Review Proposal

Main Information:

1. Proposed title: High-Entropy Alloys and Oxides as Catalysts for Water-Splitting and Fuel Cells: Synthesis, Characterization, Applications and Prospect
2. Type of Review: Review
3. Proposed submission date:2025/2/xx

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Details regarding the proposed review:

1. A short (~400-word) description of the focused topic

High-entropy materials (HEMs) due to their exceptional physicochemical properties, which include a unique electronic structure, outstanding catalytic performance, and remarkable electrochemical stability, which position HEMs as promising catalysts for applications such as water-splitting and fuel cells, underscoring their potential in electrocatalysis. Given the significant development potential and promising future of HEMs as electrocatalysts, research in this field is rapidly expanding. However, despite numerous innovative advancements, the absence of comprehensive summaries on HEMs as electrocatalysts hinders further progress. HEMs possess distinctive features like high entropy, lattice distortion, sluggish diffusion, and the cocktail effect. These characteristics significantly influence the electrocatalytic performance of HEMs, making them promising candidates to replace traditional noble metal catalysts. A controllable and facile synthesis method is crucial for the cost-effective preparation and widespread application of HEMs, as it forms the foundation for large-scale utilization. To achieve superior performance, HEM catalysts are typically designed at the nanometer scale or with nanometer-level surface topography, enhancing specific surface area and providing more active sites. Due to the inherent multi-component nature of HEMs, a broad selection of raw materials and diverse preparation strategies are available, offering extensive flexibility in synthesis approaches. The influence of each component element on the electronic structure of high-entropy materials is crucial in determining the selection of active sites during catalytic processes, directly impacting their catalytic performance. The microstructure of these materials dictates their specific surface area and adsorption capabilities, significantly influencing their catalytic efficacy. In the characterization and analysis of high-entropy materials, the complexity introduced by multiple constituent elements poses significant challenges. While basic characterization methods can determine and confirm morphology, composition, and electronic states, their limited resolution often hampers the ability to decouple contributions from individual elements accurate. High-entropy materials (HEMs), characterized by their multielement composition space, diverse active sites, and high-entropy stabilized structure, exhibit exceptional performance in electrocatalysis. These unique attributes not only enhance catalytic efficiency but also impart remarkable stability under operational conditions. Given these advantages, HEMs hold tremendous potential for further development across various applications. To unlock the full potential of HEMs in electrocatalysis and beyond, integrating their research with emerging technologies is both a challenge and an opportunity. By leveraging advancements in artificial intelligence, advanced characterization techniques, nanotechnology, additive manufacturing, and sustainable practices, we can accelerate innovation and optimize the performance of high-entropy catalysts.

2. Please provide a table of contents for the Review/Spotlight/Perspective. Briefly discuss the content of each section and highlight related key references.

Contents

1. Introduction

This section provides an overview of High-entropy materials as catalysts, highlighting their significance and potential impact in the field of electrocatalysis and energy.

2.Fundamentals of high-entropy materials as catalysts

This section introduces the basic principles and unique physical and chemical properties of HEMs, and then discusses the design of HEMs catalysts based on the above theoretical basis, such as composition and structure regulation.

2.1. Definition of High-Entropy Materials

Key References:

(1) George, E.P., Raabe, D., Ritchie, R.O.: High-entropy alloys. Nat Rev Mater. 4, 515–534 (2019). https://doi.org/10.1038/s41578-019-0121-4

2.2. Core features of High-Entropy Materials

Key References:

(2) Wang, L., Zhang, L., Lu, X., Wu, F., Sun, X., Zhao, H., Li, Q.: Surprising cocktail effect in high entropy alloys on catalyzing magnesium hydride for solid-state hydrogen storage. Chem Eng J. 465, 142766 (2023). https://doi.org/10.1016/j.cej.2023.142766.

2.3. Design Basis of High-Entropy Materials

Key References:

(3) Gao, Y., Song, Z., Hu, H., Mei, J., Kang, R., Zhu, X., Yang, B., Shao, J., Chen, Z., Li, F., Zhang, S., Lou, X.: Optimizing high-temperature energy storage in tungsten bronze-structured ceramics via high-entropy strategy and bandgap engineering. Nat Commun. 15, 5869 (2024).

3. Synthesis Strategies of High-Entropy Materials

In this section, synthesis methods are divided into dry synthesis and wet synthesis according to whether there is a solution system involved in the synthesis process. In view of the particularity of deposition techniques such as magnetron sputtering in dry synthesis, we further discuss the sputtering and non-sputtering methods in dry synthesis. By examining the selection of raw materials, the basic principle of each synthesis method, and the description of product morphology and properties, the advantages and disadvantages of different methods are compared.

3.1. Dry Synthesis of High-Entropy Catalysts

Key References:

(6) Chen Z., Zhang T., Gao X., Huang Y., Qin X., Wang Y., Zhao K., Peng X., Zhang C., Liu L., Zeng M., Yu H.: Engineering Microdomains of Oxides in High-Entropy Alloy Electrodes toward Efficient Oxygen Evolution. Adv Mater. 33, 2101845 (2021).

(7) Sun, Y., Zhang, W., Zhang, Q., Li, Y., Gu, L., Guo, S.: A general approach to high-entropy metallic nanowire electrocatalysts. Matter-Us. 6, 193–205 (2023).

3.2. Wet Synthesis of High-Entropy Catalysts

Key References:

(8) Wang, S., Huo, W., Fang, F., Xie, Z., Shang, J.K., Jiang, J.: High entropy alloy/C nanoparticles derived from polymetallic MOF as promising electrocatalysts for alkaline oxygen evolution reaction. Chem Eng J. 429, 132410 (2022).

(9) Miao, K., Jiang, W., Chen, Z., Luo, Y., Xiang, D., Wang, C., Kang, X.: Hollow-Structured and Polyhedron-Shaped High Entropy Oxide toward Highly Active and Robust Oxygen Evolution Reaction in a Full pH Range. Adv Mater. 36, 2308490 (2024).

4. Characterization and Calculation of High-Entropy Catalysts.

This section introduces basic characterization methods used to determine and confirm the morphology, composition, and electronic states of materials. In addition, advanced high-precision techniques are also be introduced to obtaining a comprehensive understanding of atomic arrangement, bonding coordination, and electronic properties in high-entropy nanoparticles.

4.1. Advanced Characterization Techniques of High-Entropy Catalysts

Key References:

(10) Zimmermann, P., Peredkov, S., Abdala, P.M., DeBeer, S., Tromp, M., Müller, C., Van Bokhoven, J.A.: Modern X-ray spectroscopy: XAS and XES in the laboratory. Coordin Chem Rev. 423, 213466 (2020).

4.2. Electronic Structure Analysis of High-Entropy Catalysts

Key References:

(11) Ding, J., Wu, D., Zhu, J., Huang, S., Rodríguez-Hernández, F., Chen, Y., Lu, C., Zhou, S., Zhang, J., Tranca, D., Zhuang, X.: High-entropy carbons: From high-entropy aromatic species to single-atom catalysts for electrocatalysis. Chem Eng J. 426, 131320 (2021).

4.3. Density Functional Theory Calculation of High-Entropy Catalysts

Key References:

(12) Li H., Han Y., Zhao H., Qi W., Zhang D., Yu Y., Cai W., Li S., Lai J., Huang B., Wang L.: Fast site-to-site electron transfer of high-entropy alloy nanocatalyst driving redox electrocatalysis. Nat Commun. 11, 5437 (2020).

5. The Electrochemical Performance of High-Entropy Catalysts

In this section we introduce the application of high entropy catalysts in three important reactions of water-splitting and fuel cell, HER, OER and ORR.

5.1. Hydrogen Evolution Reaction

Key References:

(13) Wan, Y., Wei, W., Ding, S., Wu, L., Qin, H., Yuan, X.: A Multi-Site Synergistic Effect in High-Entropy Alloy for Efficient Hydrogen Evolution. Adv Funct Mater. 2414554 (2024).

5.2. Oxygen Evolution Reaction

Key References:

(14) Ding, Y., Wang, Z., Liang, Z., Sun, X., Sun, Z., Zhao, Y., Liu, J., Wang, C., Zeng, Z., Fu, L., Zeng, M., Tang, L.: A Monolayer High-Entropy Layered Hydroxide Frame for Efficient Oxygen Evolution Reaction. Adv Mater. 2302860 (2023).

5.3. Oxygen Reduction Reaction

Key References:

(15) He, R., Yang, L., Zhang, Y., Jiang, D., Lee, S., Horta, S., Liang, Z., Lu, X., Ostovari Moghaddam, A., Li, J., Ibáñez, M., Xu, Y., Zhou, Y., Cabot, A.: A 3d-4d-5d High Entropy Alloy as a Bifunctional Oxygen Catalyst for Robust Aqueous Zinc–Air Batteries. Adv Mater. 2303719 (2023).

6. Summary and Prospects

This section addresses the current challenges and potential future directions for research on HEMs catalysts, including mechanism of high-entropy catalysts, component regulation and synthesis strategy, prospect of applications and development, and environmental impact and sustainability

6.1. Mechanism of High-Entropy Catalysts

6.2. Component Regulation and Synthesis Strategy

6.3. Prospect of Applications and Development

6.4. Environmental Impact and Sustainability

3. What is the significance of the proposed topic?

The topic of HEMs catalyst holds significant importance in the field of energy and electrocatalysis for several reasons: (1) Enhanced Catalytic Performance: HEMs exhibit superior catalytic properties due to their complex multi-component nature. The high configurational entropy from random distribution of elements leads to diverse atomic environments, which can significantly enhance catalytic efficiency in processes like hydrogen evolution, oxygen reduction, and other electrochemical reactions. (2) Increased Stability: HEMs are typically more thermodynamically stable than traditional alloys or materials, making them more resistant to degradation under harsh operating conditions. This stability is crucial for long-term applications in energy conversion and storage devices, such as fuel cells and batteries. (3) Tunability of Electronic Structure: The unique atomic distribution in HEMs allows for the adjustment of electronic properties by altering the composition. This tunability is valuable for optimizing the material for specific catalytic reactions, improving both efficiency and selectivity. (4) High Performance in Energy Conversion: In electrocatalysis, HEMs can drive critical reactions like HER, OER, and ORR. These reactions are central to renewable energy technologies, such as water splitting for hydrogen production and fuel cells.

4. Which communities are likely to find your review appealing?

Some of the communities that may find this review appealing include: (1) Catalysis and Surface Chemistry: Scientists and engineers focused on catalytic processes would be highly interested in the unique properties of HEMs. The review would appeal to those working on heterogeneous catalysis, electrocatalysis, and biocatalysis, as these materials offer new avenues for improving catalytic activity, stability, and selectivity in key reactions like HER,OER and ORR. (2) Energy and Renewable Energy: Electrochemical energy conversion and storage are major applications of high-entropy catalysts, so researchers in fields such as fuel cells, batteries, and supercapacitors would be very interested. This includes both hydrogen economy proponents and those working on solar energy, energy storage systems, and sustainable energy technologies. (3) Materials Science and Engineering: Materials scientists working on alloys, nanomaterials, and advanced composites would find this review useful in understanding how high-entropy alloys (HEAs) and nanoparticles are synthesized, characterized, and applied in a variety of technologies. Researchers in material design, particularly those interested in multicomponent systems, would also be drawn to the review's insights into structure-property relationships in high-entropy materials. (4) Nanotechnology and Nanomaterials Researchers: Researchers in nanoscience and nanotechnology would be intrigued by high-entropy nanoparticles due to their tunable properties and potential for application in catalysis, sensing, and energy conversion. The unique atomic arrangements in high-entropy nanoparticles open up exciting opportunities for nanoengineering and the design of functional nanomaterials.

5. A list of recent *reviews* published in the last five years in the proposed topic area published by the submitting authors, and how the proposed review will differ:

(1) Ren, J.-T., Chen, L., Wang, H.-Y., Yuan, Z.-Y.: High-entropy alloys in electrocatalysis: from fundamentals to applications. Chem Soc Rev. 52, 8319–8373 (2023). https://doi.org/10.1039/D3CS00557G

(2) Akrami S., Edalati P., Fuji M., Edalati K.: High-entropy ceramics: Review of principles, production and applications. Materials Science and Engineering: R: Reports. 146, 100644 (2021). https://doi.org/10.1016/j.mser.2021.100644

(3) Sun, Y., Dai, S.: High-entropy materials for catalysis: A new frontier. Sci Adv. 7, eabg1600 (2021). https://doi.org/10.1126/sciadv.abg1600

(4) Amiri, A., Shahbazian-Yassar, R.: Recent progress of high-entropy materials for energy storage and conversion. J Mater Chem A. 9, 782–823 (2021). https://doi.org/10.1039/D0TA09578H

(5) Chen, Y., Fu, H., Huang, Y., Huang, L., Zheng, X., Dai, Y., Huang, Y., Luo, W.: Opportunities for High-Entropy Materials in Rechargeable Batteries. Acs Mater Lett. 3, 160–170 (2021). https://doi.org/10.1021/acsmaterialslett.0c00484

(6) Hussain, I., Lamiel, C., Ahmad, M., Chen, Y., Shuang, S., Javed, M.S., Yang, Y., Zhang, K.: High entropy alloys as electrode material for supercapacitors: A review. J Energy Storage. 44, 103405 (2021). https://doi.org/10.1016/j.est.2021.10340

In previous reviews, the focus has typically been on the application of specific classes of high-entropy materials in catalysis and energy, or on particular reactions. For example, some reviews have addressed HEAs as catalysts for various reactions, or the use of high-entropy materials in hydrogen evolution. However, in this review, we aim to provide a comprehensive summary of the synthesis, characterization, applications, and challenges of high-entropy materials in the contexts of water-splitting and fuel cells. This review holds significant importance for guiding the development of high-entropy material catalysts, particularly for key reactions such as HER, OER, and ORR.