RATIONAL DESIGN OF ORGANIC ELECTROCATALYSTS FOR HYDROGEN AND OXYGEN ELECTROCATALYTIC APPLICATIONS

Ruiqi Cheng[1], Chaopeng Fu*[1]
1. School of Materials Science and Engineering, Shanghai Jiao Tong University
Shanghai, 200240, People's Republic of China
** E-mail: chengruiqi@sjtu.edu.cn*

ABSTRACT

Efficient electrocatalysts are critical for advancing green energy conversion technologies. Organic electrocatalysts, as novel, cost-effective alternatives to noble-metal benchmarks, have garnered considerable attention. Among these, organic frameworks (OFs) with a high degree of polymerization, crystallization, and conjugation have been proposed and developed as cost-efficient electrocatalysts. However, the relationships between their properties and electrocatalytic activities remain unclear. Our work emphasizes the urgent need to define specific structural and physicochemical properties that serve as activity indicators, facilitating the elucidation of the structure-activity relationship for the rational design of cost-efficient OFs with high electrocatalytic performance. By leveraging the unique features of organic electrocatalysts, such as controllability and compatibility, we propose valuable new strategies for implementing real-world applications like fuel cells and water electrolyzers.

KEYWORDS
Organic frameworks, Structure-activity relationship, Electrocatalysts

1. INTRODUCTION

Organic frameworks (OFs) stand out as particularly promising candidates for substituting noble metal benchmarks due to their exceptional characteristics that are advantageous for electrocatalytic applications:[1] Firstly, the molecular architecture of OFs can be precisely tailored, allowing easier control over their structure and electronic properties. Secondly, the defined chemical structure of OF backbones facilitates the identification and quantification of active species. Thirdly, OFs typically feature abundant surface functional groups, enhancing compatibility with other electrode components and improving stability in energy devices. Lastly, OFs consist mainly of earth-abundant elements (C, H, O, and N), ensuring sustainability and recyclability compared to limited metallic minerals. These advantages highlight the potential of cost-efficient OF-based electrocatalysts for practical applications. However, understanding the interplay between OF characteristics and electrocatalytic performance remains challenging.

The overall electrocatalytic activity of electrocatalysts is predominantly influenced by four key electrochemical characteristics: active site count, mass transfer, charge transfer, and thermodynamic intrinsic activity.[2] To better understand the activity origins of OF-based electrocatalysts, it is crucial to define relevant physicochemical properties as activity indicators. This allows for quantitative assessment of electrocatalytic performance and establishes a clear structure-activity relationship, guiding the rational design of cost-efficient OF-based electrocatalysts. By carefully selecting appropriate building blocks, we can optimize the four electrochemical characteristics in condensed OF-based electrocatalysts.

2. RESEARCH PROJECTS

2.1 Organic frameworks

OFs include metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). The former consists of the coordination of metal species and organic building blocks and the latter consists of covalent condensation between different building blocks. Here, we will introduce both of these OFs in the following content.

2.2 Dimensional Upgrade Induced Enriched Active Sites and Intensified Intramolecular Electron Donor-Acceptor Interaction to Boost Oxygen Reduction Electrocatalysis (*Adv. Funct. Mater. 2024, 34, 2406717)*

The molecular dimensionality of a two-dimensional COF containing a tris-triazine ring (2D-Tr-COF) was upgraded to generate its 3D counterpart (3D-Tr-COF), enabling direct comparison between 2D- and 3D-COFs. These findings reveal that slight alterations in the spatial structure (from 2D to 3D) by substituting amine building blocks lead to significant variations in molecular architecture and performance for the oxygen reduction reaction (ORR). The results indicate that 3D-Tr-COF, with enlarged lattice spacing, more active species, and a reduced degree of conjugation, possesses enriched active sites. Moreover, the intensified intramolecular electron donor-acceptor interaction between the tris-triazine ring and its neighboring imino linkage in 3D-Tr-COF optimizes the electronic/band structure and facilitates charge transfer, resulting in enhanced intrinsic activity towards ORR compared to 2D-Tr-COF. Additionally, 3D-Tr-COF exhibits promising discharging performance in aluminum-air batteries, with a maximum power density of 170.5 mW cm^{-2}.

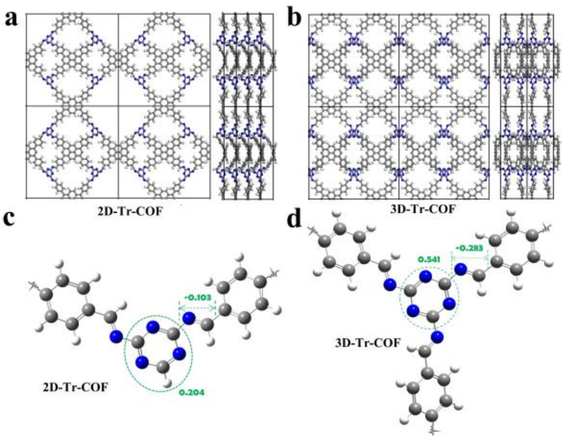

Figure 1. Illustration of the (a-b) geometry and the (c-d) intramolecular charge distribution of 2D-Tr-COF and 3D-Tr-COF.[3]

2.3 High-entropy optimizing d-orbital electronic configuration of metal organic framework for high-current-density anion exchange membrane water electrolysis (Nano Energy, Minor Revision)

Herein, we have designed a high-entropy Mil53 metal-organic framework (Mil53-HE) bifunctional electrocatalyst with enhanced performance towards oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) for overall water splitting. The improved activity and stability of Mil53-HE in water electrolysis are attributed to the optimized electronic configurations of d-orbitals in the metal centers. By introducing various kinds of elements into the metal center of Mil53 MOF, the interaction between metal ions and organic segments can be regulated. This leads to optimized electronic configurations of d-orbitals in the metal centers, further improving the activity and stability of Mil53-HE. Specifically, the overall d-band center ($\bar{E}_d$) is positively shifted, and the total number of electrons in the d-orbitals within a supercell ($\sum N_d$) is reduced. Consequently, both the oxygen and hydrogen electrocatalytic energy barriers are reduced, and structural durability under high current densities is reinforced. Additionally, the anion exchange membrane water electrolysis cell with Mil53-HE can stably operate at high current densities with low voltages (1.9 V at 0.52 A cm^{-2} and 2.1 V at 1.48 A cm^{-2}), demonstrating its feasibility for practical applications.

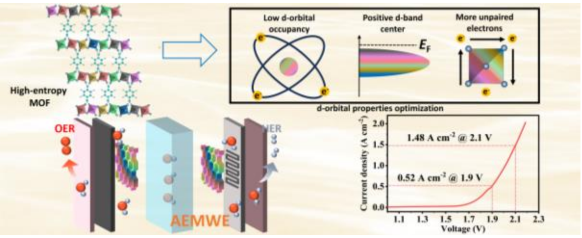

Figure 2. Illustration of the high-entropy effect in MOF towards water electrolysis.

2.4 Conclusions

For 2D-Tr-COF, we have analyzed the origin of the activity enhancement resulting from the dimensional upgrade from multiple perspectives, including the enrichment of active sites and the strengthening of intramolecular electron donor-acceptor interactions. For Mil53-HE, the high-entropy construction contributes to the optimization of d-orbital properties, including the upshift of the $\bar{E}_d$ and reduction of the $\sum N_d$. T The high-entropy Mil53-HE possesses more unpaired d-electrons, resulting in low energy barriers and small overpotentials for both the OER and HER. Additionally, more unpaired d-electrons can produce a unique entropy-stabilizing effect by preserving the metal site's electron state and covalency. Our discoveries constitute a significant advancement in increasing the availability of compatible OFs as low-cost substitutes for noble metals in electrodes for electrocatalysis in green energy storage devices.

ACKNOWLEDGEMENTS

We would like to thank the International Caffeine Society for providing us with the coins to feed our coffee machines. Note that no section number is used.

REFERENCES

1. Cheng, R.; He, X.; Li, K.; Ran, B.; Zhang, X.; Qin, Y.; He, G.; Li, H.; Fu, C., Rational Design of Organic Electrocatalysts for Hydrogen and Oxygen Electrocatalytic Applications. *Adv*. *Mater*. 2024, *36*, 2402184.
2. Cheng, R.; Min, Y.; Li, H.; Fu, C., Electronic structure regulation in the design of low-cost efficient electrocatalysts: From theory to applications. *Nano Energy* 2023, *115*, 108718.
3. Cheng, R.; Ran, B.; Zhang, X.; Han, Y.; Shao, X.; Li, H.; Fu, C., Dimensional Upgrade Induced Enriched Active Sites and Intensified Intramolecular Electron Donor-acceptor Interaction to Boost Oxygen Reduction Electrocatalysis. *Adv. Funct. Mater.* 2024, *34*, 2406717.