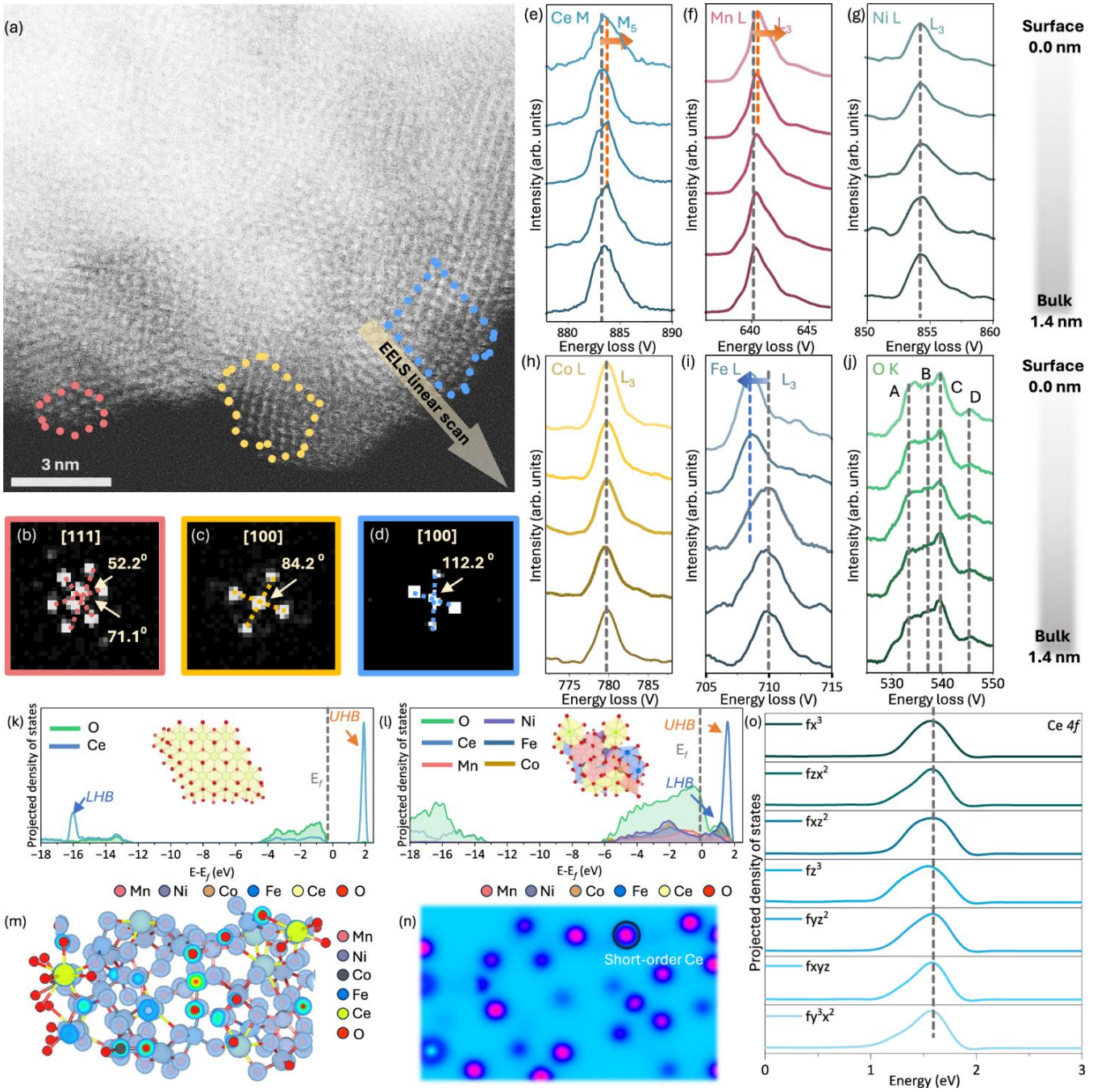

Figure 4. Atomic-scale structural and electronic structure analyses of multilevel-disordered MnNiCoFe-CeO2 [57]. a AC-HAADF image; corresponding FFT patterns for single-crystal regions: b red outlined area, c yellow outlined area, and d blue outlined areas; EELS spectra for linear scans: e Ce M-edge, f Mn L-edge, g Ni L-edge, h Co L-edge, i Fe L-edge, and j O K-edge; electronic-structure analyses: k PDOS for CeO2 (LHB = lower Hubbard band, UHB = upper Hubbard band), l PDOS for MnNiCoFe-CeO_2, m ELF of (311) plane, n charge-density differences (blue perimeter = electron density) of (111) plane, and o corresponding orbital-projected Ce4f states.

First, defect concentration should be optimized rather than maximized. Excess oxygen vacancies may increase catalytic activity or conductivity in one system but cause vacancy trapping, lattice instability, or irreversible side reactions in another. Second, mixed valence should be linked to a defined function such as charge compensation, redox storage, catalytic turnover, or surface reconstruction. Third, because an average single-phase structure cannot fully explain electrochemical response, local disorder should be assessed whenever possible. Fourth, short-range ordering should be interpreted functionally; it may improve site occupation, transport, or catalytic activity while reducing ideal configurational entropy. Fifth, especially in electrocatalysis and conversion-type battery electrodes, the operating state must be

distinguished from the pristine state. The central point is that the most direct link between HEO composition and performance is defect chemistry. Configurational entropy may assist phase formation or stabilization, but electrochemical function is ultimately expressed through migration pathways, reconstructed surfaces, redox-active environments, and local defects. Future HEO design should therefore move from "more elements" to "better-controlled defect environments," supported by local-structure evidence and operating-state validation.

6. High-Entropy Oxides for Energy Storage

6.1 Energy-Storage Design Logic

High-entropy oxides are attractive for energy-storage applications because batteries, supercapacitors, and solid electrolytes require multiple coupled properties rather than a single parameter. Redox activity, electronic or ionic transport, structural reversibility, interfacial stability, and resistance to repeated electrochemical stress are all necessary for a functional electrode or electrolyte. Many binary and ternary oxides can show strong redox activity or high theoretical capacity, yet still suffer from low conductivity, large volume change, phase instability, surface degradation, or rapid capacity fade. HEOs offer an alternative design strategy by combining redox-active, structurally stabilizing, and defect-modifying cations within a single oxide framework. Their value does not arise simply from element count. It emerges when multication disorder addresses a specific failure mechanism. Disorder can distribute reaction strain and suppress metal-particle agglomeration in conversion-type lithium-ion anodes. It can stabilize redox-active frameworks in cation-disordered cathodes if Li transport pathways remain open. It can disrupt cooperative phase transitions in layered sodium cathodes, which would otherwise cause structural damage and voltage hysteresis. In solid electrolytes, it can broaden mobile-ion site-energy distributions and reduce deep trapping. In supercapacitors, it can enhance surface or near-surface redox chemistry. These benefits are still conditional. Excessive disorder can increase voltage hysteresis, lower electronic conductivity, block ion transport, or trigger irreversible side reactions. The design goal is therefore controlled disorder rather than maximal disorder.

6.2 Lithium-ion Battery Anodes and Cathodes

The most established use of HEOs in energy storage remains lithium-ion battery anodes. Compared with several binary oxide benchmarks, the prototype rocksalt (MgCoNiCuZn)O showed that a multication oxide framework can provide high reversible capacity and improved cycling stability [4]. The storage mechanism is usually associated with conversion reactions together with partial intercalation-like or pseudocapacitive contributions. During discharge, metal–oxygen bonds are broken and reduced metal species form within a Li2O-rich matrix; partial reoxidation occurs during charge. The high-entropy framework can distribute this reaction more uniformly, reduce local stress concentration, and suppress excessive growth or aggregation of reduced metal particles [25, 55]. Figure 5 illustrates that HEO anode compositions must balance capacity-generating cations with structure-stabilizing cations. Co, Ni, Cu, Fe, and Mn can contribute to conversion capacity, whereas Mg and Zn may help preserve structural continuity and buffer volume expansion. Too many highly active cations may accelerate degradation, whereas too many weakly active cations may reduce capacity. Oxygen vacancies and pre-introduced lithium can further influence lithiation kinetics and first-cycle behaviour [58]. Most published HEO anode studies, however, remain laboratory demonstrations. Practical relevance is difficult to judge because of low-to-moderate mass loading, limited full-cell validation, and reliance on half-cell testing against lithium metal. Future anode studies should therefore prioritize first-cycle Coulombic efficiency, areal capacity, electrode density, impedance growth, post-cycling morphology, and full-cell performance.

Since HEO cathodes often rely on topotactic Li extraction and insertion rather than deep conversion, a new design logic is needed. When connected Li-rich percolation routes are maintained, multication disorder can be consistent with high capacity, as demonstrated by high-entropy or compositionally complex cation-disordered rocksalt cathodes [26]. If Li migration is blocked, voltage hysteresis is increased, or oxygen redox is destabilized, the same disorder that increases structural tolerance may turn detrimental. Thus, Li percolation, oxygen stability, electrolyte compatibility, and transition-metal redox selection must all be incorporated into HEO cathode design.

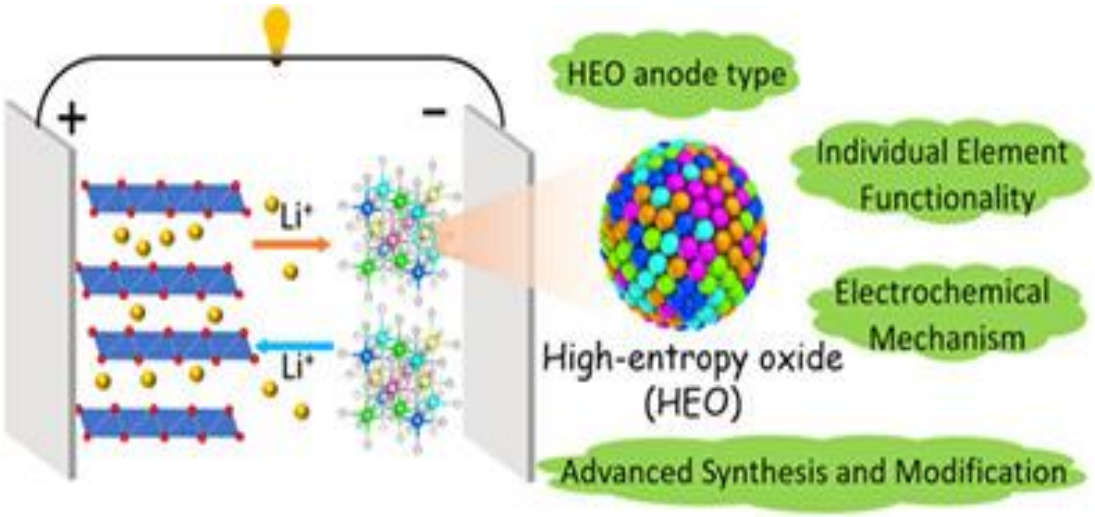

Figure 5. HEO Anode [60].

Reported disordered rocksalt cathodes demonstrate the potential of multication design; nevertheless, future research must focus more strongly on voltage fade, gas evolution, transition-metal dissolution, rate capability, energy density, and full-cell testing [59]. This is especially important because low first-cycle Coulombic efficiency remains a major barrier for conversion-type oxide anodes.

6.3 Sodium-Ion Battery Electrodes

Sodium-ion batteries provide a strong case for entropy-assisted structural stabilization because Na-ion insertion and extraction often produce larger structural rearrangements than Li-ion cycling. Layered sodium transition-metal oxides can undergo P2–O2, P2–P2′, O3–P3, and related stacking transitions, causing voltage steps, lattice strain, particle cracking, and capacity fading. The long-range structural coherence necessary for these transitions can be weakened and cycling stability enhanced by adding high-entropy disorder to the transition-metal layer. Because multication transition-metal slabs can reduce abrupt phase transitions and create smoother voltage profiles, P2-type sodium layered HEOs are especially significant [33, 37]. Only when Na-ion diffusion is maintained is this effect useful. While transition-metal migration into the sodium layer can impede transport and lower rate performance, disorder in the transition-metal layer may stabilize the framework. Another benefit noted for some high-entropy sodium layered oxides is air stability, where compositional complexity may lessen surface degradation caused by CO_2 and moisture [38]. Average voltage, redox dilution, air processing, electrolyte compatibility, and hard-carbon full-cell validation are still issues with sodium HEO cathodes, though. Future research should assess if high-entropy design enhances realistic sodium-ion full-cell performance, going beyond half-cell capacity retention.

6.4 Solid Electrolytes and Ionic Conductors

One of the most conceptually important advances in HEO energy storage is the realization that configurational disorder can improve ionic conductivity in some systems. High-entropy ionic conductors show that a disordered cation environment can broaden mobile-ion site-energy distributions and reduce deep trapping, contrary to the common assumption that disorder always impedes ion transport. Zeng and co-workers showed that a high-entropy mechanism can strongly enhance ionic conductivity by generating a more favorable distribution of local site energies for mobile ions [7]. This finding suggests that entropy can contribute not only to phase stability but also to transport-landscape engineering. The key requirement is that disorder must remain beneficial for transport. High ionic conductivity still requires sufficient mobile-ion concentration, connected migration pathways, and moderate migration barriers. A highly disordered lattice may still perform poorly if percolation is disrupted or if mobile ions are trapped by strongly binding local environments. For oxide-ion conductors, oxygen-vacancy concentration must therefore be balanced against vacancy ordering and vacancy trapping. For Li^+ and Na^+ conductors, the mobile-ion sublattice must remain connected and energetically accessible. Consequently, high-entropy solid electrolytes should be evaluated not only by conductivity, but also by bulk and grain-boundary conductivity, activation energy, transference number, electrochemical stability window, density, and electrode compatibility.

6.5 Supercapacitors and Pseudocapacitive Storage

HEOs have also been studied as pseudocapacitive electrode materials because multication oxides can provide multiple surface or near-surface redox interactions within a single framework. Spinel and nanostructured HEOs are especially relevant because transition-metal cations can participate in reversible Faradaic reactions while the oxide framework provides structural stability during cycling [61]. Promising capacitance and cycling behaviour in HEO supercapacitor electrodes are often attributed to the presence of several redox-active cations, oxygen vacancies, improved electrolyte access, and large surface area [28]. The main challenge is to separate morphology-related effects from entropy-related effects. Hollow structures, porous particles, nanofibers, and nanosheets can all enhance capacitance even in low-entropy oxides. HEO supercapacitor studies should therefore include morphology-matched controls rather than relying only on high gravimetric capacitance. Mass loading, areal capacitance, potential window, electrolyte type, rate capability, energy density, power density, Coulombic efficiency, and long-term cycling retention are all needed for a robust assessment. The key question is whether performance is dominated by one or two active species favored by morphology, or whether multiple cations genuinely contribute to redox storage.

6.6 Design Rules for Energy-Storage HEOs

Several design rules emerge for energy-storage HEOs. In conversion-type lithium-ion anodes, compositions should balance redox-active cations that provide capacity with stabilizing cations that suppress structural damage. In lithium-ion cathodes, disorder should be introduced only when Li percolation and oxygen-redox stability are maintained. In sodium-ion cathodes, transition-metal-layer disorder should suppress harmful phase transitions while preserving Na diffusion. For solid electrolytes, the goal is not disorder for its own sake, but a connected and energetically favorable mobile-ion landscape. For supercapacitors, multication redox must be paired with stable cycling, high conductivity, and accessible surface area. More broadly, HEOs are not automatically superior to simpler oxides. Their advantage appears when compositional complexity resolves a specific energy-storage bottleneck such as conversion instability, phase-transition damage, mobile-ion trapping, or limited redox-site diversity. If the limiting factor is poor conductivity, low tap density, voltage hysteresis, electrolyte instability, or excessive critical-metal content, high entropy alone will not solve it. Future studies should therefore connect each reported performance improvement to a specific structure–defect–function mechanism and support it with appropriate controls. Table 3 summarizes the energy-storage applications of HEOs, their design logic, advantages, and benchmarking requirements.

7. High-Entropy Oxides for Electrocatalysis

7.1 Electrocatalytic Relevance of High-Entropy Oxide Surfaces

High-entropy oxides are attractive electrocatalysts because catalytic reactions occur at surfaces where local atomic arrangement, metal–oxygen bonding, oxidation state, oxygen-vacancy concentration, and adsorbate binding energy determine activity. In binary or ternary oxides, the number of chemically distinct surface environments is limited. In HEOs, the surface can contain a statistical distribution of cation ensembles, each with different metal–oxygen covalency, redox flexibility, and binding strength toward intermediates such as OH*, O*, OOH*, H*, and oxygenated ORR species. This local diversity does not guarantee high catalytic activity, but it can increase the likelihood of generating near-optimal active sites. The active site must also resist passivation or dissolution, remain electronically connected, stay structurally stable, and be accessible to the electrolyte. A three-level structural model is therefore useful for interpreting HEO electrocatalysis. The first level is the bulk composition, which determines the accessible cation reservoir, lattice distortion, oxygen-vacancy propensity, and redox flexibility. The second level is the pre-reaction surface, which includes exposed facets, defect density, hydroxylation, segregation, and local cation enrichment. The third level is the operating surface, which may differ substantially from the pristine oxide because many transition-metal oxides reconstruct during electrochemical operation. This distinction is especially important for OER, where the active phase may not be the as-synthesized HEO bulk but an oxyhydroxide-like or highly oxidized surface layer. For this reason, HEO electrocatalysis should not be treated as a simple composition–activity relationship.

Table 3. Energy-storage applications: design logic, advantages, and benchmarking requirements.

Application	Relevant HEO structure	Design logic	Reported advantage	Minimum benchmarking requirement	Refs.
LIB anodes	Rocksalt and spinel HEOs	Balance redox-active cations with stabilizing cations to buffer conversion reactions and distribute strain	High reversible capacity and improved cycling stability relative to selected binary oxides	First-cycle Coulombic efficiency; areal capacity; electrode density; post-cycling structure; full-cell validation where possible	[4,25, 55, 58, 60]
LIB cathodes	Disordered rocksalt and layered HEOs	Use transition-metal disorder while preserving Li-rich percolation pathways and limiting oxygen loss	High capacity and broadened composition space for cation-disordered cathodes	Voltage hysteresis; energy density; gas evolution/oxygen stability; transition-metal dissolution; full-cell testing	[26, 59]
SIB cathodes	P2/O3 layered HEOs	Use TM-layer disorder to suppress cooperative P2-O2/O3 phase transitions and improve air stability	Smoother voltage profiles, improved structural reversibility, and better air tolerance in selected systems	Hard-carbon full cells; air-exposure protocol; phase evolution; rate performance; Na inventory control	[33,37,38,62]
Solid electrolytes and ionic conductors	Rocksalt, fluorite, and related oxide frameworks	Broaden mobile-ion site-energy distributions without creating deep traps or blocking percolation	Enhanced ionic conductivity in selected high-entropy lithium conductors	Bulk/grain-boundary separation; activation energy; transference number; density; interfacial stability	[6,7,36]
Supercapacitors	Spinel, perovskite, and nanostructured HEOs	Use multiple redox-active cations and oxygen vacancies for pseudocapacitive surface/near-surface redox	Moderate-to-high capacitance and cycling stability in nanostructured electrodes	Mass loading; areal capacitance; voltage window; ECSA/BET; rate capability; long cycling; morphology-matched controls	[28,61,63]

It is better understood as a dynamic bulk–surface–reaction system in which the parent HEO serves as a structural stabilizer, active precursor, and defect reservoir.

7.2 Oxygen Evolution Reaction as the Central HEO Electrocatalysis Platform

The oxygen evolution reaction is the most developed and best-established area of HEO electrocatalysis. The efficiency of alkaline water

electrolysis, rechargeable metal–air batteries, regenerative fuel cells, and several other coupled electrochemical conversion devices is often limited by OER. Because the reaction involves multiple proton-coupled electron-transfer steps and O–O bond formation through adsorbed oxygen intermediates, its kinetics are inherently demanding. In conventional transition-metal oxides, scaling relationships between OH*, O*, and OOH* adsorption energies often limit activity. HEOs offer a possible route around part of this limitation by generating a distribution of local binding environments rather than a single average surface site. Some surface ensembles may approach the optimal adsorption window, whereas others may bind oxygen intermediates too weakly or too strongly.

Spinel and perovskite HEOs are especially useful for OER because their transition-metal sublattices can accommodate mixed valence, oxygen vacancies, and redox-active octahedral sites. With reported overpotentials in the approximate range of 260–310 mV at 10 mA cm^{-2} under specific laboratory settings, multication spinel oxides including Fe, Co, Ni, Cr, and Mn have demonstrated promising alkaline OER activity [8, 20]. Because OER performance is highly dependent on catalyst loading, electrolyte concentration, substrate, iR correction, pre-activation, surface roughness, and current normalization, these values should be evaluated with caution. Therefore, HEO OER investigations have scientific value not only in revealing low overpotential but also in elucidating how multication chemistry governs the creation, activity, and durability of the working surface.

A central mechanistic issue is that many HEOs act as precatalysts rather than as unchanged bulk catalysts. Under anodic OER conditions, Ni-, Fe-, and Co-containing oxides may reconstruct into NiOOH-, FeOOH-, CoOOH-, or mixed oxyhydroxide-like layers. High-entropy spinel studies suggest that surface evolution and reconstruction can contribute to water-oxidation activity, and Han and co-workers showed that amorphous high-entropy electrocatalysts can promote self-reconstruction into β-NiOOH during OER [54, 64]. This does not diminish the importance of the parent HEO. Instead, it changes the design logic: under operating conditions, the parent oxide should be engineered to generate a stable and catalytically active reconstructed surface.

Within this precatalyst framework, each cation should be assigned a functional role rather than being treated as part of a generic "cocktail effect." Because NiFe oxyhydroxide-like surfaces are among the most active non-noble phases for alkaline OER, Ni and Fe often provide the most active OER sites. Mn can tune defect chemistry and oxygen exchange, while Co can improve conductivity and redox flexibility. Cr and other relatively stable cations may improve durability by suppressing dissolution, limiting uncontrolled reconstruction, or stabilizing the residual framework. The optimal HEO OER catalyst is therefore not the one with the largest number of elements, but the one that provides the best balance among active-site generation, electronic transport, defect management, and surface stability. Future OER studies should follow a clear evidence hierarchy. Low overpotential alone is not sufficient. Tafel slope, electrochemically active surface area or roughness factor, iR-corrected activity, catalyst loading, Faradaic efficiency, long-term chronopotentiometry, accelerated degradation testing, and post-OER or operando surface analysis are all needed for strong mechanistic support. Operando XAS, in situ Raman spectroscopy, dissolution analysis, and post-test XPS/TEM should be used to determine which cations oxidize, which dissolve, which enrich at the surface, and whether the active layer remains structurally stable. Without such evidence, OER activity may be incorrectly attributed to the pristine HEO rather than to the reconstructed surface.

7.3 ORR, HER, and Bifunctional Catalysis: Promising but Less Mature Directions

ORR activity in HEOs is less mature and less well defined mechanistically than OER activity. Because multication surfaces can tune oxygen adsorption, mixed-valence redox, oxygen vacancies, and metal–oxygen covalency, HEOs are attractive candidates for ORR. Under suitable support and electrolyte conditions, HEOs can function as non-precious oxygen-reduction catalysts, as shown by the sustained alkaline ORR performance of carbon-supported HEO nanoparticles [65]. Even so, HEOs should not yet be presented as direct substitutes for Pt-based catalysts in demanding ORR applications. Polarization curves, Tafel slopes, and Koutecky–Levich analysis are often used to infer ORR activity, but direct evidence for peroxide yield, four-electron selectivity, and adsorption intermediates is still limited. Strong ORR claims should therefore include rotating ring-disk electrode analysis, electron-transfer number, peroxide yield, half-wave potential, onset potential, mass activity, durability, and comparison with Pt/C or relevant non-noble benchmarks under identical testing conditions.

Another promising opportunity for HEOs is HER. Because transition-metal oxides generally exhibit weak hydrogen adsorption and limited conductivity, they are not usually the best HER catalysts. HEOs can nevertheless improve HER performance when they stabilize low-loading noble-metal species, provide defect-rich surfaces, or promote alkaline water dissociation. For example, Pt-modified high-entropy rare-earth oxides show how a multication oxide matrix can influence the coordination and stability of noble-metal active sites [66]. High-entropy double perovskites and noble-metal-free HEOs have also been explored for alkaline HER, where oxygen vacancies, mixed-valence transition metals, and reconstructed surface states may support hydrogen adsorption and the Volmer step [67]. However, HER data must be interpreted carefully because oxide surfaces may be partially reduced during operation. The active phase may be a reduced oxide, a metal/oxide interface, or a reconstructed hydroxylated layer rather than the pristine HEO. Overpotential, Tafel slope, exchange current density, electrochemical surface area, Faradaic efficiency, and long-term stability should therefore be accompanied by post-HER and operando characterization.

Because ORR and OER require distinct but related surface environments, bifunctional oxygen catalysis is a natural extension of HEO design. The air electrode in rechargeable Zn–air batteries must support OER during charging and ORR during discharge. Recent studies show that multilevel disorder engineering can improve Zn–air battery performance, and HEO-derived catalysts have therefore been explored as bifunctional ORR/OER electrodes [57, 68]. A single universal active site is unlikely to explain the benefit.

More likely, the multicomponent framework enhances structural tolerance during repeated oxidation and reduction, whereas distinct local cation ensembles support distinct oxygen-reaction pathways. HEOs can function as OER catalysts, HER catalysts, or stabilizing supports in paired catalytic systems for total water splitting [69]. However, low two-electrode voltage at 10 mA cm^{-2} should not be the sole basis for device-level claims. Electrode loading, electrolyte concentration, separator or membrane condition, gas-management specifics, operation at greater current density, Faradaic efficiency, and long-term stability should all be included.

7.4 Descriptor Distributions and Active-Site Design

The limitations of traditional single-value descriptors are especially clear in HEO electrocatalysis. Descriptors such as e_g occupancy, metal–oxygen covalency, oxygen p-band center, d-band center, and adsorption free energies help explain activity in simpler oxides. However, HEO surfaces contain many local cation configurations, oxidation states, and defect environments. The minority ensemble that actually controls catalytic turnover may be obscured by an averaged description. For example, a surface containing Ni–Fe, Co–Mn, Fe–Cr, and defect-adjacent sites with distinct adsorption energetics cannot be represented adequately by an average e_g occupancy or d-band center. Descriptor distributions are therefore more useful than descriptor averages for HEO catalysis. The aim is not to maximize uncontrolled surface diversity, but to increase the population of near-optimal active ensembles while suppressing sites that bind intermediates too strongly, too weakly, or degrade rapidly. DFT studies and descriptor-based analyses suggest that broad adsorption-energy distributions can raise the probability of generating active sites for oxygen electrocatalysis [64, 70, 71]. Excessive disorder, however, can also create sites that are inactive, insulating, unstable, or prone to degradation. Rational HEO catalyst design should therefore include statistical surface sampling, adsorption-energy distributions, oxygen-vacancy formation energies, surface-reconstruction pathways, and operando validation. This shifts the field toward predictive active-site design rather than vague "synergistic" or "cocktail" explanations.

7.5 Stability, Reconstruction, and Benchmarking Requirements

Catalyst stability is as important as initial activity. Although configurational disorder may suppress phase segregation, HEOs cannot be assumed to be electrochemically stable without direct verification under operating conditions. During OER, ORR, or HER, a material that is stable after synthesis may still dissolve, reconstruct, segregate, passivate, or be reduced. In alkaline OER, high-valence metal states and oxyhydroxide layers may form, and less stable cations may leach out. Under HER conditions, oxide surfaces may be reduced to metal/oxide interfaces.

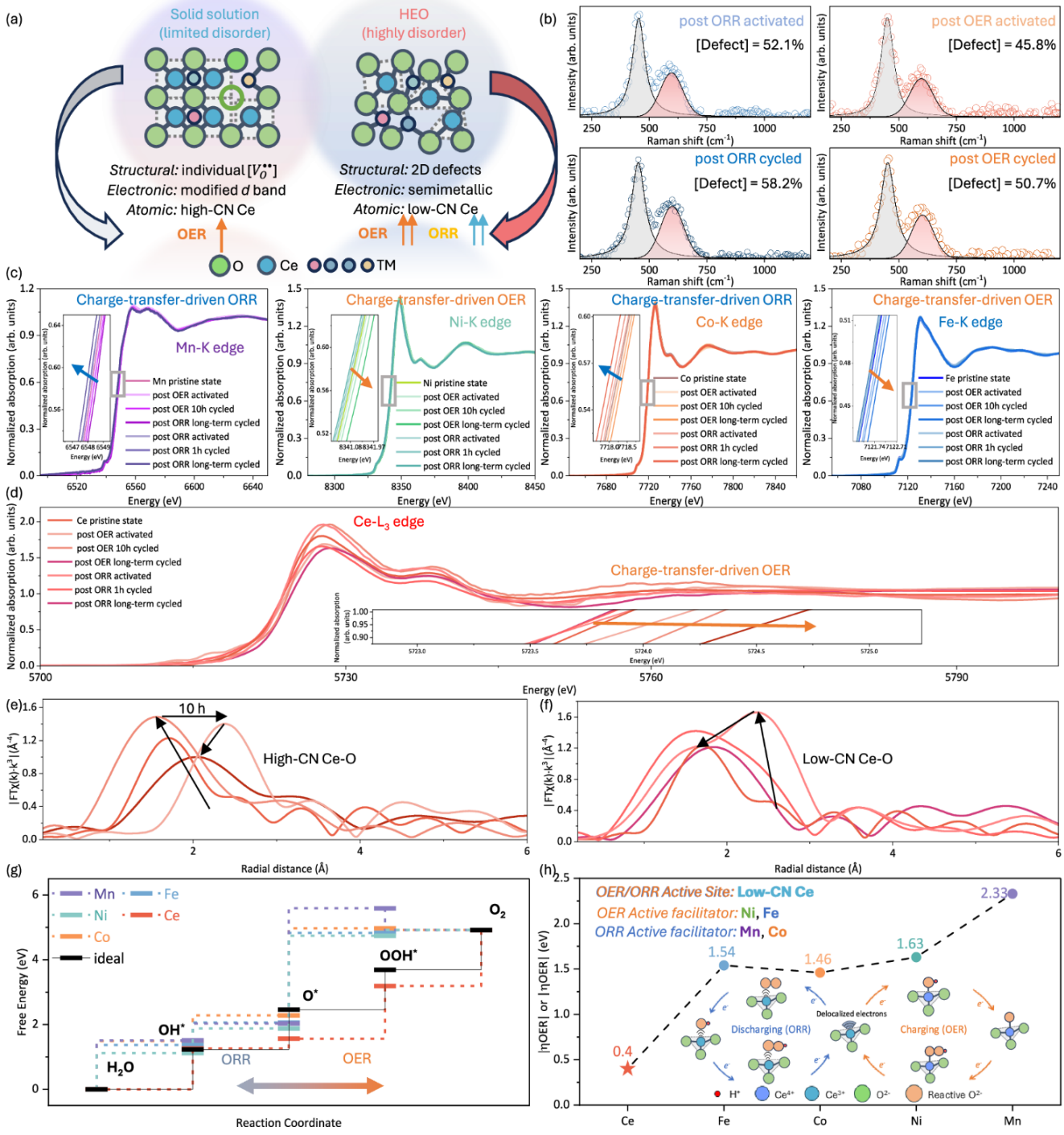

Figure 6. Active-site characterization and mechanism analysis of multilevel-disordered HEOs in OER/ORR processes [72]. Ex situ OER and ORR at different time scales: a schematic of the effect of multilevel disorder engineering; b laser Raman microspectra; c normalized Mn-K, Ni-K, Co-K, and Fe-K edge XANES spectra; d normalized Ce-L3-edge XANES spectra; e OER Fourier transform of K3-weighted Ce L3-edge EXAFS spectra; f ORR Fourier transform of K3-weighted Ce L3-edge EXAFS spectra; g calculated ORR/OER free-energy diagrams; h calculated ORR/OER overpotentials for each element.

Peroxide species, oxygenated intermediates, and repeated potential switching can gradually alter the surface during ORR and Zn–air cycling. Stability should therefore be designed through cation selection and verified experimentally rather than assumed from entropy. Figure 6 illustrates active-site characterization and mechanism analysis in a multilevel-disordered HEO during OER/ORR operation.

The revised design principle is clear: HEO electrocatalysts should be evaluated as operating-state materials. The pristine phase, activated surface, and post-reaction structure should be distinguished.

Table 4. Electrocatalytic applications: active-state mechanism and opportunity.

Reaction/application	Common HEO platform	Likely active state	Main opportunity	Validation needs	Reference
OER	Spinel, perovskite, rocksalt-derived and amorphous HEOs	Often reconstructed oxyhydroxide-like surface rather than pristine bulk oxide	Non-noble or low-noble catalysts with tunable Ni/Fe/Co/Mn/Cr roles and improved durability	Overpotential and Tafel slope with iR correction; ECSA/roughness; Faradaic efficiency; operando/post-OER XAS/Raman/XPS; dissolution analysis	[8,20,54,64,71-73]
ORR	Spinel, perovskite, fluorite-derived and carbon-supported HEO nanoparticles	Mixed-valence oxide surface with oxygen vacancies and support-dependent conductivity	Pt-free alkaline ORR and bifunctional oxygen electrodes	RRDE-derived electron-transfer number and peroxide yield; half-wave/onset potentials; durability; Pt/C benchmark under identical conditions	[57,65]
HER	Defect-rich perovskite/spinel HEOs and noble-metal-modified HEOs	Reduced/reconstructed oxide surface or stabilized noble-metal single atoms/clusters	Lower noble-metal loading and improved alkaline water-dissociation kinetics	Overpotential; Tafel slope; exchange current density; Faradaic efficiency; post-HER phase/valence analysis; Pt/C comparison	[66,67,69]
OER/ORR bifunctional catalysis	Spinel, rocksalt, perovskite, and multilevel-disordered HEOs	Different local sites or reconstructed layers support oxygen evolution and reduction	Rechargeable Zn-air batteries and regenerative oxygen electrodes	Delta E between ORR/OER metrics; charge-discharge cycling; round-trip efficiency; air-cathode architecture; post-cycling surface analysis	[57,68]
Overall water splitting	HEO/HEO, HEO/HEA, or noble-metal-modified HEO catalyst pairs	Coupled OER-active and HER-active reconstructed surfaces/interfaces	Low-noble or non-noble full-cell water-splitting systems	Cell voltage at 10/100/500 mA cm-2; long-term stability; gas Faradaic efficiency; electrode loading; industrial-current durability	[66,67,69,72,74]

For OER, stability assessment should include constant-current operation, accelerated degradation cycles, metal-dissolution analysis, Faradaic efficiency, and post-test surface characterization. For ORR, half-wave potential retention, peroxide yield, electron-transfer number, and cycling stability are required. For HER, overpotential retention, Tafel-slope evolution, hydrogen Faradaic efficiency, and post-HER structural analysis are essential. Both half-cell measurements and full-device testing should be reported for bifunctional Zn–air or water-splitting systems. The primary electrocatalytic uses of HEOs, along with their active-state processes, prospects, and validation requirements, are compiled in Table 4.

7.6 Design Rules for HEO Electrocatalysts

The electrocatalysis literature suggests several design guidelines. First, the cation set must be defined by the target reaction. In OER compositions, cations

that generate stable oxyhydroxide-like active surfaces should be prioritized, especially in Ni–Fe-rich systems. Stabilizing cations that suppress dissolution or uncontrolled reconstruction should also be included. In ORR formulations, oxygen adsorption, electronic conductivity, peroxide suppression, and alkaline durability should be optimized. In HER formulations, water dissociation, hydrogen adsorption, and resistance to reduction-induced degradation must all be considered. Second, the active surface should be designed deliberately. A HEO that appears stable in its pristine state but forms an inactive surface may be less useful than one that reconstructs into a controlled and stable working layer. Third, descriptor distributions should be optimized rather than relying only on average descriptors. Fourth, oxygen vacancies and mixed valence should be managed rather than maximized, because excessive defect concentrations can accelerate dissolution, vacancy trapping, or parasitic reactions. Finally, morphology-matched, loading-matched, and protocol-matched controls are essential for all activity claims. Only then can the intrinsic contribution of high-entropy chemistry be separated from effects due to surface area, nanostructure, electrode preparation, or testing artifacts.

8. Data-Driven Design and Computational Screening

8.1 Why Data-Driven Methods Matter for HEO Discovery

High-entropy oxides occupy a design space that is too large for conventional trial-and-error synthesis alone. Even with a limited set of transition-metal, rare-earth, alkali, alkaline-earth, and high-valence cations, thousands of equimolar and non-equimolar compositions are possible. Multi-sublattice structures, oxygen non-stoichiometry, mixed valence, synthesis atmosphere, calcination temperature, cooling rate, and defect concentration add further complexity. Data-driven approaches are useful not because they replace crystal chemistry, but because they help narrow the search space and prioritize compositions that are more likely to form the desired phase and deliver the required electrochemical function. In HEOs, computation has four particularly important roles. The first is phase prediction, which estimates whether a candidate composition will form a single-phase or predominantly single-phase oxide. The second is prediction of local structure and defect chemistry, including defect mobility, oxygen-vacancy formation, short-range ordering, and cation site preference. The third is descriptor mapping for ion-percolation pathways, redox voltage, oxygen-vacancy energetics, adsorption-energy distributions, and surface-reconstruction tendencies. The fourth is closed-loop experimental prioritization, in which active learning selects the next most informative composition on the basis of uncertainty and expected improvement. These roles are more useful to HEO research than broad claims about artificial intelligence or high-dimensional materials discovery. The main limitation is that HEO properties are rarely determined by nominal composition alone. Phase formation depends on synthesis route and thermal history, battery performance depends on electrode formulation and cycling protocol, and electrocatalytic activity depends on catalyst loading, surface area, iR correction, electrolyte, pre-activation, and operating-surface reconstruction. Data-driven HEO design must therefore integrate composition, structure, synthesis, defect chemistry, morphology, and performance metadata. A model trained only on chemical formulae may help with initial screening, but it is unlikely to produce reliable structure–performance predictions.

8.2 Phase Prediction and Formability Screening

The first task for computation-guided HEO design is to predict formability. A candidate composition must form the intended oxide framework before its electrochemical performance can be meaningfully optimized. Phase prediction is difficult because many HEOs lie close to the boundary between a disordered single phase and a multiphase mixture. Small changes in oxygen partial pressure, precursor chemistry, calcination temperature, dwell time, and cooling rate can shift the final product from a nominally single-phase oxide to a partially segregated material. CALPHAD, DFT-based thermodynamic analysis, cluster expansion, empirical descriptors, and machine-learning classification can each contribute to phase screening. Although CALPHAD is helpful in estimating phase stability from thermodynamic descriptions of lower-order systems, its accuracy is still limited for many multicomponent transition-metal oxides due to incomplete representations of mixed valence, oxygen non-stoichiometry, cation disorder, and defect formation in the databases that are currently available [13]. Although they are helpful early filters, empirical descriptors like ionic-radius variance, electronegativity difference, valence compatibility, tolerance factor, octahedral factor, and binary oxide structure

preference shouldn't be regarded as definitive evidence of phase stability. For instance, while spinel HEOs involve consideration of cation inversion and site preference, perovskite HEOs require simultaneous management of A-site and B-site chemistry, tolerance factor, charge balance, and oxygen vacancy production.

Large composition spaces can be screened by machine-learning phase classifiers trained on experimentally labeled phase outcomes and composition-derived features [75, 76]. Their main advantage is the ability to rapidly prioritize compositions that are more likely to yield layered HEOs, rocksalt, spinel, perovskite, fluorite, or pyrochlore structures. However, their reliability depends strongly on the quality of the phase labels. A composition classified as "single phase" on the basis of laboratory XRD alone may still contain amorphous secondary regions, short-range ordering, or nanoscale cation segregation. Likewise, a "failed" composition may have failed because of inappropriate synthesis conditions rather than intrinsic thermodynamic instability. Future formability models should therefore include not only composition, but also synthesis route, calcination temperature, atmosphere, dwell time, cooling rate, characterization technique, and phase-assignment confidence level.

8.3 Vacancy, Adsorption-Energy, and Transport Descriptor Distributions

Local environments, rather than average composition alone, often govern HEO functionality. Atomistic computation is especially valuable in this context. DFT, DFT+U, special quasi-random structures, cluster expansion, Monte Carlo sampling, and machine-learning interatomic potentials can be used to estimate how different cation configurations affect oxygen-vacancy formation energy, local lattice relaxation, electronic structure, ion-migration barriers, and catalytic adsorption energies [51, 52, 77, 78]. These calculations are essential because a true HEO does not contain a single type of oxygen vacancy, active site, or migration barrier. Instead, it must be described in terms of local-environment distributions. For oxygen-vacancy design, the average vacancy formation energy is not the only relevant descriptor. A HEO may display a broad range of vacancy energies because each vacancy is surrounded by a different combination of cations with distinct valence flexibility, ionic radius, and metal–oxygen bond strength. A lower mean vacancy formation energy may improve reducibility or catalytic activity, whereas an excessively broad distribution may create deep vacancy traps that reduce ion mobility. In ionic conductors, effective disorder requires more than a high vacancy concentration; it also requires connected and energetically accessible migration pathways. In battery electrodes, defect formation should enhance transport or redox kinetics without destabilizing the host framework. For electrocatalysis, adsorption-energy distributions are more informative than single averaged descriptors. Conventional quantities such as the d-band center, oxygen p-band center, e_g occupancy, metal–oxygen covalency, and the adsorption energies of OH*, O*, OOH*, or H* are useful in simpler oxides, but a single average value may obscure the minority surface configurations that control catalytic turnover in HEOs. HEO catalyst modeling should therefore assess adsorption-energy distributions across many possible local surfaces. The goal is not maximal disorder, but a distribution that increases the number of near-optimal active sites while suppressing inactive, unstable, or overbinding environments. This is especially important for OER, where the operating surface may reconstruct into oxyhydroxide-like phases and differ substantially from the pristine HEO surface.

8.4 Active Learning and Closed-Loop Optimization

One of the most useful data-driven approaches for HEO discovery is active learning. An active-learning model chooses the subsequent experiment based on expected information gain, uncertainty, and predicted performance rather than screening compositions at random. The model is updated and the new result is added to the dataset following each cycle of synthesis and characterization. Because the design space is wide, experimental synthesis can be slow, and performance depends on several coupled variables, this approach is well suited for HEOs [79]. For HEOs, active learning should be used to answer specific materials questions rather than to search blindly for the highest reported performance. In phase discovery, the model can identify compositions most likely to form a target spinel, rocksalt, perovskite, fluorite, or layered phase.

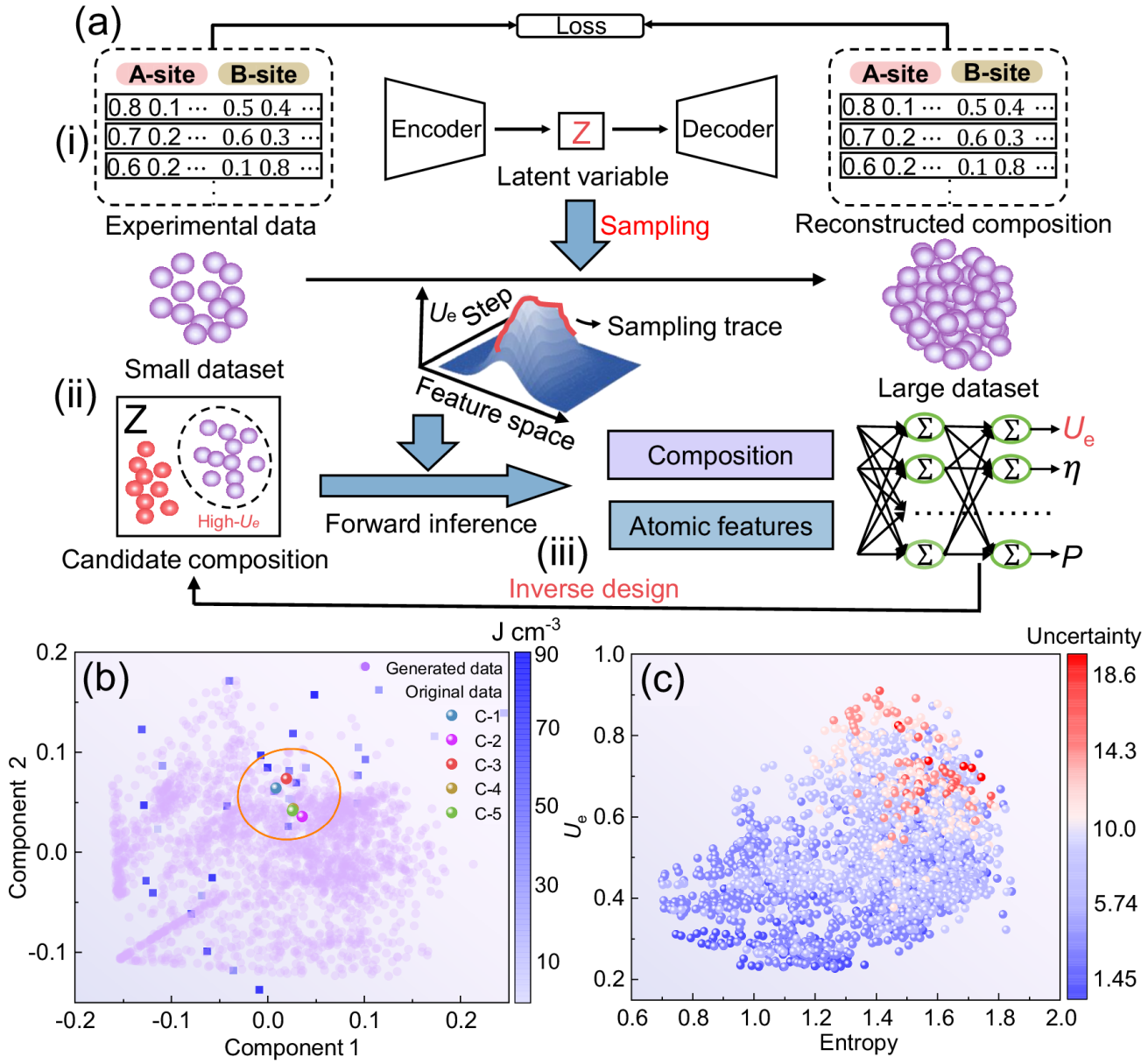

Figure 7. Overview of generative learning framework for high-entropy design [21]. **(a)** A generative learning model for the design and discovery of high-entropy dielectric materials. The framework is divided into three steps: i generation of the latent space z, ii classification and sampling of compositions, and iii forward inference and inverse design. **(b)** Latent-space distribution of the different components; purple circles represent the generated 2144 sets of high-performance data, blue squares represent the original experimental data, and solid spheres of different colours represent the five new sets of components predicted by the model. **(c)** Entropy versus normalized Ue of candidate materials, where the colour of each data point represents uncertainty.

In energy storage, it can prioritize compositions expected to preserve Li or Na percolation, reduce conversion-reaction degradation, suppress layered-phase transitions, or improve ionic conductivity. In electrocatalysis, it can identify compositions expected to generate favourable oxygen-vacancy populations, stable reconstructed OER surfaces, or balanced OER/ORR activity. In all cases, the active-learning loop should include experimental validation through phase analysis, local-structure characterization, and application-specific electrochemical testing. In high-entropy dielectric design, for example, expert-oriented trial-and-error has been combined with generative learning to identify suitable elements and compositions, as summarized in Figure 7.

Closed-loop platforms can improve HEO research by producing consistent and machine-readable data. Their value is not only faster synthesis, but better metadata control. A useful closed-loop workflow should record precursor identity, composition, pH or milling conditions, calcination profile, atmosphere, cooling rate, measured composition, phase fraction, surface area, electrode loading,

electrolyte, and testing protocol. However, full automation is not yet realistic for many HEO families because high-temperature synthesis, controlled oxygen partial pressure, long annealing, and local-structure characterization are difficult to automate completely. A more realistic near-term goal is semi-automated screening combined with human-guided crystal chemistry and targeted operando validation.

8.5 Metadata Quality, Negative Results, and Model Reliability

The main obstacle to reliable data-driven HEO design is not a lack of algorithms, but a lack of high-quality, standardized datasets. Many published studies report only successful compositions and high-performing examples, while failed syntheses, multiphase products, unstable samples, low-performing formulations, and unfavorable processing conditions are seldom documented. This creates strong survivorship bias. A model trained mostly on successful HEOs may overestimate phase formation and underestimate the importance of synthesis conditions. Negative results are scientifically valuable because they help define the boundaries between formable and non-formable compositions. Each entry in a phase-stability dataset should therefore include nominal composition, measured composition, entropy-bearing sublattice, configurational entropy, structure type, synthesis route, calcination temperature, dwell time, atmosphere, cooling rate, characterization method, and phase-purity confidence level. Energy-storage datasets should include active-material loading, electrode formulation, electrolyte, voltage window, current density, areal capacity, Coulombic efficiency, cycling protocol, and whether the test was performed in a half cell or a full cell. Electrocatalysis datasets should report catalyst loading, substrate, electrolyte concentration, reference-electrode calibration, iR correction, electrochemically active surface area or roughness factor, stability protocol, Faradaic efficiency, and post-test surface characterization. Without such metadata, models may learn laboratory-specific procedures rather than intrinsic HEO behaviour [80, 81].

Therefore, a conservative interpretation should be used in data-driven HEO design. Although composition-only models might be helpful for initial screening, they shouldn't be used to assert practical or mechanistic superiority. Both local and bulk structural information should be used to validate phase-prediction models. Metadata for testing and synthesis should be included in property models. Adsorption-energy distributions and surface reconstruction should be taken into consideration in catalyst models. Ion percolation, voltage hysteresis, interfacial compatibility, and cycling technique should all be included in battery models. The optimal computational workflows will incorporate uncertainty-aware learning, thermodynamic filters, local-structure sampling, crystal-chemical rules, and experimental feedback. Finding compositions and processing methods that result in a defined structure, regulated defect chemistry, and repeatable electrochemical function is the objective rather than producing the greatest number of candidate HEOs.

8.6 Design Rules for Computation-Guided HEO Discovery

Current data-driven HEO research suggests several design guidelines. First, regardless of projected activity or capacity, a composition that cannot reproducibly form the target structure is not a useful candidate; phase prediction should therefore precede property optimization. Second, models should treat HEOs as materials with distributions of local environments rather than as materials defined only by average composition. Ion-migration barriers, adsorption energies, and oxygen-vacancy formation energies should be represented as distributions whenever possible. Third, each model-selected composition must still be verified experimentally through synthesis, phase analysis, and function-specific testing, although active learning can reduce the experimental burden. Fourth, metadata quality should be considered part of the scientific result. Even high-performing measurements become poor training data when synthesis and benchmarking details are missing. Finally, computation should complement mechanism-driven design rather than replace it. The most useful HEO models will identify which cations, defect environments, and processing windows are most likely to solve a specific bottleneck in energy storage or electrocatalysis.

9. Challenges and Future Roadmap

9.1 From Composition Expansion to Evidence-Based Design

High-entropy oxide research has advanced rapidly, from the first demonstration of entropy-stabilized rocksalt oxides to a diverse range of multicomponent materials for batteries, solid electrolytes, supercapacitors, oxygen electrocatalysis,

hydrogen evolution, and metal-air systems. Numerous oxide frameworks, such as rocksalt, spinel, perovskite, fluorite, pyrochlore, layered, and mixed-anion structures, have been shown to be able to support substantial cation disorder. Nevertheless, the research has advanced to a point where finding additional multication compositions is no longer the main obstacle. Finding compositions that offer repeatable, mechanism-based, and practically significant advantages over lower-entropy or commonly doped oxides is the more crucial challenge.

A persistent weakness in the HEO literature is the tendency to link higher entropy directly to improved electrochemical performance without sufficient evidence separating entropy effects from other variables. Reported capacity, conductivity, overpotential, and cycling stability can all be strongly influenced by particle size, morphology, surface area, oxygen vacancies, mixed-valence states, synthesis route, electrode loading, electrolyte composition, and electrochemical protocol. Future HEO research should therefore move from composition-first reporting to evidence-based design. The critical question is not simply whether five or more elements can be mixed in one oxide, but whether a specific type of disorder solves a clearly defined electrochemical problem. This shift requires a stronger evidence hierarchy. A material should not be described as entropy-stabilized without direct thermodynamic evidence such as reversible phase formation, calorimetry, high-temperature diffraction, or validated thermodynamic modeling. Average X-ray diffraction alone is insufficient to demonstrate local chemical randomization or oxygen-vacancy distributions. Likewise, electrocatalytic activity should not be assigned to the pristine HEO bulk unless the operating surface has been identified under reaction conditions. Stronger studies should distinguish whether the observed performance is primarily due to testing conditions, entropy-assisted behavior, defect chemistry, morphology, or surface reconstruction.

9.2 Terminology, Phase Stability, and Reproducibility

A major drawback in the HEO literature is terminology. Although they may not describe the same degree of thermodynamic evidence, high-entropy oxides, entropy-stabilized oxides, and compositionally complex oxides are frequently used interchangeably. An entropy-stabilized oxide should require proof that configurational entropy directly stabilizes a single-phase structure, preferably through reversible temperature-dependent phase behaviour. At the very least, the computed configurational entropy and entropy-bearing sublattice should be expressed in a high-entropy oxide. When multicomponent chemistry is present but there is no precise entropy criterion or thermodynamic proof, the phrase "compositionally complex oxide" is more applicable [5]. This distinction is important because many electrochemical improvements may arise from conventional substitution chemistry, lattice strain, defect engineering, nanostructuring, or surface reconstruction rather than configurational entropy itself. A five-cation oxide with a single XRD pattern is not automatically entropy-stabilized. It may be kinetically retained, stabilized by favourable enthalpy, or locally segregated below the detection limit of laboratory diffraction. Future reports should therefore provide the nominal and measured composition, entropy-bearing sublattice, configurational entropy calculation, phase-purity evidence, and the experimental basis for any entropy-stabilization claim.

HEOs are frequently found near phase-separation boundaries, hence reproducibility is critical. Phase assemblage, oxygen stoichiometry, local cation distribution, particle size, and electrochemical reactivity can all be affected by slight variations in precursor identity, hydration state, milling condition, pH, calcination environment, dwell duration, heating rate, cooling rate, or post-treatment. The claimed performance difference between the HEO and the comparative material may occasionally be less than the synthesis variation. Therefore, complete synthesis information, such as precursor type and purity, mixing method, batch size, atmosphere, heat profile, post-treatment, measured composition, and phase-fraction evaluation, should be reported in future investigations. Reported HEO benefits cannot be consistently replicated or used to data-driven design without this knowledge.

9.3 Characterization, Benchmarking, and Mechanism Separation

The difference between average structure and functional structure is a significant unresolved problem. Local cation randomness, short-range ordering, oxygen-vacancy distribution, surface segregation, and operating-state stability cannot be demonstrated by laboratory XRD; yet, it is essential for determining the dominant crystal phase. While maintaining site-selective cation occupancy, local bond-length disorder, or nanoscale clustering, many HEOs may seem single-

phase by diffraction. Stronger characterization is necessary because local and surface conditions control electrochemical function. When the claim relies on local structure, oxygen vacancies, or surface reconstruction, procedures such as pair distribution function analysis, X-ray absorption spectroscopy, neutron diffraction, high-resolution STEM-EDS/EELS, atom probe tomography, Raman spectroscopy, EPR, and operando should be employed [36]. Additionally, benchmarking in the field is still uneven. Active-material loading, conductive carbon content, binder, electrolyte, voltage window, current density, cell format, and cycle number all affect battery capacity and retention. Particularly for conversion-type HEO anodes, half-cell testing against lithium or sodium metal sometimes overstates practical relevance. Density, activation energy, ionic transference number, electrochemical stability, and electrode compatibility should be included with conductivity for solid electrolytes, which must be divided into bulk and grain-boundary contributions. Without mass loading, areal capacitance, voltage window, scan rate, energy density, power density, and cycle stability, gravimetric capacitance is insufficient in supercapacitor research.

Even more stringent benchmarking is needed for electrocatalysis. OER, ORR, and HER metrics are strongly affected by catalyst loading, substrate, electrolyte concentration, reference-electrode calibration, iR correction, scan rate, pre-activation, roughness factor, and gas-evolution efficiency. Claims of superior HEO activity should therefore be supported by commercial or low-entropy reference catalysts tested under identical conditions. For OER, post-test and preferably operando characterization should determine whether the active surface is the pristine HEO, an oxyhydroxide-like layer, a dissolved/redeposited phase, or a reconstructed mixed surface. For ORR and bifunctional oxygen catalysis, rotating ring-disk measurements, peroxide yield, electron-transfer number, and full Zn–air cell data are needed. For HER, post-reaction analysis should determine whether the oxide surface remains intact or converts into reduced oxide or metal/oxide interfaces. The strongest future studies will use morphology-matched and loading-matched controls. A nanostructured HEO should not be compared with a bulk binary oxide if the objective is to prove an entropy effect. Similarly, a porous HEO catalyst should not be claimed as intrinsically superior unless surface area, particle size, electrode formulation, and testing protocol are controlled. This is essential for separating entropy-derived effects from morphology, defect concentration, and electrode architecture.

9.4 Data Quality and Computation-Guided Discovery

The HEO compositional space is too large for trial-and-error exploration alone, which makes computation and machine learning important tools. Their usefulness, however, depends entirely on data quality. Many current databases are biased toward successful syntheses and high-performing compositions because unsuccessful syntheses, multiphase products, and low-performing materials are rarely reported. This survivorship bias can cause models to overestimate phase formation and functional performance. Negative results should therefore be treated as essential scientific information because they define the limits of formability, phase stability, and property optimization. Future databases should include nominal and measured composition, structure type, synthesis route, calcination temperature, atmosphere, dwell time, cooling rate, characterization method, phase-purity confidence level, particle size, surface area, oxygen stoichiometry, valence-state data, electrode preparation, testing conditions, and performance metrics. Catalysis datasets should indicate whether the surface reconstructs during operation and should distinguish geometric current density from mass-normalized and surface-area-normalized activity. Battery datasets should include voltage window, current density, active loading, areal capacity, Coulombic efficiency, and cell configuration. Without such metadata, machine-learning algorithms may learn laboratory-specific procedural bias rather than intrinsic material behaviour [80, 81].

Distribution-based descriptors should replace average descriptors in computation-guided HEO design. The entire spectrum of local surface conditions in electrocatalysis cannot be represented by a single average d-band center, oxygen p-band center, or adsorption energy. Average disorder does not ensure mobile-ion percolation in ionic conductors. High configurational entropy in battery electrodes does not guarantee low voltage hysteresis or structural reversibility. Phase-stability prediction, local cation configuration sampling, oxygen-vacancy energetics, ion-percolation analysis, adsorption-energy distributions, and uncertainty-aware active learning should all be included in more practical models.

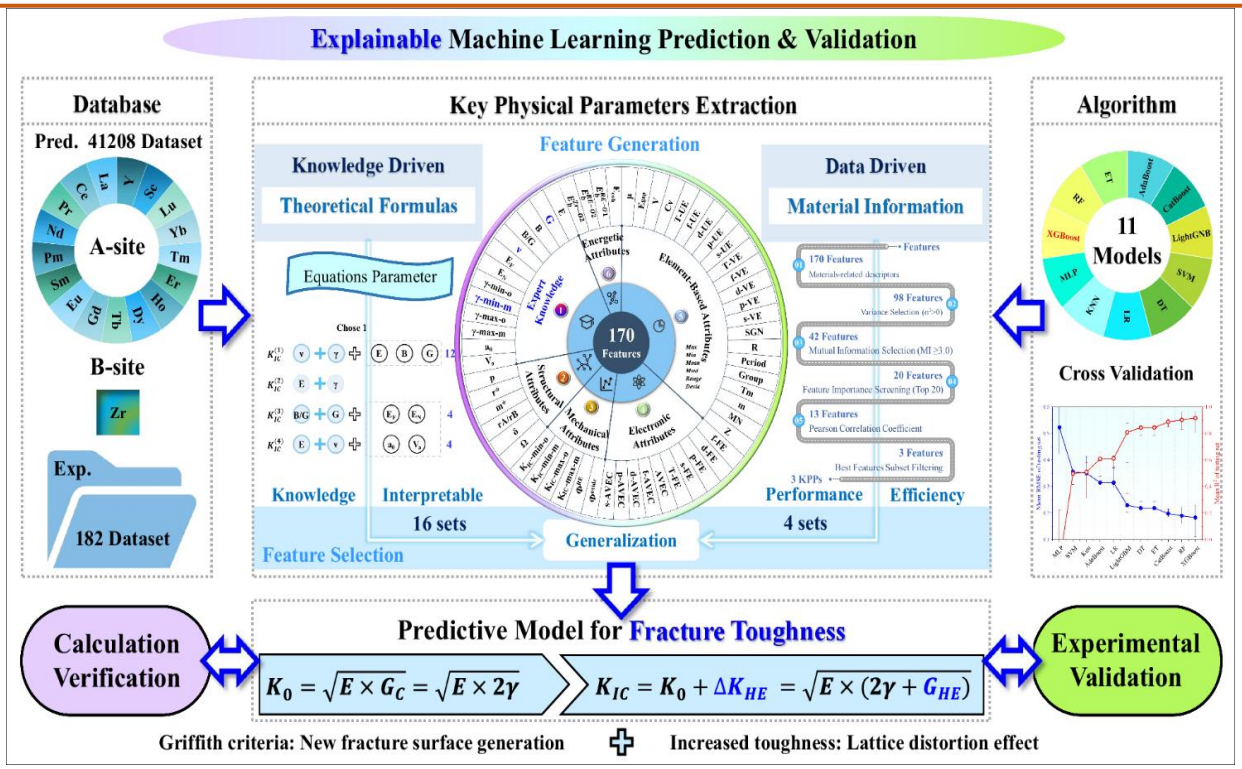

Figure 8. Hybrid domain knowledge-assisted data-driven ML for fracture toughness of HEOs [82].

The goal is to identify which composition, defect structure, and processing method can deliver a specific electrochemical function, rather than merely predicting whether a HEO can be synthesized. Figure 8 illustrates a predictive model for the fracture toughness of HEOs built from theoretical calculations, experiments, and hybrid domain-knowledge-assisted data-driven machine learning.

9.5 Scalability, Sustainability, and Device-Level Validation

Most HEO research is still performed at laboratory scale using high-purity precursors, small batch sizes, optimized thermal processing, and simplified electrochemical cells. Industrial translation must also consider cost, resource criticality, synthesis energy, batch-to-batch reproducibility, electrode fabrication, and long-term durability. In some electrocatalytic systems, HEOs may reduce reliance on Ir, Ru, or Pt, but this should be treated as a design opportunity rather than as a guaranteed economic benefit [74]. Some high-performing compositions still contain Co, Ni, rare-earth elements, or noble-metal additions, which may raise concerns about supply, cost, toxicity, or recycling. Future HEO design should therefore prioritize earth-abundant, low-criticality, and recyclable compositions whenever possible [62]. Scalable synthesis remains another unresolved challenge. Solid-state synthesis is straightforward and scalable, but it often produces coarse particles with low surface area. Sol-gel and Pechini methods improve cation mixing, but may also increase solvent use, organic waste, and batch variability. Flame spray pyrolysis, combustion synthesis, mechanochemical processing, rapid Joule heating, and photoflash methods offer promising routes to smaller particles or metastable compositions, yet their scalability, energy efficiency, compositional control, and reproducibility still need to be demonstrated. Future studies that claim practical significance should report phase purity, electrochemical performance, synthesis yield, processing temperature, batch size, precursor cost, energy demand, and compatibility with electrode fabrication. Device-level validation is essential before practical claims can be made. Battery electrodes should be tested in full cells with realistic mass loading, areal capacity, electrode density, limited electrolyte, and appropriate counter electrodes. For solid electrolytes, grain-boundary resistance, electrode compatibility, critical current density, and interfacial stability should all be evaluated. When practical performance is claimed, electrocatalysts should advance from three-electrode screening to two-electrode electrolyzers, membrane-electrode assemblies, rechargeable Zn–air batteries, or other relevant device configurations. A HEO that performs well in a half-cell, dense pellet, or glassy-carbon test may still fail under device-relevant conditions because of first-cycle loss, low tap density, electrolyte incompatibility, catalyst detachment, gas-management constraints, or surface degradation.

9.6 Roadmap for Function-Specific HEO Development

Function-specific disorder engineering should be the focal point of future HEO research. Controlling conversion-reaction reversibility, lowering first-cycle irreversible capacity, and stabilizing the metal/Li2O matrix during long-term cycling are the top priorities for lithium-ion anodes. Suppressing detrimental stacking transitions, enhancing air stability, and maintaining Na-ion diffusion should be the main goals for sodium-ion cathodes. The primary objective is to design mobile-ion energy landscapes for solid electrolytes that minimize deep trapping while preserving connected migration paths. Future research on supercapacitors should determine which cations truly take part in surface redox and whether capacitance enhancement persists once morphology is regulated.

Table 5. Research challenges and roadmap for high-entropy oxides.

Challenge	Why it limits the field	Near-term corrective action	Medium/long-term roadmap	Expected outcome	Refs.
Terminology and entropy claims	HEO, entropy-stabilized oxide, and compositionally complex oxide are often used interchangeably	Report entropy-bearing sublattice, Delta Sconf, measured composition, and evidence level	Reserve entropy-stabilized for systems with thermodynamic evidence such as reversible phase behaviour, calorimetry, or validated modeling	Cleaner claim structure and fewer overstatements	[3,5,12,13]
Local homogeneity and defect quantification	XRD alone cannot prove cation randomness, oxygen vacancy distribution, or short-range order	Combine XRD with STEM-EDS/EELS, PDF, XAS, neutron diffraction, XPS, EPR, or TGA as needed	Develop characterization packages matched to the specific claim: entropy stabilization, defect chemistry, or active surface	Stronger structure-defect-performance correlations	[18,22,32, 36,53]
Benchmarking and morphology effects	Performance may arise from surface area, particle size, porosity, loading, or electrode formulation rather than HEO chemistry	Use morphology-matched low-entropy controls and identical electrochemical protocols	Adopt community reporting standards for batteries, supercapacitors, electrolytes, OER, ORR, HER, and Zn-air cells	More reliable comparison across studies	[36,48,63, 80]
Surface reconstruction and durability	The operating catalyst may differ from the pristine HEO bulk, especially under OER/HER conditions	Use operando/in situ spectroscopy or post-test surface analysis; quantify dissolution where possible	Design HEOs as precatalysts that generate controlled, stable active surfaces	Mechanism-based catalyst design rather than composition-only screening	[54,57,64, 72,73]
Data quality and computational prediction	ML models are limited by small datasets, inconsistent labels, and missing negative results	Curate datasets with synthesis metadata, characterization confidence, and failed compositions	Integrate CALPHAD, DFT, cluster expansion, active learning, and closed-loop experimentation	More reliable phase/property prediction and inverse design	[13,75-81,83-85]
Scalability, cost, and device validation	Laboratory performance may not survive cost, criticality, manufacturability, or full-device constraints	Report precursor criticality, synthesis energy, batch reproducibility, loading, and practical device conditions	Prioritize earth-abundant compositions and validate in full cells, Zn-air batteries, electrolyzers, and solid-state configurations	Improved translation from laboratory materials to practical components	[62,69,74, 80-82, 86-88]

Designing HEO precursors that reconstruct into stable, conducting, active oxyhydroxide-like surfaces with low dissolution is the top priority for OER. Future research must determine the actual active phase and confirm reaction selectivity, durability, and device-level performance for ORR, HER, and bifunctional oxygen catalysis.

A realistic roadmap can be divided into short-, medium-, and long-term priorities. In the near term, the field should adopt morphology-matched reference materials, improve local and surface characterization, standardize terminology, and report complete synthesis information. Over the medium term, researchers should build controlled composition series to isolate cation roles, combine DFT, CALPHAD, machine learning, and operando validation, and develop curated datasets that include both successful and unsuccessful compositions. In the long term, scalable synthesis, sustainability analysis, and device-level testing should be used to evaluate HEOs. The most valuable HEOs are those that address a specific electrochemical bottleneck through the combination of selected cations, local disorder, defect chemistry, and operating-surface behavior, not simply those with the greatest number of elements. Table 5 summarizes the major challenges and corresponding roadmap priorities for future HEO development.

9. Conclusions

From the thermodynamic demonstration of entropy-stabilized rocksalt (MgCoNiCuZn)O, high-entropy oxides have evolved into a versatile design platform for batteries, solid electrolytes, supercapacitors, and electrocatalysts. Their value lies not simply in the number of elements, but in the ability of multication disorder to tune phase stability, local lattice distortion, oxygen-vacancy chemistry, mixed-valence redox, ion migration, and operating-surface reconstruction. When properly targeted, HEOs can address electrochemical limitations such as conversion-induced degradation in lithium-ion anodes, stacking transitions in layered sodium cathodes, site-energy trapping in solid electrolytes, and unstable reconstructed surfaces in oxygen electrocatalysis. High entropy should not, however, be treated as a universal explanation for performance. Particle size, surface area, morphology, oxygen vacancies, synthesis route, electrode formulation, electrolyte, and testing protocol can all strongly influence the observed response. A single-phase XRD pattern does not prove local homogeneity or operating-state stability, and a five-cation composition is not inherently entropy-stabilized. Future work should therefore prioritize function-specific disorder engineering over element-count maximization. Cations should be chosen for specific roles such as redox centers, structural stabilizers, vacancy formers, electronic modifiers, or reconstruction regulators. Because uncontrolled vacancies, segregation, or reconstruction can accelerate dissolution, side reactions, or conductivity loss, defect concentration must be optimized rather than maximized. The field should routinely report measured composition, entropy-bearing sublattice, computed configurational entropy, phase-verification method, local-structure evidence, electrochemical protocol, morphology-matched controls, and post-test characterization. With consistent terminology, rigorous reference curation, operando characterization, open datasets, scalable synthesis, and device-level validation, HEOs can progress from promising laboratory materials to reliable components for next-generation energy-storage and conversion technologies.

References

[1] D. Miracle, O. Senkov, A Critical Review of High Entropy Alloys and Related Concepts. Acta Materialia, 122, (2016) 448–511. https://doi.org/10.1016/j.actamat.2016.08.081

[2] C. Oses, C. Toher, S. Curtarolo, High-Entropy Ceramics. Nature Reviews Materials, 5(4), (2020)295–309. https://doi.org/10.1038/s41578-019-0170-8

[3] C.M. Rost, E. Sachet, T. Borman, A. Moballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, J. Maria, Entropy-Stabilized Oxides. Nature Communications, 6(1), (2015) 8485. https://doi.org/10.1038/ncomms9485

[4] A. Sarkar, L. Velasco, D. Wang, Q. Wang, G. Talasila, L. De Biasi, C. Kübel, T. Brezesinski, S.S. Bhattacharya, H. Hahn, B. Breitung, High Entropy Oxides for Reversible Energy Storage. Nature Communications, 9(1), (2018) 3400. https://doi.org/10.1038/s41467-018-05774-5

[5] M. Brahlek, M. Gazda, V. Keppens, A.R. Mazza, S.J. McCormack, A. Mielewczyk-Gryń, B. Musico, K. Page, C.M. Rost, S.B. Sinnott, C. Toher, T.Z. Ward, A. Yamamoto, What is in a Name: Defining High Entropy Oxides. APL Materials, 10(11), (2022). https://doi.org/10.1063/5.0122727

[6] B. Ouyang, Y. Zeng, The Rise of high-Entropy Battery Materials. Nature Communications, 15(1), (2024) 973. https://doi.org/10.1038/s41467-024-45309-9

[7] Y. Zeng, B. Ouyang, J. Liu, Y. Byeon, Z. Cai, L.J. Miara, Y. Wang, G. Ceder, High-Entropy Mechanism to Boost Ionic Conductivity. Science, 378(6626), (2022) 1320–1324. https://doi.org/10.1126/science.abq1346

[8] T.X. Nguyen, Y. Liao, C. Lin, Y. Su, J. Ting, Advanced High Entropy Perovskite Oxide Electrocatalyst for Oxygen Evolution Reaction. Advanced Functional Materials, 31(27), (2021). https://doi.org/10.1002/adfm.202101632

[9] A. Sarkar, Q. Wang, A. Schiele, M.R. Chellali, S.S. Bhattacharya, D. Wang, T. Brezesinski, H. Hahn, L. Velasco, B. Breitung, High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties. Advanced Materials, 31(26), (2019) e1806236. https://doi.org/10.1002/adma.201806236

[10] Y. Ma, Y. Ma, Q. Wang, S. Schweidler, M. Botros, T. Fu, H. Hahn, T. Brezesinski, B. Breitung, High-Entropy Energy Materials: challenges and New Opportunities. Energy & Environmental Science, 14(5), (2021) 2883–2905. https://doi.org/10.1039/d1ee00505g

[11] W. Bao, H. Shen, Y. Zhang, C. Qian, G. Zeng, K. Jing, D. Cui, J. Xia, H. Liu, C. Guo, F. Yu, K. Sun, J. Li, High-Entropy Oxides for Energy Storage and Conversion. Journal of Materials Chemistry A, 12(35), (2024) 23179–23201. https://doi.org/10.1039/d4ta04156a

[12] O.F. Dippo, K.S. Vecchio, A Universal Configurational Entropy Metric for High-Entropy Materials. Scripta Materialia, 201, (2021) 113974. https://doi.org/10.1016/j.scriptamat.2021.113974

[13] S.J. McCormack, A. Navrotsky, Thermodynamics of High Entropy Oxides. Acta Materialia, 202, (2020) 1–21. https://doi.org/10.1016/j.actamat.2020.10.043

[14] S.S. Aamlid, M. Oudah, J. Rottler, A.M. Hallas, Understanding the role of Entropy in High Entropy Oxides. Journal of the American Chemical Society, 145(11), (2023) 5991–6006. https://doi.org/10.1021/jacs.2c11608

[15] G.N. Kotsonis, S.S.I. Almishal, F.M.D.S. Vieira, V.H. Crespi, I. Dabo, C.M. Rost, J. Maria, High-Entropy Oxides: Harnessing Crystalline Disorder for Emergent Functionality. Journal of the American Ceramic Society, 106(10), (2023) 5587–5611. https://doi.org/10.1111/jace.19252

[16] N. Sharma, J. Link, I. Heinmaa, R. Stern, T. Chakrabarty, S. Marik, Spin Glass and Complex Magnetism in a High-Entropy Spinel Oxide with Five Cations at both Tetrahedral and Octahedral Sites. Applied Physics Letters, 126(5), (2025). https://doi.org/10.1063/5.0242505

[17] S. Sen, M. Palabathuni, K.M. Ryan, S. Singh, High Entropy Oxides: Mapping the Landscape from Fundamentals to Future Vistas. ACS Energy Letters, 9(8), (2024) 3694–3718. https://doi.org/10.1021/acsenergylett.4c01129

[18] H. Gao, N. Guo, Y. Gong, L. Bai, D. Wang, Q. Zheng, Sub-Angstrom-Scale Structural Variations in high-Entropy Oxides. Nanoscale, 15(48), (2023) 19469–19474. https://doi.org/10.1039/d3nr05176e

[19] S.S. Almishal, J.T. Sivak, G.N. Kotsonis, Y. Tan, M. Furst, D. Srikanth, V.H. Crespi, V. Gopalan, J.T. Heron, L. Chen, C.M. Rost, S.B. Sinnott, J. Maria, Untangling Individual Cation Roles in Rock Salt High-Entropy Oxides. Acta Materialia, 279, (2024) 120289. https://doi.org/10.1016/j.actamat.2024.120289

[20] J. Baek, M.D. Hossain, P. Mukherjee, J. Lee, K.T. Winther, J. Leem, Y. Jiang, W.C. Chueh, M. Bajdich, X. Zheng, Synergistic effects of Mixing and Strain in High Entropy Spinel Oxides for Oxygen Evolution Reaction. Nature Communications, 14(1), (2023) 5936. https://doi.org/10.1038/s41467-023-41359-7

[21] W. Li, Z. Shen, R. Liu, X. Chen, M. Guo, J. Guo, H. Hao, Y. Shen, H. Liu, L. Chen, C. Nan, Generative Learning Facilitated Discovery of High-Entropy Ceramic Dielectrics for Capacitive Energy Storage. Nature Communications, 15(1), (2024) 4940. https://doi.org/10.1038/s41467-024-49170-8

[22] M.R. Chellali, A. Sarkar, S.H. Nandam, S.S. Bhattacharya, B. Breitung, H. Hahn, L. Velasco, On the homogeneity of High Entropy Oxides: An Investigation at the Atomic Scale. Scripta Materialia, 166, (2019) 58–63.

https://doi.org/10.1016/j.scriptamat.2019.02.039

[23] S.S. Almishal, M. Furst, Y. Tan, J.T. Sivak, G. Bejger, J. Petruska, S.V.G. Ayyagari, D. Srikanth, N. Alem, C.M. Rost, S.B. Sinnott, Thermodynamics-Inspired High-Entropy Oxide Synthesis. Nature Communication, 16, (2025) 8211. https://doi.org/10.1038/s41467-025-63567-z

[24] H. Wu, Q. Lu, Y. Li, J. Wang, Y. Li, R. Jiang, J. Zhang, X. Zheng, X. Han, N. Zhao, J. Li, Y. Deng, W. Hu, Rapid Joule-Heating Synthesis for Manufacturing High-Entropy Oxides as Efficient Electrocatalysts. Nano Letters, 22(16), (2022) 6492–6500. https://doi.org/10.1021/acs.nanolett.2c01147

[25] Q. Li, D. Ning, D. Wong, K. An, Y. Tang, D. Zhou, G. Schuck, Z. Chen, N. Zhang, X. Liu, Improving the Oxygen Redox Reversibility of Li-rich Battery Cathode Materials via Coulombic Repulsive Interactions Strategy. Nature Communications, 13(1), (2022) 1123. https://doi.org/10.1038/s41467-022-28793-9

[26] Z. Lun, B. Ouyang, D. Kwon, Y. Ha, E.E. Foley, T. Huang, Z. Cai, H. Kim, M. Balasubramanian, Y. Sun, J. Huang, Y. Tian, H. Kim, B.D. McCloskey, W. Yang, R.J. Clément, H. Ji, G. Ceder, Cation-Disordered Rocksalt-Type High-Entropy Cathodes for Li-Ion Batteries. Nature Materials, 20(2), (2020) 214–221. https://doi.org/10.1038/s41563-020-00816-0

[27] G.H.J. Johnstone, M.U. González-Rivas, K.M. Taddei, R. Sutarto, G.A. Sawatzky, R.J. Green, M. Oudah, A.M. Hallas, Entropy Engineering and Tunable Magnetic Order in the spinel High-Entropy Oxide. Journal of the American Chemical Society, 144(45), (2022) 20590–20600. https://doi.org/10.1021/jacs.2c06768

[28] C. Triolo, M. Maisuradze, M. Li, Y. Liu, A. Ponti, G. Pagot, V. Di Noto, G. Aquilanti, N. Pinna, M. Giorgetti, S. Santangelo, Charge Storage Mechanism in Electrospun Spinel-Structured High-Entropy (MN0.2Fe0.2Co0.2Ni0.2ZN0.2)3O4 Oxide Nanofibers as Anode Material for Li-Ion Batteries. Small, 19(46), (2023) e2304585. https://doi.org/10.1002/smll.202304585

[29] H. Zheng, Y. Liu, Z. Ma, E. Debroye, J. Ye, L. Zhang, T. Liu, High-Entropy Perovskite Oxides as a Family of Electrocatalysts for Efficient and Selective Nitrogen Oxidation. ACS Nano, 18(27), (2024) 17642–17650. https://doi.org/10.1021/acsnano.4c02231

[30] Y. Yang, H. Bao, H. Ni, X. Ou, S. Wang, B. Lin, P. Feng, Y. Ling, A Novel Facile Strategy to Suppress Sr Segregation for High-Entropy Stabilized $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ cathode. Journal of Power Sources, 482, (2021) 228959. https://doi.org/10.1016/j.jpowsour.2020.228959

[31] A.J. Wright, Q. Wang, C. Hu, Y. Yeh, R. Chen, J. Luo, Single-Phase Duodenary High-Entropy Fluorite/Pyrochlore Oxides with an Order-Disorder Transition. Acta Materialia, 211, (2021) 116858. https://doi.org/10.1016/j.actamat.2021.116858

[32] B. Jiang, C.A. Bridges, R.R. Unocic, K.C. Pitike, V.R. Cooper, Y. Zhang, D. Lin, K. Page, Probing the Local Site Disorder and Distortion in Pyrochlore High-Entropy Oxides. Journal of the American Chemical Society, 143(11), (2020) 4193–4204. https://doi.org/10.1021/jacs.0c10739

[33] H. Wang, X. Gao, S. Zhang, Y. Mei, L. Ni, J. Gao, H. Liu, N. Hong, B. Zhang, F. Zhu, W. Deng, G. Zou, H. Hou, X. Cao, H. Chen, X. Ji, High-Entropy Na-Deficient layered oxides for Sodium-Ion batteries. ACS Nano, 17(13), (2023) 12530–12543. https://doi.org/10.1021/acsnano.3c02290

[34] J. Wang, Y. Cui, Q. Wang, K. Wang, X. Huang, D. Stenzel, A. Sarkar, R. Azmi, T. Bergfeldt, S.S. Bhattacharya, R. Kruk, H. Hahn, S. Schweidler, T. Brezesinski, B. Breitung, Lithium Containing Layered High Entropy Oxide Structures. Scientific Reports, 10(1), (2020) 18430. https://doi.org/10.1038/s41598-020-75134-1

[35] E.Y. Pikalova, E.G. Kalinina, N.S. Pikalova, E.A. Filonova, High-Entropy Materials in SOFC technology: Theoretical Foundations for their Creation, Features of synthesis, and Recent Achievements. Materials, 15(24), (2022) 8783. https://doi.org/10.3390/ma15248783

[36] J.P. Barber, W.J. Deary, A.N. Titus, G.R. Bejger, S.S.I. Almishal, C.M. Rost, Disorder by Design: Unveiling local structure and functional insights in high entropy oxides. Materials Horizons, 12(24), (2025) 10453–10477. https://doi.org/10.1039/d5mh01033k

[37] J. Wang, S.L. Dreyer, K. Wang, Z. Ding, T. Diemant, G. Karkera, Y. Ma, A. Sarkar, B. Zhou, M. V. Gorbunov, A. Omar, D. Mikhailova, V. Presser, M. Fichtner, H. Hahn, T. Brezesinski, B. Breitung, Q. Wang, P2-type Layered High-Entropy Oxides as sodium-ion Cathode Materials. Materials Futures, 1(3), (2022) 035104. https://doi.org/10.1088/2752-5724/ac8ab9

[38] J. Zhan, J. Huang, Z. Li, J. Yuan, S. Dou, H. Liu, C. Wu, Air-Stable High-Entropy Layered Oxide Cathode with Enhanced Cycling Stability for Sodium-Ion Batteries. Nano Letters, 24(32), (2024) 9793–9800. https://doi.org/10.1021/acs.nanolett.4c00968

[39] Z. Ding, J. Bian, S. Shuang, X. Liu, Y. Hu, C. Sun, Y. Yang, High Entropy Intermetallic–Oxide Core–Shell nanostructure as superb oxygen evolution reaction catalyst. Advanced Sustainable Systems, 4(5), (2020). https://doi.org/10.1002/adsu.201900105

[40] G. Wang, J. Qin, Y. Feng, B. Feng, S. Yang, Z. Wang, Y. Zhao, J. Wei, Sol–Gel Synthesis of Spherical Mesoporous High-Entropy oxides. ACS Applied Materials & Interfaces, 12(40), (2020) 45155–45164. https://doi.org/10.1021/acsami.0c11899

[41] X. Yang, H. Wang, Y. Song, K. Liu, T. Huang, X. Wang, C. Zhang, J. Li, Low-Temperature synthesis of a porous High-Entropy Transition-Metal oxide as an anode for High-Performance Lithium-Ion batteries. ACS Applied Materials & Interfaces, 14(23), (2022) 26873–26881. https://doi.org/10.1021/acsami.2c07576

[42] A. Khandelwal, G. Mathew, S. Bhattacharya, A. Colsmann, G.C. Marques, M. Botros, F. Strauss, J. Xing, J.S. Raju, A. Ponnusamy, J. Aghassi-Hagmann, T. Brezesinski, S. Schweidler, B. Breitung, Synthesis-Driven functionality in High-Entropy materials. Small, 21(44), (2025) e01703. https://doi.org/10.1002/smll.202501703

[43] A.H. Phakatkar, M.T. Saray, M.G. Rasul, L.V. Sorokina, T.G. Ritter, T. Shokuhfar, R. Shahbazian-Yassar, Ultrafast Synthesis of High Entropy Oxide Nanoparticles by flame Spray Pyrolysis. Langmuir, 37(30), (2021) 9059–9068. https://doi.org/10.1021/acs.langmuir.1c01105

[44] J. Baek, Y. Jiang, D. Ka, Y. Li, Y. Wang, S. Kim, A.W. Potter, Z. Zhuo, J. Guo, X. Zheng, Ultrafast Photoflash Synthesis of High-Entropy Oxide Nanoparticles. ACS Nano, 19(5), (2025) 5839–5850. https://doi.org/10.1021/acsnano.4c18277

[45] L. Lin, K. Wang, R. Azmi, J. Wang, A. Sarkar, M. Botros, S. Najib, Y. Cui, D. Stenzel, P. A. Sukkurji, Q. Wang, H. Hahn, S. Schweidler, B. Breitung, Mechanochemical synthesis: route to novel rock-salt-structured High-Entropy Oxides and Oxyfluorides. Journal of Materials Science, 55(36), (2020) 16879–16889. https://doi.org/10.1007/s10853-020-05183-4

[46] L. Miao, J.T. Sivak, G. Kotsonis, J. Ciston, C.L. Ophus, I. Dabo, J. Maria, S.B. Sinnott, N. Alem, Chemical Environment and Structural Variations in High Entropy Oxide Thin Film Probed with Electron Microscopy. ACS Nano, 18(23), (2024) 14968–14977. https://doi.org/10.1021/acsnano.4c00787

[47] Y. Wang, H. He, H. Lv, F. Jia, B. Liu, Two-Dimensional Single-Crystalline Mesoporous High-Entropy Oxide Nanoplates for Efficient Electrochemical Biomass Upgrading. Nature Communications, 15(1), (2024) 6761. https://doi.org/10.1038/s41467-024-50721-2

[48] S.N. Gonzalez, C.M. Block, R.P. O'Hayre, R.M. Richards, Synthesis Methods for Electrochemically Applicable High Entropy Oxides. Langmuir, 40(45), (2024) 23573–23582. https://doi.org/10.1021/acs.langmuir.4c02299

[49] G. Shen, Z. Wen, Z. Wang, L. Shu, Strain-Engineered Flexoelectricity and Oxygen Vacancy Dynamics for Modulating Interfacial Charge Transport in $BaTiO_3$. Journal of Materiomics, 12(2), (2025) 101145. https://doi.org/10.1016/j.jmat.2025.101145

[50] A. Stangl, D. Muñoz-Rojas, M. Burriel, In situ and Operando Characterisation Techniques for Solid Oxide Electrochemical Cells: Recent Advances. Journal of Physics Energy, 3(1), (2020) 012001. https://doi.org/10.1088/2515-7655/abc1f5

[51] M. Zhang, X. Duan, Y. Gao, S. Zhang, X. Lu, K. Luo, J. Ye, X. Wang, Q. Niu, P. Zhang, S. Dai, Tuning Oxygen Vacancies in Oxides by Configurational Entropy. ACS Applied Materials & Interfaces, 15(39), (2023) 45774–45789. https://doi.org/10.1021/acsami.3c07268

[52] B. Baldassarri, J. He, A. Gopakumar, S. Griesemer, A.J.A. Salgado-Casanova, T. Liu, S.B. Torrisi, C. Wolverton, Oxygen Vacancy Formation

Energy in Metal Oxides: High-Throughput Computational Studies and Machine-Learning Predictions. Chemistry of Materials, 35(24), (2023) 10619–10634. https://doi.org/10.1021/acs.chemmater.3c02251

[53] C.M. Rost, Z. Rak, D.W. Brenner, J. Maria, Local structure of the $Mg_xNi_xCo_xCu_xZn_xO$(x =0.2) Entropy-Stabilized Oxide: An EXAFS study. Journal of the American Ceramic Society, 100(6), (2017) 2732–2738. https://doi.org/10.1111/jace.14756

[54] M. Han, C. Wang, J. Zhong, J. Han, N. Wang, A. Seifitokaldani, Y. Yu, Y. Liu, X. Sun, A. Vomiero, H. Liang, Promoted Self-Construction of β-NiOOH in Amorphous High Entropy Electrocatalysts for the Oxygen Evolution Reaction. Applied Catalysis B: Environmental, 301, (2022) 120764. https://doi.org/10.1016/j.apcatb.2021.120764

[55] P. Ghigna, L. Airoldi, M. Fracchia, D. Callegari, U. Anselmi-Tamburini, P. D'Angelo, N. Pianta, R. Ruffo, G. Cibin, D.O. De Souza, E. Quartarone, Lithiation mechanism in High-Entropy Oxides as Anode Materials for Li-Ion Batteries: An Operando XAS study. ACS Applied Materials & Interfaces, 12(45), (2020) 50344–50354. https://doi.org/10.1021/acsami.0c13161

[56] S. Wang, T. Chen, C. Kuo, C. Lin, S. Huang, M. Lin, C. Wang, H. Chen, Operando Synchrotron Transmission X-ray Microscopy Study on (Mg, Co, Ni, Cu, Zn)O High-Entropy Oxide Anodes for Lithium-ion Batteries. Materials Chemistry and Physics, 274, (2021) 125105. https://doi.org/10.1016/j.matchemphys.2021.125105

[57] X. Zheng, S.S. Mofarah, R.F. Webster, J. Zhang, C. Cazorla, Y. Nie, S. Wang, Y. Jiang, T. De Villenoisy, J. Wang, Y. Yao, T. Zhao, L. Dai, S.L.Y. Chang, C. Zhao, D. Chu, L. Sheppard, P. Koshy, C.C. Sorrell, Transforming Disorder in the Design of Advanced High-Entropy Oxide Electrocatalysts for zinc-air Batteries. Nature Communications, 17(1), (2026). https://doi.org/10.1038/s41467-026-69849-4

[58] X. Liu, Y. Xing, K. Xu, H. Zhang, M. Gong, Q. Jia, S. Zhang, W. Lei, Kinetically Accelerated Lithium storage in High-Entropy (LiMgCoNiCuZn)O enabled by Oxygen Vacancies. Small, 18(18), (2022) e2200524. https://doi.org/10.1002/smll.202200524

[59] Z. Cai, Y. Zhang, Z. Lun, B. Ouyang, L.C. Gallington, Y. Sun, H. Hau, Y. Chen, M.C. Scott, G. Ceder, Thermodynamically Driven Synthetic Optimization for Cation-Disordered Rock Salt Cathodes. Advanced Energy Materials, 12(21), (2022). https://doi.org/10.1002/aenm.202103923

[60] X. Liu, X. Li, Y. Li, H. Zhang, Q. Jia, S. Zhang, W. Lei, High-Entropy Oxide: A Future Anode Contender for Lithium-Ion Battery. EcoMat, 4(6), (2022). https://doi.org/10.1002/eom2.12261

[61] Y. Yin, W. Zhang, X. Zhang, M.M. Theint, J. Yang, Z. Yang, J. Li, S. Liang, X. Ma, Low-Dimensional High Entropy Oxide $(FeCoCrMnNi)_3O_4$ for Supercapacitor Applications. Dalton Transactions, 52(26), (2023) 9005–9016. https://doi.org/10.1039/d3dt00909b

[62] A. Joshi, S. Chakrabarty, S.H. Akella, A. Saha, A. Mukherjee, B. Schmerling, M. Ejgenberg, R. Sharma, M. Noked, High-Entropy Co-Free O3-Type Layered Oxyfluoride: a Promising Air-Stable Cathode for Sodium-Ion Batteries. Advanced Materials, 35(51), (2023) e2304440. https://doi.org/10.1002/adma.202304440

[63] A. Amiri, R. Shahbazian-Yassar, Recent Progress of High-Entropy Materials for Energy Storage and Conversion. Journal of Materials Chemistry A, 9(2), (2020) 782–823. https://doi.org/10.1039/d0ta09578h

[64] J. Wang, S. Sun, S. Xi, Y. Sun, S.J.H. Ong, Z.W. Seh, Z.J. Xu, High-Entropy Spinel Oxides for water Oxidation: Surface Entropy Evolution and Activity Promotion. The Journal of Physical Chemistry C, 128(12), (2024) 4978–4987. https://doi.org/10.1021/acs.jpcc.4c00670

[65] T. Li, Y. Yao, B.H. Ko, Z. Huang, Q. Dong, J. Gao, W. Chen, J. Li, S. Li, X. Wang, R. Shahbazian-Yassar, F. Jiao, L. Hu, Carbon-Supported High-Entropy Oxide Nanoparticles as stable Electrocatalysts for Oxygen Reduction Reactions. Advanced Functional Materials, 31(21), (2021). https://doi.org/10.1002/adfm.202010561

[66] Y. Jiang, Z. Liang, H. Fu, M. Sun, S. Wang, B. Huang, Y. Du, PT-Modified High Entropy rare Earth Oxide for Efficient Hydrogen Evolution in PH-Universal Environments. Journal of the American Chemical Society, 146(13), (2024)

9012–9025. https://doi.org/10.1021/jacs.3c13367

[67] N. Sun, Z. Lai, W. Ding, W. Li, T. Wang, Z. Zheng, B. Zhang, X. Dong, P. Wei, P. Du, Z. Hu, C. Pao, W. Huang, H. Wang, M. Lei, K. Huang, R. Yu, Alkali Metals Activated High Entropy Double Perovskites for Boosted Hydrogen Evolution Reaction. Advanced Science, 11(42), (2024) e2406453. https://doi.org/10.1002/advs.202406453

[68] H. Ge, L. Zheng, G. Yuan, W. Shi, J. Liu, Y. Zhang, X. Wang, Polyoxometallate Cluster Induced High-Entropy Oxide Sub-1 nm Nanosheets as Photoelectrocatalysts for Zn–Air Batteries. Journal of the American Chemical Society, 146(15), (2024) 10735–10744. https://doi.org/10.1021/jacs.4c00652

[69] X. Yang, R. Guo, R. Cai, Y. Ouyang, P. Yang, J. Xiao, Engineering High-Entropy Materials for Electrocatalytic Water Splitting. International Journal of Hydrogen Energy, 47(28), (2022) 13561–13578. https://doi.org/10.1016/j.ijhydene.2022.02.123

[70] C. Chen, Z. Xu, G. Hai, W. Huang, C. Pao, H. Li, K. Jiang, N. Zhang, T. Liu, Tailoring the d Band Center of High-Entropy Perovskite Oxide Nanotubes for Enhanced Nitrate Electroreduction. Small, 21(2), (2024) e2407964. https://doi.org/10.1002/smll.202407964

[71] F. Liu, M. Yu, X. Chen, J. Li, H. Liu, F. Cheng, Defective High-Entropy Rocksalt Oxide with Enhanced Metal–Oxygen Covalency for Electrocatalytic Oxygen Evolution. Chinese Journal of Catalysis, 43(1), (2022) 122–129. https://doi.org/10.1016/s1872-2067(21)63794-4

[72] J. Hu, T. Guo, X. Zhong, J. Li, Y. Mei, C. Zhang, Y. Feng, M. Sun, L. Meng, Z. Wang, Z. Wang, B. Huang, L. Zhang, Z. Wang, Z. Wang, In Situ Reconstruction of High-Entropy Heterostructure Catalysts for Stable Oxygen Evolution Electrocatalysis under Industrial Conditions. Advanced Materials, 36(14), (2024) e2310918. https://doi.org/10.1002/adma.202310918

[73] T. Zhang, F. Wang, P. Fu, Z. Li, L. Li, Z. Cao, L. Tang, D. Wei, H. Cong, High-Entropy Modified Spinel-Type Co_3O_4 Nanowires Enhance Activity and Stability for Water Oxidation. Advanced Functional Materials, 36(37), (2026) e30208. https://doi.org/10.1002/adfm.202530208

[74] Y. Sun, S. Dai, High-Entropy Materials for Catalysis: A New Frontier. Science Advances, 7(20), (2021). https://doi.org/10.1126/sciadv.abg1600

[75] A.F. Manchón-Gordón, P. Panadero-Medianero, J.S. Blázquez, Descriptors for Predicting Single- and Multi-Phase Formation in High-Entropy Oxides: A Unified Framework Approach. Materials, 18(16), (2025) 3862. https://doi.org/10.3390/ma18163862

[76] X. Duan, Y. Li, J. Zhao, M. Zhang, X. Wang, L. Zhang, X. Ma, Y. Qu, P. Zhang, Machine Learning Accelerated Discovery of Entropy-Stabilized Oxide Catalysts for Catalytic Oxidation. Journal of the American Chemical Society, 147(1), (2024) 651–661. https://doi.org/10.1021/jacs.4c12838

[77] J.T. Sivak, S.S.I. Almishal, M.K. Caucci, Y. Tan, D. Srikanth, J. Petruska, M. Furst, L. Chen, C.M. Rost, J. Maria, S.B. Sinnott, Discovering High-Entropy Oxides with a Machine-Learning Interatomic Potential. Physical Review Letters, 134(21), (2025) 216101. https://doi.org/10.1103/physrevlett.134.216101

[78] J.H. Yang, T. Chen, L. Barroso-Luque, Z. Jadidi,G. Ceder, Approaches for Handling High-Dimensional Cluster Expansions of Ionic Systems. Npj Computational Materials, 8(1), (2022). https://doi.org/10.1038/s41524-022-00818-3

[79] S. Nie, Y. Xiang, L. Wu, G. Lin, Q. Liu, S. Chu, X. Wang, Active Learning Guided Discovery of High Entropy oxides Featuring High H2-Production. Journal of the American Chemical Society, 146(43), (2024) 29325–29334. https://doi.org/10.1021/jacs.4c06272

[80] Q. Wang, L. Velasco, B. Breitung, V. Presser, High-Entropy Energy Materials in the Age of Big Data: A Critical Guide to Next-Generation Synthesis and Applications. Advanced Energy Materials, 11(47), (2021). https://doi.org/10.1002/aenm.202102355

[81] C. Liu, S. Li, Y. Zheng, M. Xu, H. Su, X. Miao, Y. Liu, Z. Zhou, J. Qi, B. Yang, D. Chen, C. Nan, Y. Lin, Advances in High Entropy Oxides: Synthesis, Structure, Properties and beyond. Progress in Materials Science, 148, (2024) 101385. https://doi.org/10.1016/j.pmatsci.2024.101385

[82] Y. Zhang, K. Ren, W.Y. Wang, X. Gao, J. Wang, Y. Wang, H. Song, X. Liang, J. Li, Smart design A2Zr2O7-type High-Entropy Oxides through Lattice-Engineering Toughening Strategy. Npj Computational Materials, 10, (2024) 277. https://doi.org/10.1038/s41524-024-01462

[83] O.A. Dicks, S.S. Aamlid, A.M. Hallas, J. Rottler, Expanding the Search Space of High Entropy Oxides and Predicting Synthesizability using Machine Learning Interatomic Potentials. Computational Materials Science, 267, (2026) 114581. https://doi.org/10.1016/j.commatsci.2026.114581

[84] H. Zhao, L. Li, T. Zhang, J. Yao, X. Peng, J. Peng, M. Zhu, B. Xu, X. Liu, H. Yu, Discovering high-entropy electrocatalysts through a batch-alloy targeting approach. Science Advances, 11(28), (2025) eadx6121. https://doi.org/10.1126/sciadv.adx6121

[85] P. Tukur, Y. Wei, Y. Zhang, H. Chen, Y. Lin, S. He, Y. Mo, J. Wei, Machine Learning-Guided discovery of High-Entropy Perovskite Oxide Electrocatalysts via Oxygen Vacancy Engineering. Small, 21(21), (2025) e2501946. https://doi.org/10.1002/smll.202501946

[86] W. Wang, Q. Zhang, L. Yang, G. Liang, X. Xiong, Y. Cheng, L. Wu, C. Lin, R. Che, How do the Four Core Factors of High Entropy Affect the electrochemical properties of Energy-Storage materials. Advanced Science, 12(1), (2024) e2411291. https://doi.org/10.1002/advs.202411291

[87] T. Cai, A. Chen, S. Liang, J. Mu, L. Wang, W. He, K. Tao, J. Li, F. Huang, Machine Learning for Design and Full Chain Research of High-Entropy Na-Ion Cathodes. Advanced Materials, 37(44), (2025) e08717. https://doi.org/10.1002/adma.202508717

[88] H. Guo, Z. Guo, G. Xue, H. Wang, J. Gong, K. Chu, J. Qin, Y. Guan, H. Dong, Y. Chen, Y. Miao, C. Zhang, H. Liu, T. Liu, J. Hofkens, F. Lai, Entropy-Driven Stabilization of Noble Metal Single Atoms: Advancing Ammonia Synthesis and Energy Output in Zinc-Nitrate Batteries. Advanced Materials, 37(28), (2025) e2500224. https://doi.org/10.1002/adma.202500224

Author Contribution Statement

Both the authors equally contributed and approved the final version of this work.

Does this article screened for similarity?

Yes

Conflict of interest

The Author's declares that there is no conflict of interest anywhere.

About the License