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## Revisiting Necessity of High-Entropy Electrocatalysts

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### Abstract

High-entropy alloys are often presumed stable and intrinsically beneficial for electrocatalysis. This Comment argues that in situ structural evolution can diminish configurational entropy, necessitating rigorous identification of active phases under operando conditions before attributing catalytic performance to high-entropy effects.

High-entropy alloys (HEAs) have recently emerged as compelling candidates in the field of electrocatalysis owing to their ability to form compositionally complex solid solutions that integrate a diverse array of surface active sites within a single-phase structure.<sup>1-3</sup> Thermodynamically, their high configurational entropy suppresses phase segregation, and kinetically, sluggish diffusion effect confers kinetic stability, leading to expectations of superior physical and chemical stability over conventional alloys.<sup>4</sup> However, experimental studies under electrocatalytic conditions have revealed critical concerns.<sup>5,6</sup> During reactions such as the oxygen evolution reaction (OER) at anodic potentials or hydrogen evolution reaction (HER) and CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) in cathodic environments, HEAs have been shown to undergo surface reconstructions.<sup>7-12</sup> These transformations raise a fundamental question: *can the high-entropy configuration still be regarded as the catalytically active phase if an HEA undergoes significant structural or compositional changes during reaction?* Moreover, once the in situ-formed active structure is a simpler phase, it is essential to consider whether comparable performance could be achieved using a conventional catalyst. This knowledge gap is particularly critical, as such transformations are intimately linked to catalytic properties and mechanistic insights. This Comment calls for a more critical evaluation of HEA design in electrocatalysis, with particular emphasis on how structural and compositional changes may compromise the intended high-entropy state. By clarifying the conceptual foundations of high-entropy catalyst design and outlining plausible transformation pathways, we aim to promote more rigorous investigation of HEAs as functional and reliable electrocatalysts.

### **Entropy-driven principles in electrocatalyst design**

*Unique Surface Ensembles.* Unlike monometallic/binary alloys, HEAs create a vast array of local atomic configurations on a single catalyst surface.<sup>13</sup> This inherent structural heterogeneity results in a wide distribution of adsorption energies for reaction intermediates rather than a narrow or singular binding energy profile. Theoretically, such diversity enhances the likelihood of encountering surface sites with near-optimal adsorption energies for specific intermediates.<sup>3</sup>

Consequently, HEAs have the potential to circumvent the limitations imposed by conventional volcano-type relationships by spanning a broader region of the activity-binding energy curve.

*Breaking Scaling Relations.* Another compelling feature of HEAs is their potential to overcome the limitations imposed by linear scaling relationships between adsorbed reaction intermediates. The distinct chemical roles of neighboring elements can create synergistic effects, enabling the concerted tuning of catalytic activity beyond the reach of conventional alloys. Furthermore, the multifunctional nature of HEA surfaces provides the possibility for versatile active sites to participate in discrete stages of a reaction pathway.

*Stability Expectations.* HEAs are also widely regarded as intrinsically stable materials. At elevated temperatures, the high configurational entropy favors the formation of a single-phase, chemically disordered structure, while at lower temperatures, sluggish atomic diffusion provides kinetic barriers that suppress phase separation and elemental migration.<sup>3</sup> These characteristics have led to the expectation that HEAs are inherently resistant to degradation pathways commonly observed in conventional alloys during electrocatalysis.

Building on these proposed advantages, HEAs have been actively investigated in electrocatalytic applications benefitting from so-called “synergistic effects” or the “high-entropy effect”.<sup>14</sup> However, a critical assumption underlying numerous reports is that the HEA maintains its single-phase, multi-elemental configuration during reactions. The following sections critically assess the validity of this assumption under practical electrochemical conditions and explore potential transformation pathways that may undermine the fundamental integrity of HEA electrocatalysts.

### **Traits that may lead to entropy loss**

*Dealloying and leaching.* Electrocatalytic operation can trigger irreversible surface degradation through dealloying and leaching, particularly during anodic reactions like OER, which directly dismantle the multi-elemental complexity of HEAs. High anodic potentials and reactive oxygen species drive selective dissolution of the most electrochemically vulnerable metals, as predicted by Pourbaix diagrams, yielding a structurally and compositionally simplified surface oxide with reduced configurational entropy (Fig. 1). For instance, IrFeCoNiCu HEA nanoparticle under acidic

OER conditions leach *3d* transition metals, forming an Ir-enriched surface oxide shell,<sup>15</sup> questioning the original high-entropy contribution despite enhanced stability. Similarly, the Cantor alloy (CoCrFeNiMn) in alkaline conditions loses Cr and Mn,<sup>16</sup> resulting in a Ni/Fe/Co oxyhydroxide surface that reduces the HEA to a conventional ternary oxide. Although such restructuring may occasionally improve activity (e.g., exposing active IrO<sub>x</sub> species), it often disrupts synergistic interactions or causes irreversible material loss, undermining the intended benefits of high-entropy design.

*Surface reconstruction, oxidation, and formation of new phases.* Under anodic potentials, *3d* transition metals in HEAs readily form oxyhydroxide layers (Fig. 1), widely recognized as OER-active phases. This type of restructuring is unequivocal, as evidenced by in situ Raman studies of a MoZnFeCoNi HEA, which demonstrates the formation of M-OOH species during OER.<sup>17</sup> Cathodic processes like CO<sub>2</sub>RR operate via distinct mechanisms: local pH elevation and CO adsorption can drive surface remodeling. An AgAuCuPdPt HEA aerogel showed high CO<sub>2</sub>RR activity, but no operando evidence confirmed retention of the high-entropy configuration.<sup>18</sup> Similarly, a CuMoRuFeW HEA nanorod enhanced C<sub>2</sub> product formation without verifying the active surface structure.<sup>19</sup> Although the inherent site diversity of HEAs is theorized to facilitate multi-carbon pathways by stabilizing varied intermediates, the actual surface under operation is likely a reconstructed one, challenging the stability of the initial high-entropy configuration.

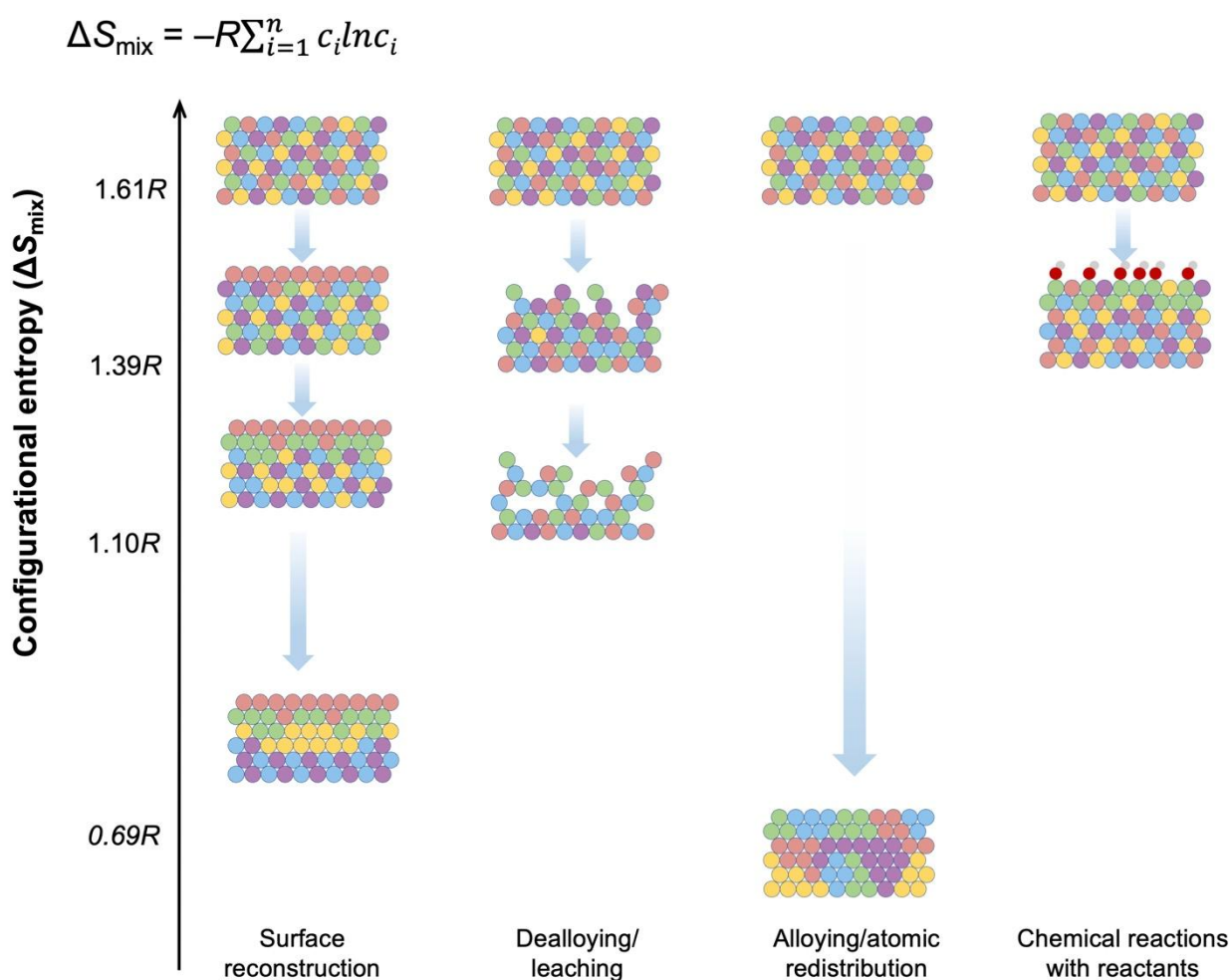
*Alloying and atomic redistribution.* Enhanced elemental diffusivity in HEAs under electrochemical conditions, driven by differences in surface energy, atomic mobility, and concentration gradients,<sup>20</sup> leads to surface segregation and heterogeneous atomic arrangements (Fig. 1).<sup>21</sup> For example, simulations of the AgAuCuPdPt HEA reveal that Ag (lowest surface energy) migrates to the surface and forms nanoclusters, Au accumulates subsurface, while Pt, Cu, and Pd remain depleted from the surface.<sup>22</sup> These segregation trends, governed by relative surface energies, create a surface composition starkly different from the equimolar bulk. Such dynamic redistribution critically modulates electrocatalytic behavior and must be accounted for in mechanism analysis and catalyst design.

*Chemical reactions with reactants.* Chemical interactions with reactants can induce new phases or adsorbate-driven segregation (Fig. 1). Elements with strong affinity for specific adsorbates, such as hydrogen during HER, may preferentially enrich at the surface, either by occupying surface sites or by lowering surface energy in hydrogen-rich environments. A representative example is a sub-nanometric PdRhMoFeMn metallene, which showed exceptional HER activity across wide pH ranges.<sup>23</sup> Operando X-ray absorption spectroscopy and Density Functional Theory (DFT) simulations revealed distinct roles for each metal component in reaction steps. However, the stability of the multi-elemental configuration, particularly in light of Pd's known hydride formation, was not directly confirmed, leaving open the possibility of potential surface restructuring under working conditions.

In short, dealloying/leaching, surface reconstruction and new phase formation are particularly pronounced under anodic OER, where transition-metal-based HEAs typically transform into surface oxides or hydroxides. During HER and CO<sub>2</sub>RR, HEAs are generally more stable. Nonetheless, minor restructuring and elemental redistribution induced by the adsorption of specific intermediates may still occur. When configurational entropy is significantly reduced, the benefits commonly ascribed to high-entropy design may be questionable and be less relevant to the actual

reaction mechanism. Accordingly, we should revisit the necessity of high-entropy electrocatalyst design.

**Fig. 1 | Schematic of potential pathways for entropy loss in HEAs under electrocatalytic conditions.** The thermodynamic driving force for these transformations is underpinned by the change in configurational entropy ( $\Delta S_{\text{mix}}$ ). For a multi-component alloy system (represented by colored spheres) with an equimolar composition,  $\Delta S_{\text{mix}}$  can be simplified as  $R\ln(n)$ , where  $R$  is the



molar gas constant and  $n$  is the number of types of elements. The ideal  $\Delta S_{\text{mix}}$  values for binary, ternary, quaternary and quinary systems are calculated as  $0.69R$ ,  $1.10R$ ,  $1.39R$ , and  $1.61R$ , respectively. The arrows depict representative degradation routes from a high-entropy solid solution towards lower-entropy states.

### **Necessity of high-entropy electrocatalyst design**

With the evidence above, it is necessary to revisit a central question in the field: *Is the high-entropy configuration necessary for electrocatalysis?* Some HEAs serve as precursors that transform into the active phase, while others leverage the disordered multi-elemental structure. This distinction has generated ongoing debate within the electrocatalysis community.

*Viewpoint 1: the role of HEAs as “pre-catalysts” should be clearly defined.* Many high-entropy configurations are unstable under reaction conditions, effectively functioning as pre-catalysts. For instance, IrFeCoNiCu during OER reconstructs into an Ir-enriched oxyhydroxide layer.<sup>15</sup> If the same Ir-rich surface could be prepared directly on a simple support, would the catalytic performance differ in a meaningful way? Yet, the HEA precursor may still add value: the resulting Ir shell might contain surface defects or residual heteroatoms that enhance activity beyond pure Ir nanoparticles. In this context, the HEA serves as a sacrificial template that evolves into an optimized state, akin to dealloying that creates nanoporous metals.

*Viewpoint 2: claims of unique catalytic synergies caused by HEAs require rigorous operando validation.* Advocates for high-entropy electrocatalysts highlight examples where the multicomponent configuration remains intact during reaction. The PdRhMoFeMn metallene exemplifies this paradigm, achieving exceptional HER activity while maintaining its multi-element configuration.<sup>23</sup> However, such claims require rigorous operando validation. Systems with sustained high-entropy catalysis should be clearly distinguished from reconstructed ones.

The central question remains: Does a catalyst truly need five or more randomly mixed elements? Often, only a subset of the constituent elements dominates the surface chemistry, suggesting that carefully designed ternary or quaternary alloys could suffice. Additionally, early computational predictions of entropic stabilization and sluggish diffusion increasingly conflict with experimental evidence of dynamic restructuring under operating conditions.<sup>24,25</sup> This gap highlights the need for predictive models that incorporate dynamic surface effects under realistic conditions. Recent work has suggested the incorporation of adsorbate-induced effects, such as surface-bound oxygen or hydrogen promoting selective segregation, into predictive stability models.<sup>26</sup> While entropic

stabilization may preserve bulk disorder, surface regions remain vulnerable to transformation, especially during prolonged reaction. A nuanced view of HEA stability is therefore essential.

### **Outlook and future directions**

The classical structure-based paradigm assumes active sites are static and environment is secondary. Yet, catalysts often evolve dynamically under reaction conditions, which challenges traditional descriptors derived from equilibrium DFT models. HEA electrocatalysts are best understood as inherently dynamic systems, where surfaces evolve into active phases that bear little resemblance to the initial high-entropy design. The necessity of a high-entropy configuration must thus be rigorously demonstrated, not assumed. Looking ahead, the field must prioritize identifying the true active phase using operando techniques to track structural evolution and surface chemistry at high resolution.<sup>27-30</sup> Key challenges include determining the optimal number of elements and whether the five-element definition is functionally necessary. Embracing this dynamic perspective will enable rational design where high-entropy configuration provides a definitive, rather than circumstantial advantage in electrocatalysis.

## References

- 1 George, E. P., Raabe, D. & Ritchie, R. O. High-Entropy Alloys. *Nat. Rev. Mater.* **4**, 515-534 (2019).
- 2 Sun, X. & Sun, Y. Synthesis of Metallic High-Entropy Alloy Nanoparticles. *Chem. Soc. Rev.* **53**, 4400-4433 (2024).
- 3 Löffler, T., Ludwig, A., Rossmeisl, J. & Schuhmann, W. What Makes High-Entropy Alloys Exceptional Electrocatalysts? *Angew. Chem. Int. Ed.* **60**, 26894-26903 (2021).
- 4 Hsu, W.-L., Tsai, C.-W., Yeh, A.-C. & Yeh, J.-W. Clarifying the Four Core Effects of High-Entropy Materials. *Nat. Rev. Chem.* **8**, 471-485 (2024).
- 5 Wang, J. *et al.* Spatially and Temporally Understanding Dynamic Solid–Electrolyte Interfaces in Carbon Dioxide Electroreduction. *Chem. Soc. Rev.* **52**, 5013-5050 (2023).
- 6 Wang, J., Tan, H.-Y., Zhu, Y., Chu, H. & Chen, H. M. Linking the Dynamic Chemical State of Catalysts with the Product Profile of Electrocatalytic CO<sub>2</sub> Reduction. *Angew. Chem. Int. Ed.* **60**, 17254-17267 (2021).
- 7 Zhao, X. *et al.* Multiple Metal–Nitrogen Bonds Synergistically Boosting the Activity and Durability of High-Entropy Alloy Electrocatalysts. *J. Am. Chem. Soc.* **146**, 3010-3022 (2024).
- 8 Liu, H. *et al.* Unveiling Atomic-Scaled Local Chemical Order of High-Entropy Intermetallic Catalyst for Alkyl-Substitution-Dependent Alkyne Semihydrogenation. *J. Am. Chem. Soc.* **146**, 20193-20204 (2024).
- 9 Wang, Y. *et al.* Ordering-Dependent Hydrogen Evolution and Oxygen Reduction Electrocatalysis of High-Entropy Intermetallic Pt<sub>4</sub>FeCoCuNi. *Adv. Mater.* **35**, 2302067 (2023).
- 10 Hu, J. *et al.* In Situ Reconstruction of High-Entropy Heterostructure Catalysts for Stable Oxygen Evolution Electrocatalysis under Industrial Conditions. *Adv. Mater.* **36**, 2310918 (2024).

- 11 Liang, J. *et al.* Reconstruction of High Entropy Alloys on a Metal-Organic Framework Approaching Active Oxygen Reduction Electrocatalysts. *Nano Lett.* **24**, 7293-7301 (2024).
- 12 Song, B. *et al.* Revealing High-Temperature Reduction Dynamics of High-Entropy Alloy Nanoparticles Via in Situ Transmission Electron Microscopy. *Nano Lett.* **21**, 1742-1748 (2021).
- 13 Cao, G., Yang, S., Ren, J.-C. & Liu, W. Electronic Descriptors for Designing High-Entropy Alloy Electrocatalysts by Leveraging Local Chemical Environments. *Nat. Commun.* **16**, 1251 (2025).
- 14 Yan, X., Zhou, Y. & Wang, S. Nano-High Entropy Materials in Electrocatalysis. *Adv. Funct. Mater.* **35**, 2413115 (2025).
- 15 Maulana, A. L. *et al.* Understanding the Structural Evolution of Irfeconicu High-Entropy Alloy Nanoparticles under the Acidic Oxygen Evolution Reaction. *Nano Lett.* **23**, 6637-6644 (2023).
- 16 Luan, C. *et al.* Revealing Dynamic Surface and Subsurface Reconstruction of High-Entropy Alloy Electrocatalysts During the Oxygen Evolution Reaction at the Atomic Scale. *ACS Catal.* **14**, 12704-12716 (2024).
- 17 Mei, Y. *et al.* MoZn-Based High Entropy Alloy Catalysts Enabled Dual Activation and Stabilization in Alkaline Oxygen Evolution. *Sci. Adv.* **10**, eadq6758.
- 18 Li, H. *et al.* High-Entropy Alloy Aerogels: A New Platform for Carbon Dioxide Reduction. *Adv. Mater.* **35**, 2209242 (2023).
- 19 Qin, J., Hu, D., Xiang, D. & Kang, X. CuMoRuFeW High Entropy Alloy Surfaced Nanorods: Superior Electrochemical CO<sub>2</sub> Reduction to Ethylene. *Chin. J. Struct. Chem.* **44**, 100571 (2025).
- 20 Chida, Y. *et al.* Experimental Study Platform for Electrocatalysis of Atomic-Level Controlled

- High-Entropy Alloy Surfaces. *Nat. Commun.* **14**, 4492 (2023).
- 21 Feng, J., Wang, X. & Pan, H. In-Situ Reconstruction of Catalyst in Electrocatalysis. *Adv. Mater.* **36**, 2411688 (2024).
- 22 Dahale, C., Goverapet Srinivasan, S., Mishra, S., Maiti, S. & Rai, B. Surface Segregation in the Agaucupdpt High Entropy Alloy: Insights from Molecular Simulations. *Mol. Syst. Des. Eng.* **7**, 878-888 (2022).
- 23 Li, Y. *et al.* Operando Elucidation of Hydrogen Production Mechanisms on Sub-Nanometric High-Entropy Metallenes. *Nat. Commun.* **15**, 10222 (2024).
- 24 Batchelor, T. A. A. *et al.* High-Entropy Alloys as a Discovery Platform for Electrocatalysis. *Joule* **3**, 834-845 (2019).
- 25 Lu, Z., Chen, Z. W. & Singh, C. V. Neural Network-Assisted Development of High-Entropy Alloy Catalysts: Decoupling Ligand and Coordination Effects. *Matter* **3**, 1318-1333 (2020).
- 26 Sun, Y. & Dai, S. High-Entropy Materials for Catalysis: A New Frontier. *Sci. Adv.* **7**, eabg1600.
- 27 Wang, J. *et al.* In Situ X-Ray Spectroscopies Beyond Conventional X-Ray Absorption Spectroscopy on Deciphering Dynamic Configuration of Electrocatalysts. *Nat. Commun.* **14**, 6576 (2023).
- 28 Tung, C.-W. *et al.* Spin Crossover-Driven Diiron Electrocatalyst Boosts Sustainable Water Oxidation. *Nat. Sustain.* **8**, 793-805 (2025).
- 29 Wang, J. *et al.* Resolving Dynamic Behavior of Electrocatalysts Via Advances of Operando X-Ray Absorption Spectroscopies: Potential Artifacts and Practical Guidelines. *Adv. Mater.* **37**, 2418797 (2025).
- 30 Hsu, C.-S. *et al.* Activating Dynamic Atomic-Configuration for Single-Site Electrocatalyst in Electrochemical CO<sub>2</sub> Reduction. *Nat. Commun.* **14**, 5245 (2023).

**Competing Interests Statement**

The authors declare no competing interests.

**Author Contributions**

H.M.C. and J.W. conceived and wrote the manuscript, J.W. and F.Z.T. revised the manuscript.

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