Chemical Synthesis

Research Highlight

Machine learning identifies efficient Ru-based electrocatalysts

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Water electrolysis for green hydrogen production enables the conversion of the renewable energy into clean fuel. Relative to the conventional alkaline water electrolyzers, proton exchange membrane (PEM) electrolyzers possess a more compact design and are capable of delivering a greater current density and higher voltage efficiency[1]. Regrettably, the sluggish kinetics of anodic oxygen evolution reaction (OER) and the degradation of catalysts in acidic and strongly oxidative environments largely hinder the upgrading of PEM[2]. Currently, Iridium oxides (IrO_2), bearing an activity-stability compromise, are the primary catalysts for OER, yet the high cost and continuously growing demand urge us to find a feasible alternative[3]. In this context, Ru-based catalysts with the merits of approximately 100-fold greater abundance, 8-fold lower cost, and more appealing activity than IrO_2 come into view[4]. Unfortunately, Ru-based catalysts, such as RuO_2, tend to form soluble $Ru^{>4+}$ species in the OER process, giving rise to a severe decay in catalytic performance. Notwithstanding the improvement in activity by some strategies, their lifespan remains limited to merely several hours at current densities higher than 10 mA·cm^{-2}[5-7]. Challenges persist in the development of Ru-based catalysts that are both highly active and stable. In contrast to traditional experimental trial-and-error methods or expensive and slow density function theory (DFT) approaches, high-throughput

theoretical calculation techniques combined with machine learning (ML) have significantly improved the efficiency of catalyst design[8], providing potential for accelerating the development of efficient Ru-based catalysts.

Now, in their article published in *Journal of the American Chemical Society*, Abed *et al.* rapidly figured out the suitable composition of desirable Ru-based catalysts with the assistance of a ML computational pipeline [Figure 1A][9]. Initially, the trained pipeline identified the Ru-Cr-Ti-O_x as a good candidate with enhanced durability. And experimentally, the $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_2$ was synthesized successfully, delivering a current density of 100 mA·cm^{-2} at the overpotential of 267 mV and tiny decay in a 200-hour stability test. Compared to RuO_2, this catalyst significantly extended lifespan and reduced overpotential. Evidenced by the theoretical calculations and in situ characterizations jointly, the Cr additives allow for the reduction in overpotential by decreasing reaction energy barriers and the Ti dopants slow down the mass dissolution of Ru by boosting metal-oxygen covalency, both of which endow the $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_2$ catalyst with high activity and long-term stability.

To achieve this, firstly, a computational model employing a crystal graph convolutional neural network modified with a hyperbolic tangent activation function and dropout algorithm (CGCNN-HD) was trained, validated and tested using a data set of 36,465 metal oxide structures. The Pourbaix energy (ΔG_{pbx}), referring to the energy of formation per atom, serves as a proxy to predict the electrochemical stability. All structures underwent a preprocessing and scaling procedure using the lattice scaling approach, with the predicted property shifted within a 95% confidence interval to minimize the errors caused by nonideal structures. With the trained model, a M-M_2-O chemical space, which maintained the rutile oxide structure constant while substituting 46 elements, was explored to generate a dataset of 2,070 hypothetical compounds. A total of 195 rutile oxide structures were selected based on the energy above hull criteria [Figure 1B]. Focusing on the ΔG_{pbx} of the Ru-containing structures, it was revealed that doping Ti, Sn, Ge and Cr improved the Pourbaix stability and resulted in the increase of the metal-oxygen covalency. Among these, Ti demonstrated the largest computational improvement and Cr exhibited enhancing activity in previous studies; thus, experimental validation was concentrated on the Ru-Cr-Ti-O_x family of catalysts.

A series of Ru-Cr-Ti-O_x materials preserving the rutile oxide structure were synthesized by a sol-gel method starting by tuning the amount of Cr in the Ru-Cr-O_2 and then optimizing the Ti proportion. The $Ru_{0.75}Cr_{0.25}O_x$ and $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$ possessing optimized overpotential and enhanced stability were attained. The results of morphological characterization show that they maintained a similar rutile structure, in which the doped elements are uniformly distributed in the particles with a crystallite size of 3.5-5.0 nm, smaller than that of commercial RuO_2. Both could provide more than 400 A·g_{Ru}^{-1} of a mass activity at 1.48 V *vs*. Reversible hydrogen electrode (RHE), being approximately four folds higher than that of RuO_x (79 A·g_{Ru}^{-1}) [Figure 1C]. Intriguingly, the doping of Cr and Ti species each played a distinct role. Specifically, incorporating Cr remarkably increased the electrochemical active surface area and lowered the formation energy barrier of HOO*, the critical intermediate in the rate-determining step, thereby elevating the mass activity drastically. In the chronoamperometry test at the current density of 100 mA·cm^{-2}, RuO_x and $Ru_{0.75}Cr_{0.25}O_x$ were completely deactivated in the initial 40 h [Figure 1D], indicating that the Cr species was not a key component in improving the stability of Ru-based materials. Meanwhile, the Ti-doped counterpart exhibited good stability within 200 h, benefiting from the extremely slow dissolution of Ru [Figure 1E]. Unveiled by the X-ray absorption near-edge structure (XANES) results of O K-edge and calculations, the Ti species apparently increased the metal-oxygen covalence in the rutile oxide structure from 85.20% of RuO_2 to 93.62% in $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$ [Figure 1F]. Moreover, in situ differential electrochemical mass spectroscopy measurements (DEMS) using the ^{18}O isotope disclosed that the Ti incorporation in
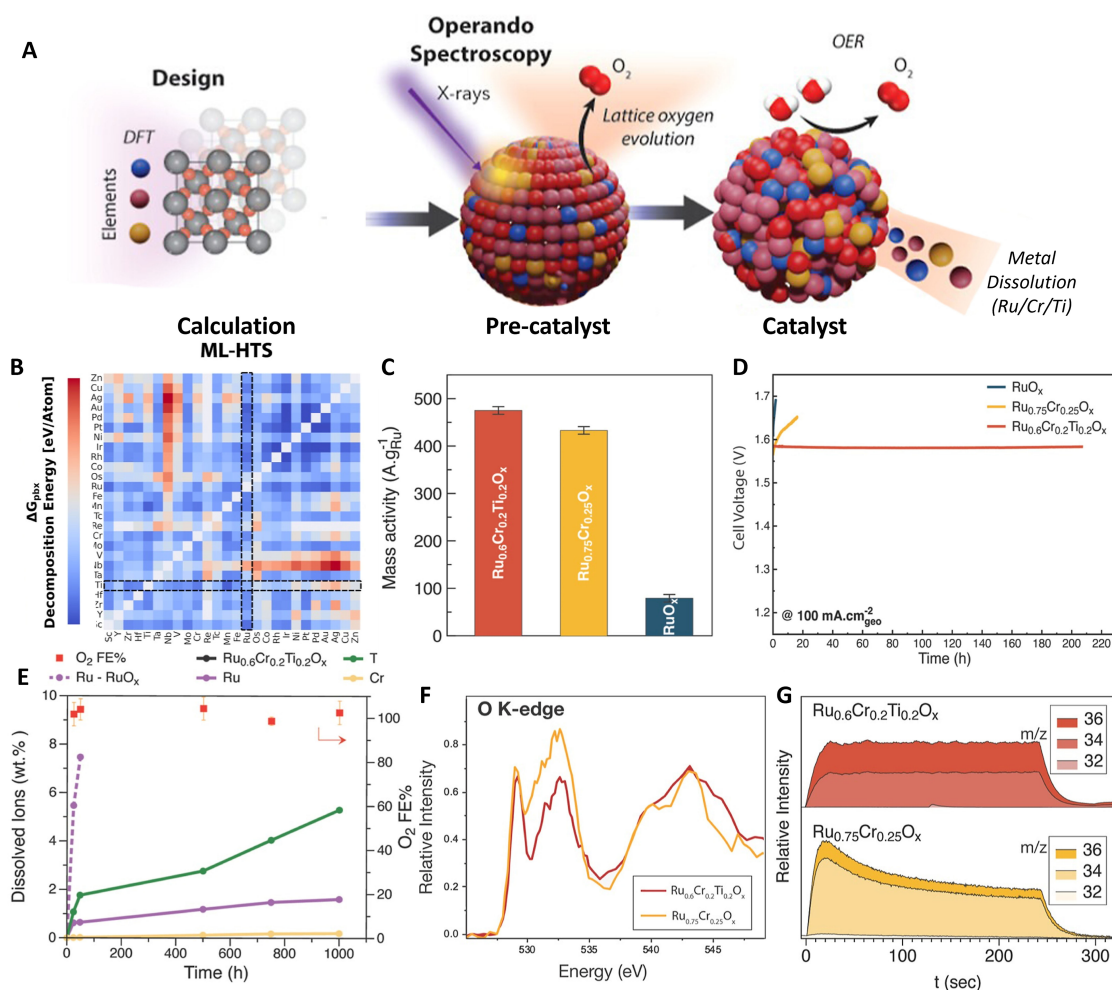
Figure 1. ML-aided framework identifies Ru-based acidic water oxidation catalysts. (A) Schematic of the design process of Ru-based catalysts from the ML-aided calculation model to the real catalyst; (B) The model named CGCNN-HD's heatmaps of Pourbaix electrochemical stability (ΔG_{pbx}) for the subset; (C) Mass activity at 1.48 V *vs.* RHE for $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$, $Ru_{0.75}Cr_{0.25}O_x$, and RuO_x; (D) Stability test at a constant current density of 100 mA·cm$_{geo}^{-2}$; (E) Accumulative total dissolved ions for RuO_x and $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$; (F) O K-edge STXM spectroptychography XANES comparison between $Ru_{0.75}Cr_{0.25}O_x$ and $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$; (G) DEMS signals of the reaction products using a $H_2^{18}O$ aqueous sulfuric acid electrolyte. This figure is quoted with permission from Abed *et al.*[9]. ML: Machine learning; CGCNN-HD: crystal graph convolutional neural network modified with a hyperbolic tangent activation function and dropout algorithm; RHE: reversible hydrogen electrode; STXM: scanning transmission X-ray microscopy; XANES: X-ray absorption near-edge structure; DEMS: differential electrochemical mass spectroscopy measurements.

$Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$ suppressed participation degree of lattice oxygen by ~66%, compared to $Ru_{0.75}Cr_{0.25}O_x$ [Figure 1G], allowing for a more rigid metal-oxygen framework and higher kinetic barriers for oxide dissolution, making the $Ru_{0.6}Cr_{0.2}Ti_{0.2}O_x$ more stable. In short, Cr additives account for the boosted reaction activity and Ti dopants are responsible for the enhancement in stability of the Ru-M-O materials. The excellent OER performance in experiment is well in line with the screening results of ML.

In summary, Abed *et al.* presented an inspiring approach for exploiting multi-component catalysts[9]. The guidance of ML enables the devising of efficient and durable catalysts to become more targeted, reducing the workload and time-consuming processes largely. Notably, the efficacy of ML models depends largely on the quantity and quality of training data. Despite the exponential growth in published experimental electrocatalytic data annually, a limited amount is currently accessible for ML training. Closer collaboration

between experiments and ML simulations is needed. Besides, the selected descriptors require careful consideration, and the applicability of the ΔG_{pbx} discussed in this work to other systems deserves to be verified. Although there remains considerable exploration ahead, the prospect for ML-assisted development of efficient catalysts is undoubtedly attractive.

DECLARATIONS

Authors' contributions
Made substantial contributions to conception and writing of the highlight: Zhang M, Wan Y, Lin Y

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
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Consent for publication
Not applicable.

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