Highlight

Record-breaking bifunctional oxygen electrocatalyst accomplished by a data-driven approach for zinc-air batteries

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Rechargeable zinc-air batteries (ZABs) have recently drawn great attention in energy research due to their high theoretical capacity, low costs, and inherently safe nature.[1-3] However, the sluggish cathode reactions necessitate the development of bifunctional oxygen electrocatalysts with lower ΔE indicator values. The ΔE indicator is commonly employed to quantitatively evaluate the electrocatalytic activity of a bifunctional oxygen electrocatalyst, representing the overall overpotential from oxygen reduction reaction (ORR) to oxygen evolution reaction (OER). This ΔE value is defined as the difference between the potential needed to reach an OER current density of 10 mA cm² (E_{10}) and the half-wave potential of ORR ($E_{1/2}$) [4, 5] For an extended period, benchmarking was conducted using state-of-the-art noble metal-based electrocatalysts (Pt/C for ORR and Ir/C for OER), which have a ΔE value of 0.77 V. The high cost and scarcity of noble metals sparked efforts to develop non-noble metal-based electrocatalysts capable of surpassing existing performance records. A comparable performance to noble metal catalysts was first reported in 2011 by Dai et al., who achieved a ΔE indicator of 0.80 V using Co_3O_4 nanocrystals loaded on graphene.[6] Inspired by the early success, although various attempts were made to integrate multiple active sites into composite electrocatalysts for enhanced bifunctional activity, the next record ΔE value of 0.72 V was only reported in 2017 by Kuang et al.[7] Furthermore, a new record was established in 2021 with CoNC@LDH, achieving a record-low ΔE of 0.63 V.[8] Since then, no other reports have achieved better bifunctional oxygen electrocatalysts, prompting a shift towards a data-driven approach to identify the most effective material combinations for setting a new record.

Recently, Liu et al. introduced a data-driven approach to design a bifunctional oxygen electrocatalyst, setting a record with a ΔE of 0.57 V. They achieved this by systematically investigating the "component-performance" relationship of previously reported bifunctional oxygen electrocatalysts.[9] The proposed data-driven approach aids in statistically identifying advanced active sites for ORR and OER electrocatalytic activity, facilitating rational integration to create the best-performing bifunctional oxygen electrocatalyst. It is undeniably proven to be a paradigm-shifting strategy for surpassing traditional experimental methods in optimizing the bifunctional activity of electrocatalysts. By pre-determining critical activity factors and optimal integration strategies, this approach allows for a focused effort on designing and developing only the highest-performing materials, which is also crucial for other bifunctional photo-electrocatalytic materials, such as bifunctional water-splitting catalysts. [10]

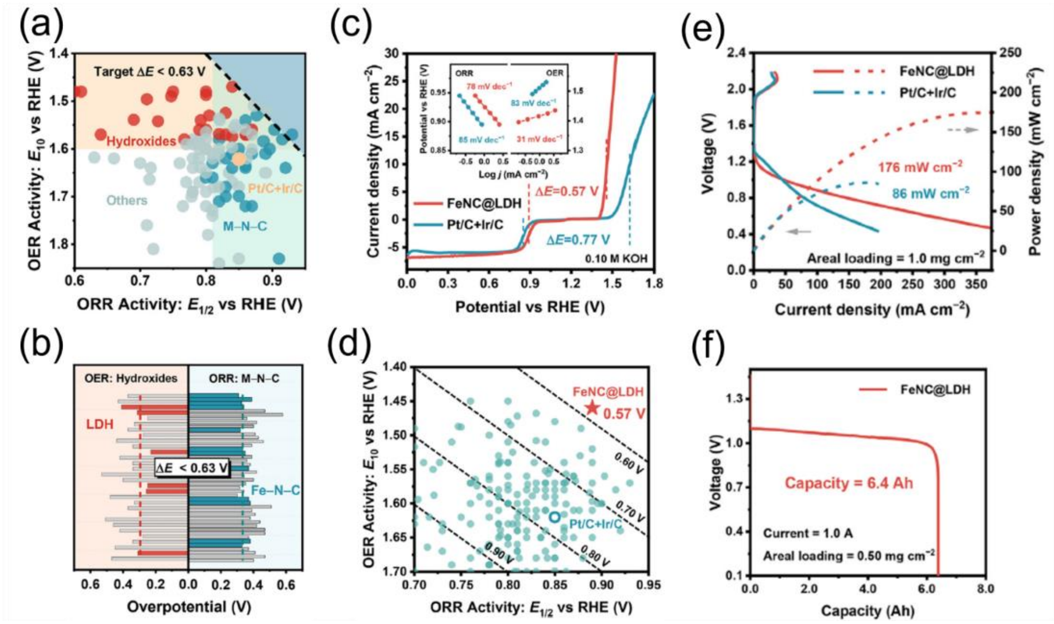

Fig. 1. Data-driven statistical analysis of (a) Previously reported bifunctional oxygen electrocatalysts performances, (b) Performance distribution of the specific active sites in the "M-N-C" and "Hydroxides" subcategories. (c) Experimental bifunctional electrocatalytic activity evaluation of FeNC@LDH in comparison with the state-of-the-art Pt/C+Ir/C electrocatalysts. (d) Data-driven analysis chart of bifunctional electrocatalysts with the new record set by FeNC@LDH. Electrochemical performances of ZABs, (e) LSV curves and calculated discharge power density of stack-type ZABs with the FeNC@LDH in comparison with Pt/C+Ir/C cathodes. (f) Galvanostatic discharge performance of ZABs with an input current of 1.0 A. Reproduced with permission from ref [9].

In detail, the authors initially conducted a systematic analysis of the component-performance relationship using bifunctional performance indicators from 247 previously reported oxygen electrocatalysts. By aiming to achieve a ΔE value lower than the previous record of 0.63 V, they traced the performance distributions, as illustrated in **Fig. 1a**. To enhance understanding, the electrocatalysts were categorized by type and marked with different colors. This approach allowed the authors to identify the optimal groups for each category, concluding that hydroxides were best for OER and M-N-C ("M" refers to metal atoms coordinated with planar N/C atoms and anchored within carbon skeleton) materials for ORR, with $E_{10} \leq 1.60$ V and $E_{1/2} \geq 0.83$ V, respectively. It should be noted that most of their composites achieved $\Delta E \leq 0.77$ V, surpassing the performance of the noble-metal benchmark. This indicates that integrating hydroxides and M-N-C components can significantly enhance bifunctional electrocatalytic activity. To further evaluate the specific active sites, the subcategories of hydroxides and M-N-C electrocatalysts were examined by plotting their reported overpotentials, as shown in **Fig. 1b**. It is observed that layered double hydroxide (LDH) sites and atomically dispersed Fe-N-C sites demonstrate relatively higher electrocatalytic activity within their respective subgroups. By evaluating the electrocatalytic activity of various reported LDH sites for OER, NiFe LDH has been identified as the most effective choice, demonstrating the highest OER activity with $E_{10} \leq 1.50$ V. Furthermore, the cation modulation strategy was systematically studied using a data-driven approach to understand the doping effects of various elements in NiFe LDH. The study identified Ce-doped NiFe LDH as the state-of-the-art OER catalyst, exhibiting the highest OER electrocatalytic activity with $E_{10} = 1.45$ V. Ultimately, employing the data-driven approach, the authors statistically identified Fe-N-C and NiFeCe LDH sites as high-activity active sites for ORR and OER electrocatalysis, respectively.

Applying their theoretical insights, the authors experimentally fabricated a FeNC@LDH composite using a two-step synthesis process. The FeNC and Ce-doped NiFe LDH were first synthesized separately through thermal annealing and co-precipitation methods, respectively. The final composite was then fabricated by integrating the LDH and FeNC components through an ultrasonication-assisted method. To validate the effectiveness of the data-driven approach, the bifunctional electrocatalytic activity of the designed FeNC@LDH electrocatalyst was experimentally tested. As anticipated, the FeNC@LDH electrocatalyst sets a newfound record for bifunctional electrocatalytic activity, achieving a ΔE as low as 0.57 V. This performance is attributed to its superior individual electrocatalytic activities in OER (E_{10} = 1.46 V vs. RHE) and ORR ($E_{1/2}$ = 0.89 V vs. RHE) **(Fig. 1c)**. The record-breaking ΔE achieved with the FeNC@LDH electrocatalyst has been incorporated into the data-driven analysis chart, as shown in **Fig. 1d.** Rechargeable ZABs assembled with the FeNC@LDH electrocatalyst delivered peak current density of 176 mW/cm^2 **(Fig. 1e)**, discharge rate performance up to 50 mA/cm^2, and long-cycling lifespan of 607 cycles (at 10 mA/cm^2 and 10 mAh/cm^2). From a practical perspective, the authors demonstrated ampere-hour-scale ZABs with a capacity of 6.4 Ah per cell **(Fig. 1f)**, promoting the success of the data-driven approach in advancing the research for rechargeable ZABs.

Overall, Liu et al.'s work demonstrates a data-driven approach that establishes statistical guidelines for designing record-breaking bifunctional oxygen electrocatalysts. This method not only introduces new design principles for bifunctional oxygen electrocatalysts but also validates the concept experimentally by achieving a new ΔE record of 0.57 V with FeNC@LDH. Given its success, this data-driven approach is likely to be applicable to other bifunctional electrocatalytic systems, such as water-splitting catalysts, where understanding specific OER and HER activities is crucial. We believe that data-driven statistical analysis represents a highly promising direction for designing materials that exhibit record-high catalytic activity.

Declaration of competing interest

There are no conflicts to declare.

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Graphical Abstract

A data-driven approach has been proposed to break the record for the bifunctional oxygen electrocatalyst performance indicator ΔE by statistically analyzing previously reported electrocatalysts for ampere hour scale zinc-air batteries.