

Review Article

High entropy intermetallic compounds: A discovery platform for structure–property correlations and materials design principles in electrocatalysis

Ridha Zerdoumi¹, Alfred Ludwig^{2,3} and Wolfgang Schuhmann¹

The electrocatalytic properties of multi-metal materials are predominantly influenced by electronic and geometric effects related to surface and sub-surface atoms. A comprehensive understanding of these effects and their complex interplay is paramount for the efficient development of high-performance catalysts. Along with compositionally complex solid solutions (CCSS), often called high-entropy alloys (HEAs), high-entropy intermetallic compounds (HEIMCs) are an emerging class of materials with distinctive properties originating from both high-entropy alloys and intermetallic compounds. The ordered intermetallic structure is beneficial for identifying structure–property correlations of catalytic surfaces. This minireview provides a summary of the current knowledge of high entropy intermetallic compounds and their role in catalysis, with a particular focus on the key tunable parameters essential for achieving high-performance materials.

Addresses

¹ Analytical Chemistry-Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

² Chair for Materials Discovery and Interfaces, Institute for Materials, Faculty of Mechanical Engineering, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

³ Center for Interface-Dominated High-Performance Materials, ZGH, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

Corresponding authors: Schuhmann, Wolfgang (wolfgang.schuhmann@rub.de); Zerdoumi, Ridha (ridha.zerdoumi@rub.de)

Current Opinion in Electrochemistry 2024, 48:101590

This review comes from a themed issue on **Electrocatalysis (2024)**

Edited by **Pawel J. Kulesza** and **Iwona Rutkowska**

For complete overview about the section, refer [Electrocatalysis \(2024\)](#)

Available online 6 September 2024

<https://doi.org/10.1016/j.coelec.2024.101590>

2451-9103/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Keywords

Intermetallic compounds, High entropy materials, Electronic effect, Geometric effect, Electrocatalysis.

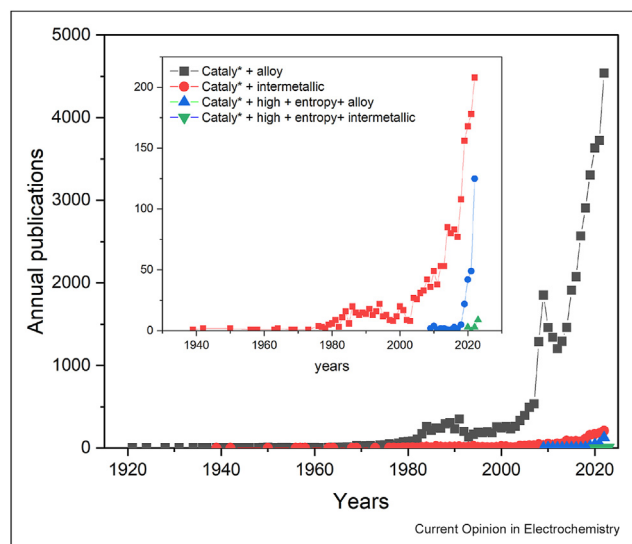
Introduction

Electrocatalysis plays a crucial role in the development of sustainable and clean energy conversion techniques through the discovery of new electrocatalytic materials and tailoring their properties for particular electrochemical reactions of interest. This is essential for addressing the global-growing energy demand, while simultaneously mitigating climate change. Noble-metal-based materials are extensively used in electrochemical energy conversion owing to their high activity, selectivity, and durability. These properties can be further enhanced by alloying noble metals with other non-noble elements. The enhancement can be attributed to the alteration of their electronic and geometric effects, both of which play a crucial role in determining the overall catalytic performance. Alongside the enhancement of their electrocatalytic properties, alloying could contribute to substantial cost reduction through the utilization of less expensive and more abundant elements.

Based on their atomic arrangement, multi-metallic systems can be broadly classified into two major categories: substitutional solid solutions (alloys) with a disordered atomic arrangement and intermetallic compounds characterized by an ordered arrangement of atoms. The progressive incorporation of different metallic components in both categories leads to ternary, quaternary, and eventually high entropy materials (quinary and beyond), specifically high entropy alloys (HEA) and high entropy intermetallic compounds (HEIMCs), respectively.

The trend in research on the use of these categories as catalyst materials is depicted in [Figure 1](#), illustrating a rapid growth in annual research articles. In 2022, there were over 200 articles addressing catalysis using intermetallic compounds and 125 dedicated to HEAs. While the number for HEAs is comparatively lower, the recent increase since 2009 suggests a growing interest in the field compared to intermetallic compounds. However, both figures pale in comparison to alloy catalysts, which boast over 4500 articles. Remarkably, the first study on the catalysis of HEIMCs was reported in 2020, and as of 2022, only three additional studies have been reported.

Figure 1



Annual publications of research papers on catalysis and alloys (black), intermetallic compounds (red), high entropy alloys (blue), and high entropy intermetallic compounds (green). Publications containing these words or parts of them in the title, keywords, or abstract were counted using the Scopus database. Copyright © 2023 Elsevier. All rights are reserved.

This indicates that the field of HEIMC catalysis is still in its infancy. In this minireview, a summary of the current status of HEIMCs is provided, offering an overview of their role as electrocatalyst materials, with a particular focus on the main tunable parameters for achieving high-performance electrocatalysts.

The crystal structure of solid solutions is derived from the crystal structures of the constituent elements, with randomly occupied atomic sites. These structures predominantly adopt the *Cu*-type (fcc), *Mg*-type (hcp), and *W*-type (bcc) of crystal structures. In contrast, intermetallic compounds crystallize into distinct crystal structures that differ from those of their constituting elements. The complexity of these structures ranges from unit cells containing one to more than 20,000 atoms [1,2]. The formation of such structures is governed by a combination of electronic and geometric factors, such as the optimization of chemical bonding and the ratio of atomic sizes. The ordered crystal structure of intermetallic compounds also results in new 'scaffolds' for the electronic structure, which can lead to unique physicochemical properties that can be significantly different from those of their constituent elements or solid solution counterparts. Moreover, the ordered atomic arrangement reduces the segregation tendency [3], and well-defined electronic structures and distinct chemical bonding are all features endowing intermetallic compounds with special catalytic properties.

The increase in the number of metallic components of solid solutions leads to the formation of compositionally complex solid solutions (CCSSs; frequently referred to as HEAs). They consist of five or more metallic elements, distributed homogeneously in the lattice, with a random occupancy of the atomic positions in the crystal structure (Figure 2). The electronic structure of CCSSs can be tuned to a great extent by modifying their elemental composition, which results in materials with unique electrocatalytic [4–10], magnetic [11,12], thermal [13], and mechanical properties [14–17]. This capability enables a paradigm shift from “*applying the materials we have*” to “*engineering the materials we need*.” [18] In addition to unique electronic properties, the presence of multiple active sites (multifunctionality) in the form of poly-elemental surface atom arrangements can enable multiple reactions and/or reaction steps at the same time [19,20].

In intermetallic compounds, the increase in the number of metallic components leads to the formation of HEIMCs. Early reports date back to 1984 [21,22], while the term HEIMCs was coined by Firstov et al. in 2015 [23–25], followed by reviews mainly focusing on mechanical and thermal properties [26–31]. Their application in electrocatalysis was reported in 2020 [32,33], with only a limited number of more studies reported since then [34–43*]. Unlike HEAs, the constituent elements in HEIMCs are distributed separately across two or more distinct sublattices, with at least one sublattice featuring a random distribution depending on the base intermetallic structure (Figure 2). The diverse crystal structures of HEIMCs, together with the vast space of possible elemental combinations, enable multidimensional tuning of electronic and geometric properties to achieve high-performance catalysts. This provides the field of heterogeneous catalysis with crossbreed properties originating from both high-entropy alloys and intermetallic compounds.

Concepts in materials design principles for heterogeneous catalysis

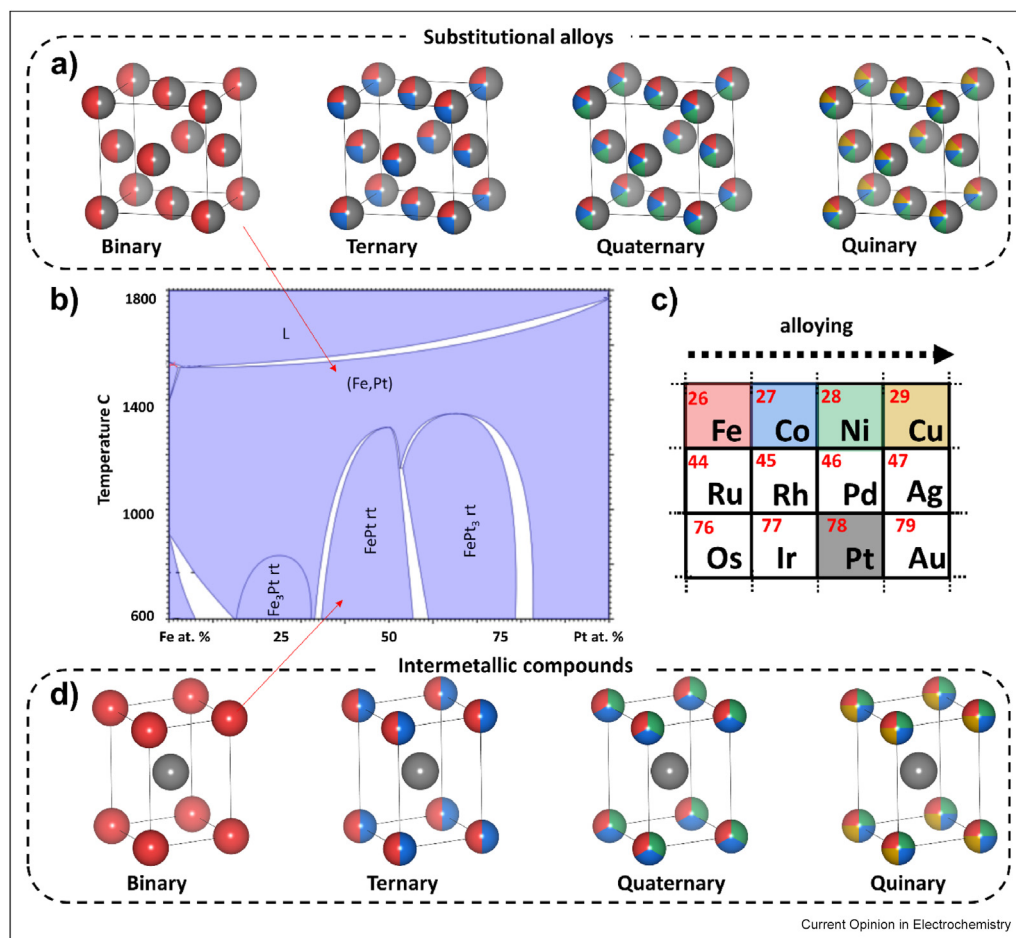
Understanding the factors that govern multi-metallic materials at the atomic level is crucial for designing more stable, selective, and efficient catalysts. This section elaborates more on these factors. They include the conventional electronic and geometric effects, which are common in both intermetallic compounds and solid solutions, the ordering and steric effects specific to intermetallic compounds, and the mixing and multifunctional effects, which are more prominent in high entropy materials.

Electronic effects

Ligand effects

Electronic effects can be classified into *ligand* and *strain effects*. *Ligand effects* refer to the modification of the

Figure 2



From binary to multinary catalysts: Substitution in the Pt–Fe solid solution phase from binary to quinary $\text{Pt}_{50}(\text{FeCoNiCu})_{50}$ HEA with Cu-type crystal structure (a). Pt–Fe phase diagram showing the Fe–Pt disordered phase (alloy) and the FePt ordered intermetallic phase (b). Substitution by increasing the number of constituent metallic components from Fe to Cu (c). Substitution in the FePt intermetallic phase from binary to quinary $\text{Pt}(\text{FeCoNiCu})$ HEIMC with CuAu-type crystal structure. The Fe–Pt phase diagram is reproduced from the AtomWork database of the National Institute for Materials Science (NIMS) (<http://crystdb.nims.go.jp/>).

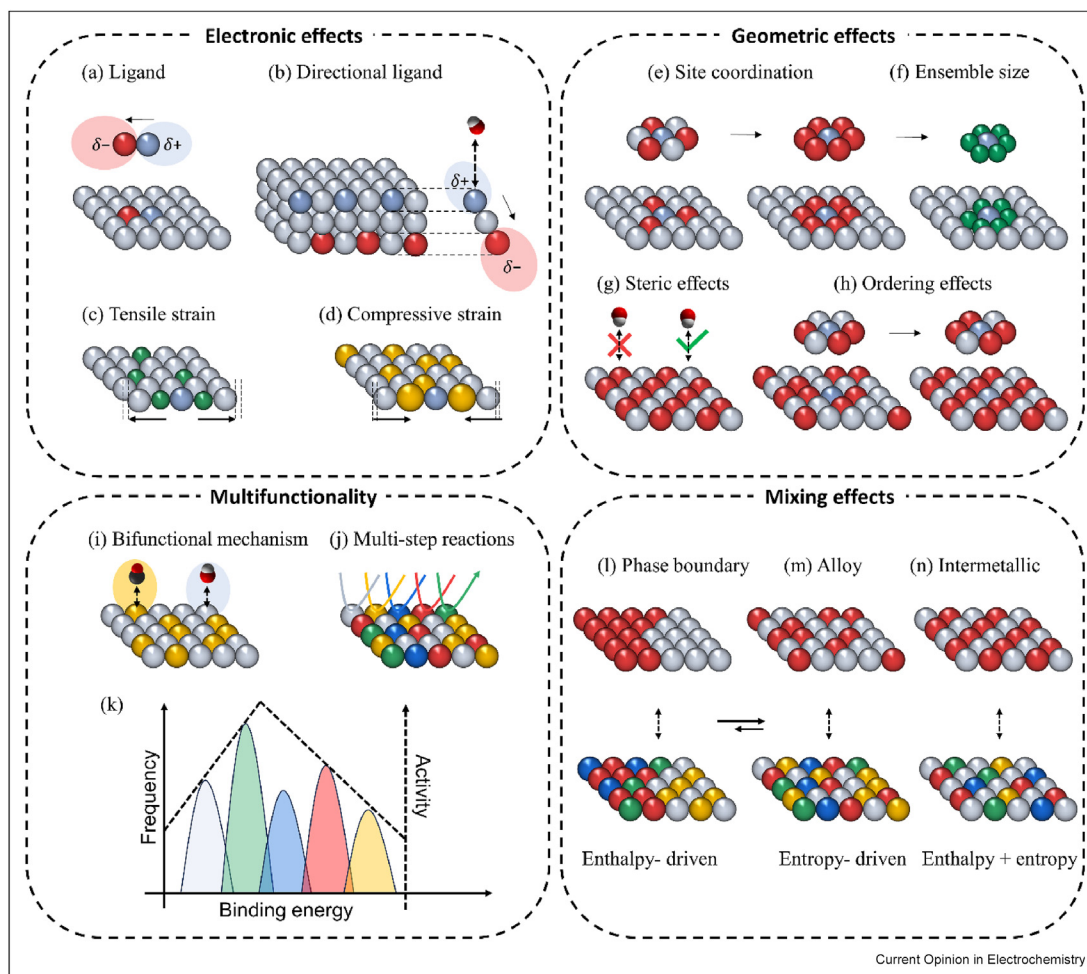
electronic states of the base metal by orbital degeneration and/or hybridization when alloyed with a different metal (Figure 3a). This induces electronic charge transfer between the neighboring atoms and thus affects their electronic band structure. In coordination and organic chemistry, the term “inductive effect” is more common. In 1995, Hammer and Nørskov introduced the “*d*-band” theory to establish a correlation between catalytic activity and the *d*-band center [44]. The position of the *d*-band center relative to the Fermi level was found to be decisive in achieving suitable adsorption energies according to the Sabatier principle [45]. Later in an experimental study, Stamenkovic *et al.* [46*] reported a volcano relationship between the *d*-band center values and the oxygen reduction reaction (ORR) activity for Pt_3M ($\text{M} = \text{Ti}, \text{V}, \text{Fe}, \text{Co}, \text{and Ni}$). Recently, Rossmeisl *et al.* [47*] reported a new type of ligand effect in metallic alloys. In the so-called

“directional ligand effects” (Figure 3b), three atomic positions in the third layer of a fcc (111) structure relative to the adsorption site were found to have significantly increased influence on reactivity over any second or third nearest atomic position. This phenomenon cannot be simply explained by the *d*-band model and requires additional theoretical and experimental investigations for a comprehensive understanding.

Strain effects

Strain effects can originate from the mismatch of lattice parameters at the interface of two different metallic phases. The negligible difference in the lattice mismatch has a more significant electronic influence on the shift of the *d*-band center, rather than a direct geometric influence on the orientation of adsorbed reaction intermediates [48]. Thus, a strain effect is classified as an electronic effect, even though it originates from a

Figure 3



Schematic illustration of alloying effects on catalysis, including electronic effects (a–d), geometric effects (e–h), multifunctionality (i–k), and mixing effects (l–n).

“geometric” factor. Strain effects are commonly observed in core–shell structures due to the crystal lattice mismatch of the core and the shell. They can further be classified as compressive strain when the lattice parameters of the core structure are smaller than those of the shell (Figure 3c), or as tensile strain when they are larger (Figure 3d). Recent ORR studies on Pt-lanthanide alloys [49**] and Cu/Pt near-surface alloys [50] provide experimental evidence of the volcano relation in electrocatalysis achieved through fine-tuning of strain in a Pt overlayer.

Geometric effects

Ensemble effects

In addition to the electronic structure, the specific arrangement of the surface atoms (atomic ensembles) acting as an active site is crucial for heterogeneous catalysis. Depending on the atomic radii, the incorporation of a second metal into the structure of the base

metal (M) results in a modification of both the coordination number in the M–M coordination shell (Figure 3e) and the size of the M ensemble (Figure 3f), which has a direct influence on the adsorption configurations of chemical species involved in the reaction.

Steric effects

While electronic and geometric effects can be associated with both alloys and intermetallic compounds, steric and ordering effects are unique to intermetallic compounds. Owing to their ordered atomic arrangement, the different constituent atoms of intermetallic compounds are regularly distributed within the crystal lattice (Figure 3g). This strong preferential site occupation, known as “site equality” [51], can be modified to favor specific reaction pathways over others by providing favorable adsorption configurations via elemental substitution. The establishment of such a precisely controlled atomic environment can introduce steric constraints to some specific

adsorption configurations, consequently enabling controlled stereoselective reactions.

Ordering effects

For the same elemental compositions, certain metallic systems can either form single-phase disordered alloys or ordered intermetallic compounds. An example is the Pt_3M and PtM_3 intermetallic phases and the Pt-M alloy phase in the Pt-M system, where $\text{M} = \text{Fe}, \text{Ni}, \text{Co}$ (Pt-Fe phase diagram in Figure 1). Typically, the intermetallic phase exhibits higher activity than the alloy phase. Since the chemical composition and the crystal structure of both phases are similar, their electronic structure is more or less alike. The enhanced activity of the intermetallic phase is attributed to the “ordering effect” [52], a unique property of intermetallic compounds [53–55]. The origin of this effect can be explained by maximizing the number of Pt-M contacts. The ordered structure of intermetallic compounds has a larger number of nearest-neighbor contacts between the first and the second metals compared to any disordered alloy structure (Figure 3h). This establishes a platform for maximum charge transfer between different constituents, thus resulting in improved catalytic properties.

Multifunctional effects

Multifunctional effects (Figure 3i and j) are defined as effects that cannot be classified as electronic or geometric. They can be promoted by increasing the number of metallic components, which is beneficial for multi-step reactions. In conventional binary systems, they are known as *bifunctional effect* or *bifunctional mechanism* (Figure 3i). The poisoning of Pt active sites during oxidation of small organic molecules by strongly adsorbed CO is a typical example of bifunctionality in electrocatalysis [56]. The incorporation of more oxophilic metals with less affinity for CO facilitates the adsorption of oxygen species, significantly lowering the energy barrier for the complete oxidation of adsorbed CO to CO_2 . In high entropy materials, the presence of multiple active sites from different elements enhances the catalytic properties by facilitating simultaneous reactions and/or reaction steps [57]. Remarkably, it provides another option to break the limitation of the linear scaling relationships in electrocatalysis by choosing the appropriate crystal structure and elemental composition to design multinary systems with maximized multifunctionality (Figure 3k). Moreover, differences in electronic properties, such as electronegativity among the constituent elements induce strong local electron interactions, which can convert inactive sites to active sites in electrocatalysis [58**].

High entropy mixing effects

The formation of thermodynamically stable phases is a competition process between enthalpy and entropy ($\Delta G = \Delta H - T\Delta S$). The configurational entropy (ΔS_{mix}) can be expressed as: ($\Delta S_{\text{mix}} = R \ln n$) where R

and n are the gas constant and the number of constituent elements, respectively. Hence, $\Delta S_{\text{mix}} = 1.39R$ and $1.61R$ for equiatomic alloys with four and five elements, respectively. When the number of constituent elements increases, the configurational entropy (ΔS_{mix}) can dominate and stabilize the phase at high temperature, as the entropy term ($-T\Delta S$) becomes sufficiently negative to overcome the mixing enthalpy (ΔH_{mix}) and make the mixing free energy (ΔG_{mix}) negative. As a result, even combinations of metals with a low miscibility or a large miscibility gap in the binary phase diagrams tend to mix well at high temperatures and form stable single-phase alloys as the number of constituent elements increases (Figure 3l, m). This leads to an indirect effect on electrocatalysis by providing additional platforms with various compositions and electronic configurations, thus yielding new possibilities for binding energies and potentially enhanced catalytic properties.

Disentangling electronic and geometric effects

Electronic and geometric effects play a crucial role in the electrocatalytic properties of materials. However, disentangling these effects is challenging, as they are often interrelated due to their coexistence in multi-metal catalysts. Consequently, enhanced properties are frequently ascribed to synergistic or “cocktail” effects, without a clear explanation of the role of alloying and the distinct contribution of each element. In literature, several approaches have been proposed to address this issue, among them the gradual substitution in isostructural intermetallic compounds [59**]. In this approach, the substitution of elements from the same group allows for a stepwise variation of the unit cell parameters for the same number of valence electrons. Conversely, substitution within the same period by neighboring elements enables a systematic variation of the number of valence electrons with negligible changes in geometrical parameters. Substitution by varying both period and group allows for addressing electronic and geometric effects simultaneously. This approach is also applicable to complex solid solutions, providing insights into whether the reaction is predominantly influenced by electronic and/or geometric factors [60]. Understanding these fundamental contributions is essential and lays the foundation for materials design in electrocatalysis through a knowledge-based approach. This involves the development of appropriate descriptors for electronic and geometric effects, along with a comprehensive understanding of their complex interactions.

Special electrocatalytic attributes of high-entropy intermetallic compounds

After classifying various types of multi-metallic materials and delving further into their design principles for electrocatalysis, this section provides a comparative analysis of the distinctive properties of HEIMCs in relation to intermetallic compounds, substitutional alloys, and HEAs. In the case of HEIMCs, the formation enthalpy

(ΔH_f) of the base intermetallic compound is negative enough to overcome the mixing effect driven by entropy (ΔS_{mix}). Thus, the formation of HEIMCs is driven by both enthalpy and entropy (Figure 3n). Consequently, these materials can exhibit unique properties originating from both high-entropy materials and intermetallic compounds. Their main advantages over intermetallic compounds and HEAs are summarized in the following.

New electronic properties

Similar to HEAs, the extensive composition space of possible chemical combinations in HEIMCs provides an additional level for tuning electronic properties, which is crucial for electrocatalysis. Importantly, the modification of electronic properties extends beyond the simple *fcc*, *bcc*, and *hcp* crystal structures typical of HEAs. Instead, it encompasses complex crystal structures of intermetallic compounds. This enables a wider exploration of multi-ary combinations arranged in a more diverse array of crystal structures, delving into unexplored territories in electrocatalysis with the potential to unveil new electronic, and consequently, electrocatalytic properties.

Scaling relation

For an efficient catalytic reaction, the catalyst should have a moderate binding energy with reaction intermediates, i.e. neither too weak nor too strong. This is often represented in volcano plots, where the catalytic activity is plotted against the binding energy of a reaction intermediate (Figure 3k). The maximum of the volcano corresponds to the optimal binding energy. The reaction intermediates often interact differently with different types of metal site ensembles on catalytic surfaces. Thus, different scaling relationships may exist for multifunctional surfaces compared to pure metal or oxide surfaces. For high entropy materials, these scaling relationships involve contributions from different constituents, thus increasing the number of independent descriptors required to describe the corresponding binding energies. This provides an extra dimension of flexibility to the volcano plots with more independent variables to optimize binding energies and might lead to the identification of materials with new properties.

Given the constraint of HEAs to the simple *fcc*, *bcc*, and *hcp* crystal structures, the configuration of various multifunctional metal site ensembles on their surface is constrained within these structures. In contrast, HEIMCs, characterized by their complexity in both chemical composition and crystal structure diversity, can serve as a materials platform with more possible ensemble arrangements. Moreover, these ensembles can also be organized into independent crystal sublattices, adding extra layers of flexibility for tuning binding energies. The emerging electronic properties resulting from these chemical and structural complexities in HEIMCs offer promising alternative avenues to overcome the limitations of scaling relationships, paving the way for the

development of new materials beyond the traditional "volcano" paradigm.

Synergy between multifunctionality, steric and ordering effects

Multifunctionality is a distinctive feature of high entropy materials, whereas steric and ordering effects are characteristics of intermetallic compounds. Remarkably, HEIMCs stand out as an exclusive materials platform where these effects can be combined. Multifunctionality arises from the random elemental distribution in one (or more) sublattices, while ordering and steric effects emerge from the ordered distribution on the second sublattice. The crystal structure diversity of HEIMCs allows these effects to be combined in different arrangements, resulting in a wide range of electronic interactions. The ordering effect ensures maximum nearest-neighbor heteroatom contacts between the ordered and the disordered sublattices, leading to improved activity and selectivity. Simultaneously, the randomness of the disordered sublattice provides the necessary multifunctionality. In a synergistic way, this exclusive combination can lead to the activation of some electrocatalytic reactions that may not be as thermodynamically favorable on intermetallic compounds or HEAs alone. Moreover, the partial preferential substitution in the ordered sublattice can lead to achieving the highest site density of single atoms by isolating adjacent metal atoms into single atom sites (site isolation). This allows coupling the catalytic benefits from intermetallic compounds and single-atom catalysts together with the multifunctionality arising from the random distribution in both sublattices. All of these attributes make HEIMCs an appropriate materials platform for a rational design approach of electrocatalytic materials. This involves understanding different reaction steps in the target reaction and tuning electronic and crystal structures of the catalyst. Through the selection of the appropriate metallic components and their crystal structures, a "multidimensional" control of the reaction path towards more selective, active and durable catalytic materials can be achieved.

Summary and outlook

In this minireview, the fundamental concepts underlying the design principles of multi-metal materials for catalysis are summarized. These materials are categorized into disordered solid solutions and ordered intermetallic compounds. Increasing the number of constituent elements in both categories results in the formation of high-entropy alloys and high-entropy intermetallic compounds, respectively. The formation of solid solutions is predominantly driven by entropy, while the formation of intermetallic compounds is driven by enthalpy. Consequently, the formation of high-entropy intermetallic compounds is driven by both enthalpy and entropy. As a result, these materials exhibit

physicochemical properties originating from both high-entropy materials and intermetallic compounds.

The physicochemical properties of multimetallic materials, including their electrocatalytic properties, are governed by four effects: electronic, geometric, multifunctionality, and high entropy (mixing) effects. Multifunctionality arises from the presence of multiple active sites from different elements, which enhances the catalytic properties by facilitating simultaneous reaction steps. This offers an additional approach to designing multinary systems capable of breaking the limitation of the linear scaling relationships in catalysis through the selection of an appropriate crystal structure and elemental composition with maximum multifunctionality. Mixing effects arise from the increase of the mixing entropy through an increase in the number of constituent elements. The increased mixing entropy enhances the miscibility of the elements, resulting in improved stability of the formed phase and the potential development of new, enhanced catalytic properties.

High-entropy materials represent a comparatively novel approach to the design of multi-metallic materials, beyond traditional binary and ternary combinations. In particular, HEIMCs constitute a distinctive class of high-entropy materials inheriting properties from both intermetallic compounds and high-entropy alloys. They hold a significant potential to revolutionize the field of electrocatalysis, serving as an exclusive platform for the synergy of multifunctionality, steric and ordering effects. Nevertheless, achieving a comprehensive understanding of the complex electronic interactions and the individual contributions of each element to overall catalytic properties is required. Unraveling this complexity requires a multidisciplinary approach combining appropriate descriptors for electronic and/or geometric effects in model studies together with high-throughput experimentation and fundamental mechanistic studies.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Wolfgang Schuhmann reports financial support was provided by European Research Council. Wolfgang Schuhmann reports financial support was provided by Deutsche Forschungsgemeinschaft. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

The authors acknowledge the financial contribution of the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (CasCat [833408]), and from the Deutsche Forschungsgemeinschaft (DFG) in the framework of the CRC247 [388390466] and CRC1625 [506711657].

References

Papers of particular interest, published within the period of review, have been highlighted as:

- * of special interest
- ** of outstanding interest

1. Weber T, Dshemuchadse J, Kobas M, Conrad M, Harbrecht B, Steurer W: **Large, larger, largest - a family of cluster-based tantalum copper aluminides with giant unit cells. I. Structure solution and refinement.** *Acta Crystallogr B: Struct. Sci. Cryst. Eng. Mater.* 2009, **65**:308–317.
2. Conrad M, Harbrecht B, Weber T, Jung DY, Steurer W: **Large, larger, largest - a family of cluster-based tantalum copper aluminides with giant unit cells. II. The cluster structure,** *Acta Crystallogr. B. Struct. Sci. Cryst. Eng. Mater.* 2009, **65**:318–325.
3. Armbrüster M, Schlögl R, Grin Y: **Intermetallic compounds in heterogeneous catalysis-a quickly developing field.** *Sci Technol Adv Mater* 2014, **15**, 34803.
4. Batchelor TA, Pedersen JK, Winther SH, Castelli IE, Jacobsen KW, Rossmeisl J: **High-entropy alloys as a discovery platform for electrocatalysis.** *Joule* 2019, **3**:834–845.
5. Lu Z, Chen ZW, Singh CV: **Neural network-assisted development of high-entropy alloy catalysts: decoupling ligand and coordination effects.** *Matter* 2020, **3**:1318–1333.
6. Sun Y, Dai S: **High-entropy materials for catalysis: a new frontier.** *Sci Adv* 2021, **7**.
7. Wang B, Yao Y, Yu X, Wang C, Wu C, Zou Z: **Understanding the enhanced catalytic activity of high entropy alloys: from theory to experiment.** *J Mater Chem A* 2021, **9**:19410–19438.
8. Wang K, Huang J, Chen H, Wang Y, Yan W, Yuan X, Song S, Zhang J, Sun X: **Recent progress in high entropy alloys for electrocatalysts.** *Electrochem Energy Rev* 2022, **5**:1–28.
9. Xin Y, Li S, Qian Y, Zhu W, Yuan H, Jiang P, Guo R, Wang L: **High-entropy alloys as a platform for catalysis: progress, challenges, and opportunities.** *ACS Catal* 2020, **10**: 11280–11306.
10. Yang X, Guo R, Cai R, Ouyang Y, Yang P, Xiao J: **Engineering high-entropy materials for electrocatalytic water splitting.** *Int J Hydrogen Energy* 2022, **47**:13561–13578.
11. Chaudhary V, Chaudhary R, Banerjee R, Ramanujan RV: **Accelerated and conventional development of magnetic high entropy alloys.** *Mater Today* 2021, **49**:231–252.
12. Kumari P, Gupta AK, Mishra RK, Ahmad MS, Shahi RR: **A comprehensive review: recent progress on magnetic high entropy alloys and oxides.** *J Magn Magn Mater* 2022, **554**, 169142.
13. Chen J, Zhou X, Wang W, Liu B, Lv Y, Yang W, Xu D, Liu Y: **A review on fundamental of high entropy alloys with promising high-temperature properties.** *J Alloys Compd* 2018, **760**: 15–30.
14. George EP, Curtin WA, Tasan CC: **High entropy alloys: a focused review of mechanical properties and deformation mechanisms.** *Acta Mater* 2020, **188**:435–474.
15. Li W, Xie Di, Li D, Zhang Y, Gao Y, Liaw PK: **Mechanical behavior of high-entropy alloys.** *Prog Mater Sci* 2021, **118**, 100777.
16. Sathiyamoorthi P, Kim HS: **High-entropy alloys with heterogeneous microstructure: processing and mechanical properties.** *Prog Mater Sci* 2022, **123**, 100709.
17. Miracle DB, Senkov ON: **A critical review of high entropy alloys and related concepts.** *Acta Mater* 2017, **122**:448–511.

18. Bishop-Moser J, Miracle D: *Manufacturing high entropy alloys: pathway to industrial competitiveness*. 2018.
 19. Löffler T, Ludwig A, Rossmeisl J, Schuhmann W: **What makes high-entropy alloys exceptional electrocatalysts?** *Angew Chem, Int Ed* 2021, **60**:26894–26903.
 20. Löffler T, Savan A, Garzón-Manjón A, Meisch M, Scheu C, Ludwig A, Schuhmann W: **Toward a paradigm shift in electrocatalysis using complex solid solution nanoparticles.** *ACS Energy Lett* 2019, **4**:1206–1214.
 21. Liu CT, Stiegler JO: **Ductile ordered intermetallic alloys.** *Science* 1984, **226**:636–642.
 22. Liu CT: **Physical metallurgy and mechanical properties of ductile ordered alloys (Fe, Co, Ni)₃V.** *Int Met Rev* 1984, **29**: 168–194.
 23. Firstov G, Timoshevski A, Kosorukova T, Koval Y, Matviychuk Y, Verhovlyuk P: **Electronic and crystal structure of the high entropy TiZrHfCoNiCu intermetallics undergoing martensitic transformation.** *MATEC Web Conf.* 2015, **33**:6006.
 24. Firstov GS, Kosorukova TA, Koval Y, Odnosum VV: **High entropy shape memory alloys.** *Mater Today Proc* 2015, **2**: S499–S503.
 25. Firstov GS, Kosorukova TA, Koval YN, Verhovlyuk PA: **Directions for high-temperature shape memory alloys' improvement: straight way to high-entropy materials?** *Shap. Mem. Superelasticity* 2015, **1**:400–407.
 26. Yang T, Cao BX, Zhang TL, Zhao YL, Liu WH, Kong HJ, Luan JH, Kai JJ, Kuo W, Liu CT: **Chemically complex intermetallic alloys: a new frontier for innovative structural materials.** *Mater Today* 2022, **52**:161–174.
 27. Wang H, He Q-F, Yang Y: **High-entropy intermetallics: from alloy design to structural and functional properties.** *Rare Met* 2022, **41**:1989–2001.
 28. Zhou N, Jiang S, Huang T, Qin M, Hu T, Luo J: **Single-phase high-entropy intermetallic compounds (HEICs): bridging high-entropy alloys and ceramics.** *Sci Bull* 2019, **64**:856–864.
 29. Liu J, Wang X, Singh A, Xu H, Kong F, Yang F: **The Evolution of Intermetallic compounds in high-entropy alloys: from the secondary phase to the main phase.** *Metals* 2021, **11**:2054.
 30. Wright AJ, Luo J: **A step forward from high-entropy ceramics to compositionally complex ceramics: a new perspective.** *J Mater Sci* 2020, **55**:9812–9827.
 31. Ostovari Moghaddam A, Fereidonnejad R, Cabot A: **Semi-ordered high entropy materials: the case of high entropy intermetallic compounds.** *J Alloys Compd* 2023, **960**, 170802.
 32. Ding Z, Bian J, Shuang S, Liu X, Hu Y, Sun C, Yang Y: **High entropy intermetallic-oxide core-shell nanostructure as superb oxygen evolution reaction catalyst.** *Adv. Sustain. Syst.* 2020, **4**, 1900105.
- This work represents the first report on the use of a high entropy intermetallic phase as an electrocatalyst.
33. Jia Z, Yang T, Sun L, Zhao Y, Li W, Luan J, Lyu F, Zhang L-C, Kruzic JJ, Kai J-J, Huang JC, Lu J, Liu CT: **A Novel multinary intermetallic as an active electrocatalyst for hydrogen evolution.** *Adv Mater* 2020, **32**, 2000385.
 34. Wang Y, Zhang X-Y, He H, Chen J-J, Liu B: **Ordered mesoporous high-entropy intermetallics for efficient oxygen reduction electrocatalysis.** *Adv Energy Mater* 2023, 2303923.
 35. Cui M, Yang C, Hwang S, Yang M, Overa S, Dong Q, Yao Y, Brozena AH, Cullen DA, Chi M, Blum TF, Morris D, Finrock Z, Wang X, Zhang P, Goncharov VG, Guo X, Luo J, Mo Y, Jiao F, Hu L: **Multi-principal elemental intermetallic nanoparticles synthesized via a disorder-to-order transition.** *Adv Sci* 2022, **8**, eabm4322.
 36. Feng G, Ning F, Pan Y, Chen T, song J, Wang Y, Zou R, Su D, Xia D: **Engineering structurally ordered high-entropy intermetallic nanoparticles with high-activity facets for oxygen reduction in practical fuel cells.** *J Am Chem Soc* 2023, **145**: 11140–11150.
 37. Shi H, Sun X-Y, Liu Y, Zeng S-P, Zhang Q-H, Gu L, Wang T-H, Han G-F, Wen Z, Fang Q-R, Lang X-Y, Jiang Q: **Multicomponent intermetallic nanoparticles on hierarchical metal network as versatile electrocatalysts for highly efficient water splitting.** *Adv Funct Mater* 2023, **33**, 2214412.
 38. Soltani N, Rahman JU, Carvalho PA, Finstad T: **Towards multicomponent intermetallic nanoparticles as efficient and low-cost catalysts.** *J Alloys Compd* 2023, **956**, 170254.
 39. Zhang Q, Shen T, Song M, Wang S, Zhang J, Huang X, Lu S, Wang D: **High-entropy L12-Pt(FeCoNiCuZn)₃ intermetallics for ultrastable oxygen reduction reaction.** *J Energy Chem* 2023, **86**:158–166.
 40. Wang Y, Gong N, Liu H, Ma W, Hippalgaonkar K, Liu Z, Huang Y: **Ordering-dependent hydrogen evolution and oxygen reduction electrocatalysis of high-entropy intermetallic Pt₄FeCo-CuNi.** *Adv Mater* 2023, **35**, 2302067.
 41. Wang D, Chen Z, Wu Y, Huang Y-C, Tao L, Chen J, Dong C-L, Singh CV, Wang S: **Structurally ordered high-entropy intermetallic nanoparticles with enhanced C–C bond cleavage for ethanol oxidation.** *SmartMat* 2023, **4**, e1117.
 42. Liu J, Lee C, Hu Y, Liang Z, Ji R, Soo XYD, Zhu Q, Yan Q: **Recent progress in intermetallic nanocrystals for electrocatalysis: from binary to ternary to high-entropy intermetallics.** *Smart-Mat* 2023, **4**, e1210.
 43. Yang C-L, Wang L-N, Yin P, Liu J, Chen M-X, Yan Q-Q, Wang Z-S, Xu S-L, Chu S-Q, Cui C, Ju H, Zhu J, Lin Y, Shui J, Liang H-W: **Sulfur-anchoring synthesis of platinum intermetallic nanoparticle catalysts for fuel cells.** *Science* 2021, **374**:459–464.
- This work reports an effective synthesis method for a wide range of Pt-based HEIMC nanoparticles. The strong Pt–S bonds within sulfur-doped carbon supports stabilize small Pt-alloy nanoparticles (<5 nm) to annealing temperatures up to 1000 °C. A total of 46 Pt-M combinations (20 binary, 10 ternary, 10 quaternary, 5 quinary, and 1 senary) were synthesized successfully and tested for the oxygen reduction reaction.
44. Hammer B, Nørskov JK: **Electronic factors determining the reactivity of metal surfaces.** *Surf Sci* 1995, **343**:211–220.
 45. Sabatier P: **Hydrogénations et déshydrogénations par catalyse.** *Ber. Dtsch. Chem. Ges.* 1911, **44**:1984–2001.
 46. Stamenkovic VR, Mun BS, Arenz M, Mayrhofer KJJ, Lucas CA, Wang G, Ross PN, Markovic NM: **Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces.** *Nat Mater* 2007, **6**:241–247.
- In this work, a series of Pt3M (M = Ni, Co, Fe, Ti, V) alloys were used to demonstrate the volcano relationship in electrocatalysis between the experimentally determined surface electronic structure (d-band center) and activity for the oxygen-reduction reaction.
47. Clausen CM, Batchelor TAA, Pedersen JK, Rossmeisl J: **What Atomic positions determines reactivity of a surface? Long-range, directional ligand effects in metallic alloys.** *Adv Sci* 2021, **8**, 2003357.
- This work reports a new type of ligand effects, The so-called “Long-range, directional ligand effects.” Statistical analysis of 2000 DFT calculations combined with host/guest calculations, showed that three atomic positions in the third layer of an fcc (111) metallic structure fourth-nearest to the adsorption site display significantly increased influence on reactivity over any second or third nearest atomic positions.
48. Mavrikakis M, Hammer B, Nørskov JK: **Effect of strain on the reactivity of metal surfaces.** *Phys Rev Lett* 1998, **81**: 2819–2822.
 49. Escudero-Escribano M, Malacrida P, Hansen MH, Vej-Hansen UG, Velázquez-Palenzuela A, Tripkovic V, Schiøtz J, Rossmeisl J, Stephens IEL, Chorkendorff I: **Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction.** *Science* 2016, **352**:73–76.
- This work presents a new set of highly active Pt-alloys for ORR. The lattice parameter of the bulk alloys is systematically controlled by lanthanide contraction to modulate the strain of a Pt overlayer, thereby influencing the activity, stability, and reactivity of these materials.
50. Jensen KD, Tymoczko J, Rossmeisl J, Bandarenka AS, Chorkendorff I, Escudero-Escribano M, Stephens IEL: **Elucidation of the oxygen reduction volcano in alkaline media using**

- a copper-platinum (111) alloy. *Angew Chem Int Ed* 2018, **57**: 2800–2805.
51. Karamad M, Tripkovic V, Rossmeisl J: **Intermetallic alloys as CO electroreduction catalysts—role of isolated active sites.** *ACS Catal* 2014, **4**:2268–2273.
 52. Watanabe M, Tsurumi K, Mizukami T, Nakamura T, Stonehart P: **Activity and stability of ordered and disordered Co-Pt alloys for phosphoric acid fuel cells.** *J Electrochem Soc* 1994, **141**: 2659–2668.
 53. Kim J, Lee Y, Sun S: **Structurally ordered FePt nanoparticles and their enhanced catalysis for oxygen reduction reaction.** *J Am Chem Soc* 2010, **132**:4996–4997.
 54. Hodnik N, Jeyabharathi C, Meier JC, Kostka A, Phani KL, Rečnik A, Bele M, Hočevar S, Gabersček M, Mayrhofer KJJ: **Effect of ordering of PtCu₃ nanoparticle structure on the activity and stability for the oxygen reduction reaction.** *Phys Chem Chem Phys* 2014, **16**:13610–13615.
 55. Koh S, Toney MF, Strasser P: **Activity–stability relationships of ordered and disordered alloy phases of Pt₃Co electrocatalysts for the oxygen reduction reaction (ORR).** *Electrochim Acta* 2007, **52**:2765–2774.
 56. Wang K, Gasteiger HA, Markovic NM, Ross PN: **On the reaction pathway for methanol and carbon monoxide electrooxidation on Pt-Sn alloy versus Pt-Ru alloy surfaces.** *Electrochim Acta* 1996, **41**:2587–2593.
 57. Löffler T, Waag F, Gökce B, Ludwig A, Barcikowski S, Schuhmann W: **Comparing the activity of complex solid solution electrocatalysts using inflection points of voltammetric activity curves as activity descriptors.** *ACS Catal* 2021, **11**: 1014–1023.
 58. Zhu H, Sun S, Hao J, Zhuang Z, Zhang S, Wang T, Kang Q, Lu S, Wang X, Lai F, Liu T, Gao G, Du M, Wang D: **A high-entropy atomic environment converts inactive to active sites for electrocatalysis.** *Energy Environ Sci* 2023, **16**:619–628.
- This study proposes a high-entropy atomic environment regulation strategy to convert inactive to active sites for electrocatalysis. Integrating the low-electronegativity Mn and high-electronegativity Cu with Fe, Co, and Ni-base metals to form a FeCoNiCuMn HEA nanoparticles (NPs) would drive the inactive Cu to electron-enriched active sites through the strong local electron interaction induced by electronegativity differences.
59. Zerdoumi R, Matselko O, Rößner L, Sarkar B, Grin Y, Armbrüster M: **Disentangling electronic and geometric effects in electrocatalysis through substitution in isostructural intermetallic compounds.** *J Am Chem Soc* 2022, **144**: 8379–8388.
- This work reports a systematic approach for the evaluation of individual and combined contributions of electronic and geometric effects in electrocatalysis. Three substitutional series of isostructural intermetallic compounds were used to control the unit cell volume and the number of valence electrons per unit cell to establish a systematic structure–property correlation in electrocatalysis.
60. Zerdoumi R, Savan A, Amalraj M, Tetteh EB, Lourens F, Krysiak OA, Junqueira JRC, Ludwig A, Schuhmann W: **Combinatorial screening of electronic and geometric effects in compositionally complex solid solutions toward a rational design of electrocatalysts.** *Adv Energy Mater* 2024, **14**, 2302177.