Motif-driven scalable design of rutile high-entropy oxide catalysts for oxygen evolution reaction

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1. Introduction

The discovery of efficient multi-cation oxide catalysts is hindered by the exponential growth of chemical space arising from compositional diversity, surface heterogeneity, and competing reaction pathways, rendering brute-force density functional theory (DFT) enumeration impractical. Here, to bypass this computational bottleneck, we develop a motif-based analytical framework for the scalable prediction of adsorption energetics on rutile-type multi-cation oxides. Using physically constrained multitask symbolic regression by sure independence screening and sparsifying operator (SISSO), we derive a unified analytical expression that maps the adsorption energies of key oxygen evolution reaction (OER) intermediates directly from intrinsic elemental properties and local coordination motifs. This model enables nearly zero-DFT-cost prediction of catalytic activity and reaction pathway preferences across vast compositional spaces. Subsequent large-scale screening identifies cost-performance Pareto-optimal oxides, and experimental validation confirms the predicted activity trends. This work establishes an interpretable paradigm for scalable framework for catalyst screening, overcoming the limitations of explicit first-principles calculations in complex multi-element systems.

2. Substantial section

The rational design of multi-cation rutile oxides as oxygen evolution reaction (OER) catalysts is fundamentally constrained by the explosive growth of chemical and configurational space. As the number of constituent elements increases, the number of possible compositions grows combinatorially, while each composition hosts a multitude of chemically nonequivalent surface sites arising from diverse local coordination environments[1]. This complexity is further amplified by the coexistence of multiple reaction mechanisms on oxide surfaces, including the conventional adsorbate-evolving mechanism (AEM) and lattice-oxygen–involved pathways such as the bridging oxygen activation/deactivation (BOAD) mechanism.[2] Together, these factors render the surface chemistry of multi-cation metal oxides intrinsically heterogeneous and highly nonuniform.

In principle, density functional theory (DFT) provides a rigorous framework to evaluate adsorption energetics and catalytic activity. However, the exponential proliferation of compositions and surface motifs makes brute-force DFT enumeration computationally infeasible. The fundamental bottleneck is therefore not whether a single surface configuration can be calculated, but whether reliable adsorption energies and activity rankings can be obtained at scale across thousands of compositions and chemically distinct sites. Without such scalable access to adsorption energetics, high-throughput screening of diverse multi-element systems remains largely intractable.

Since explicit DFT evaluation across this astronomical number of specific configurations is practically impossible, the ultimate imperative is to discover a universal analytical expression that maps local coordination motifs directly to adsorption energetics. Such an equation would recognize that adsorption energies are not macroscopic material constants, but local-motif-dependent quantities governed by the central active site and the modulating perturbations from its nearest-neighbor cations.

Here, to definitively bypass the severe computational bottleneck of DFT, we develop a general and interpretable analytical framework based on this motif-centric perspective (Fig 1). Rather than constructing black-box machine learning models, we employ multitask symbolic regression via the sure independence screening and sparsifying operator (SISSO)[3, 4] on a limited calibration dataset. This allows us to distill a sparse, unified, and physically interpretable mathematical equation that governs the adsorption energies of key OER intermediates (*O, *OH, and *OOH) using only intrinsic elemental properties and local coordination descriptors.[5]

Because the theoretical OER overpotential can be directly derived from the adsorption free energies of these intermediates, this unified analytical expression enables rapid, zero-DFT prediction of catalytic activity and discrimination between AEM and BOAD pathways across vast compositional spaces. This capability further allows cost-performance Pareto optimization, making it possible to identify high-efficiency multi-cation candidates for experimental validation without resorting to exhaustive first-principles calculations. By transforming expensive DFT enumeration into a motif-based analytical theory grounded in elemental properties, this work establishes a scalable and physically transparent route toward rational design of the complex electrocatalysts.

2.1 Figures and tables

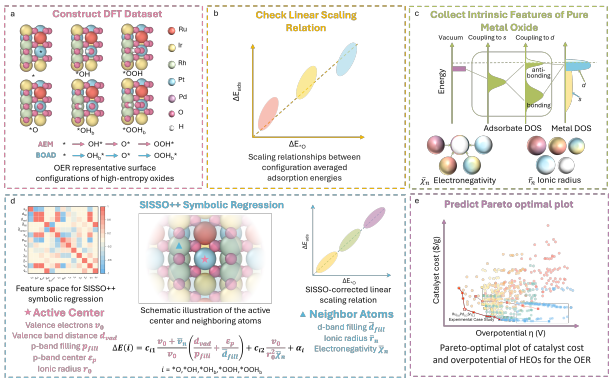

Fig. 1: Data-driven discovery framework for HEOOER catalysts.

References

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