

Structural design, green synthesis and performance control of electrocatalytic materials of nickel and copper metal-organic frames

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Abstract: At present, the research and development of low cost, high activity and high stability oxygen reduction electrocatalytic materials is the key to the commercialization of fuel cells. For platinum-free catalysts, metal organic framework (MOFs) has many advantages, such as diverse structure, large specific surface area, low cost and resistance to methanol poisoning. On the basis of previous studies on electrocatalysts containing nickel and copper, the applicant intends to construct and design organic frame materials containing nickel and copper by means of green synthesis, and regulate their surface structure, morphology, conductivity, lattice constant and electronic structure, so as to improve the adsorption performance of MOFs materials on O₂ and improve catalytic activity. At the same time, the key technology for preparing electrocatalysts will be explored, and the crystal growth mechanism was discussed. By studying the correlation between the different composition, structure and electron distribution state of the catalyst and the electrocatalytic performance, the catalytic activity center and the possible catalytic reaction mechanism of the catalyst will be revealed. The structure-activity relationship of the prepared catalyst was revealed. The improvement mechanism of its catalytic performance will be illustrated by quantitative chemical calculation. The research of this project should be provide experimental and theoretical basis for the design and preparation of nickel and copper based MOFs electrocatalytic materials with low cost and good performance.

Key words: Fuel cell; Electrocatalytic materials; The platinum; Metal organic frames; Morphology effects

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I. Introduction

In recent years, the massive consumption of fossil fuels has brought serious energy and environmental problems, and therefore, the development and application of clean energy technologies is urgent [1]. Fuel cell has many advantages such as high efficiency, no pollution, no noise, high reliability and modularity. It is the fourth generation of power generation mode after thermal power, hydropower and nuclear power. It has a very wide application prospect in portable electronic equipment, fixed power stations, electric vehicles and aerospace fields [2-3]. The core reaction process of the fuel cell system — The reaction rate of oxygen reduction reaction (ORR) is slow (the cathode reaction rate is more than 6 orders of magnitude slower than the anode reaction rate), which seriously restricts the development and application of fuel cell technology. In order to speed up the reaction speed, it is necessary to use electrocatalyst. Among many catalytic materials, the precious metal platinum based catalyst is the most effective [4,5]. However, due to the high price and limited reserves of platinum, and in the actual application process, the catalyst is easy to poisoning, poor stability and other shortcomings, which affect the performance and service life of the energy system, this problem has also become the bottleneck to achieve large-scale commercialization of fuel cells [6-8]. Therefore, the development of non-precious metal ORR catalysts with low cost, rich material sources, high activity and stability is of great theoretical and practical significance.

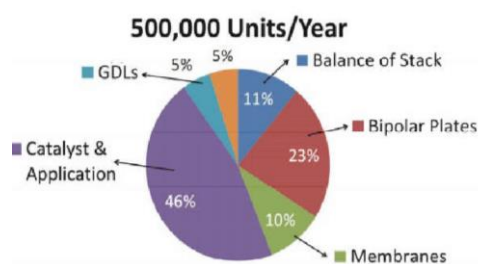


Figure 1 Cost schematic diagram of each component of the proton exchange membrane fuel cell

At present, in the field of platinum catalytic materials research, a series of in the alkaline conditions have good ORR catalytic activity and stability of non-precious metal catalyst: including doped carbon materials, transition metal oxides, nitrogen oxides, carbide have been found [9-13], among them, the metal doped carbon base catalyst is more attention. However, in the current widely used acidic media, the ORR activity and stability of carbon-based catalysts are poor due to the corrosion of carbon materials and the continuous dissolution of transition metals [14]. Deng yida, professor wen-bin hu team by precise adjustment of bimetallic ZnCo-ZIFs precursor amount of zinc doping, successfully realized the cobalt atoms at the atomic level, the nitrogen doped carbon base prepared different cobalt atoms aggregation of cobalt based catalyst: cobalt nanoparticles, cobalt atomic clusters and cobalt single atoms, this strategy makes the TM catalyst size effect to single atom scale. It is shown that the single atom cobalt has high chemical activity, and its coordination with N in the substrate ensures its stability, excellent electrical conductivity of the carbon base, and rich pore structure and large specific surface area. This work provides a reference for the regulation of particle size through the spatial separation effect, and useful for the deep understanding of the nanocatalyst size-performance relationship [15].

Compared with other non-precious metal ORR catalysts, "metal-organic frame nanomaterials" (MOFs) stand out. They have the advantages of rich and orderly porous structure, excellent acid and alkali corrosion resistance, large surface area, wide sources, [16], and are considered to have the potential to replace the traditional platinum-based catalysts, and become one of the hot research directions in the field of new energy technology. However, the poor conductivity and stability of most MOFs themselves, which limited their further application in the field of electrochemistry. In 2012, American scientists discovered that Metal-organic Frameworks (MOFs), like metals, could conduct electricity, as shown in Figure 2, creating a revolutionary breakthrough for renewable energy harvesting and storage[17].

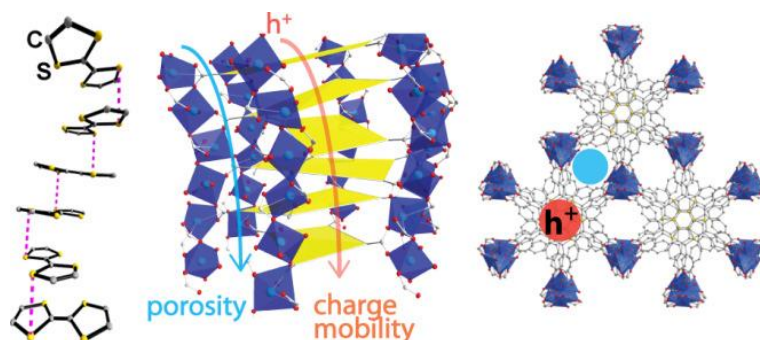


Figure 2 The conductive MOFs found by American scientists

II. Preparation methods of metal-organic frame materials (MOFs)

The controllable preparation of multi-dimensional nickel and copper-based metal-organic frame nanomaterials mainly include solvent thermal method, microwave synthesis method, electrochemical synthesis method, ultrasonic synthesis method, etc. First, the study is to make the synthesis process greener by changing the solvent, metal salt and ligand. Secondly, the effects of using different preparation processes and processes on the yield, structure and morphology, and crystallinity of MOFs catalysts with the same reactants are studied. Through the effective doping of the second transition metal, the final product pore structure and conductivity by the appropriate electrochemical process and the green solution is the preferred electrochemical process of the catalyst.

2.1 Optimization of the solvent

Finding environmentally friendly solvents or developing less / solvent-free synthesis method is the only way for the green synthesis and even industrial production of MOFs. Screening of solvents with high efficiency and low toxicity is a feasible route, e. g., for HKUST-1 synthesis using MetA and copper acetate, dihydrol-glucoside (Cyrene) is used as a solvent instead of conventional DMF, and the product specific surface area is higher than the latter.

2.2 Optimization of the metal sources and the ligands

Avoid chloride and nitrate, because chloride is generally highly corrosive, nitrate is easy to cause an explosion. A preface direction of ligand optimization lies in the recycling or utilization of its recycled ligands from discarded resources. For example, we can place the discarded PET plastic and metal salts in a microwave reactor to obtain the degradation product — terephthalic acid, while self-assemble with metal ions in the process. In March 2020, a team of researchers from the School of Science at Clemson University demonstrated that a new double-spiral metal organic frame architecture in a partially oxidized form can conduct electricity and is expected to become a new generation of semiconductors. The work was published in ACS Applied Materials & Interfaces and became a cover article. They introduced a butterfly-like tetrathiofulvalene (ExTTF) convex ligand into the MOF, creating a unique S-shaped charge transport path that extends along adjacent joints. Thus yields a novel double helical structure that is conductive once it is partially oxidized by the guest iodine molecule. When the ExTTF ligands on one side of each double helix are iodine-oxidized, while those on the other remain neutral, they form intermolecular charge-transfer chains along the seam. Electrons flow along this path in an intermolecular fashion, enabling better electrical conductivity of metallic organic frames.”

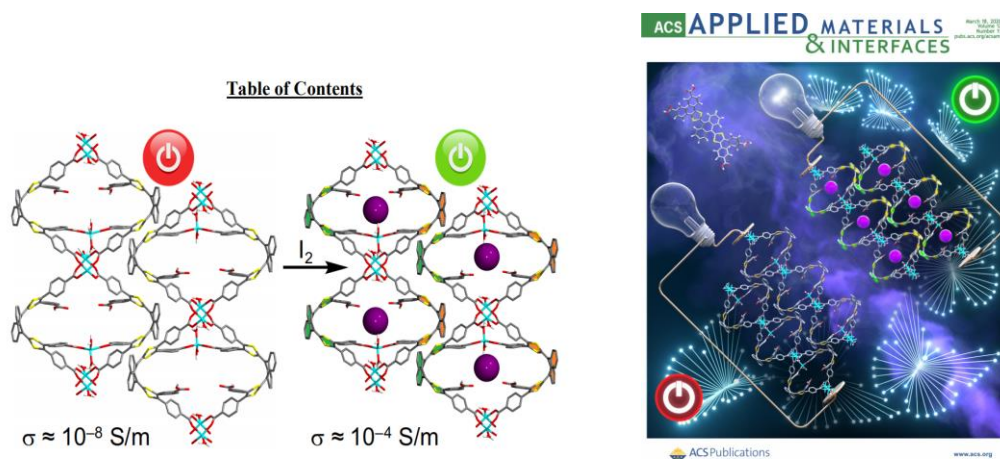


Figure 3 The double-helical structure of the conductive MOFs

The research team of Chinese scholar Liu Qinghua used the light-induced lattice distortion strategy to introduce lattice stress into the lattice of some transition metal-based — metal organic frame compounds, successfully activating the catalytic activity of the metal node of the compound, and realizing its electrodriven oxygen reduction catalysis with high quality activity and high stability. The NiFe-MOFs compounds show excellent electrocatalytic oxygen reduction and oxygen precipitation activities, and are expected to become efficient cathodic oxygen reduction catalysts for industrial fuel cells, providing a new approach for the development of non-precious metal catalysis [18]. Their research results have effectively improved China's national competitiveness in related fields, and laid a foundation for the smooth development of non-platinum electrocatalytic materials. Recently, professor G. Li's group from Zhengzhou University was invited to publish a review paper entitled "Proton conductive carboxylate-based metal organic frameworks" in Coordination Chemistry Reviews, which summarized the research and application progress of carboxylic acid MOFs in proton conduction. A comprehensive overview of the design and preparation strategy, structural stability, proton conductivity, mechanism and application is given. Based on the latest research results, the new progress of proton conductivity mechanism by using single crystal proton conductivity test, molecular dynamics fitting, solid-state nuclear magnetic test and quasi-elastic neutron scattering is summarized. At the same time, the application progress of this kind of metal organic framework in fuel cell is introduced. At present, the research of scholars at home and abroad on this topic mostly focuses on the synthesis of MOFs materials and the photocatalytic properties of [20,21], while the relationship between the electrical conductivity, structure and catalytic activity, catalyst active site and catalytic mechanism are rarely reported. For the catalytic reaction, the active center, catalytic mechanism and structure-activity relationship of the catalyst are an important theoretical

basis to guide the catalyst design and modification. Copper and nickel in the first cycle transition elements have low prices, are rich in reserves, and have strong redox capacity, and their complexes have the potential to serve as electrocatalysts. Nickel, as a non-precious metal, has variable oxidation and original price, is an ideal substitute for the same precious metals palladium and platinum. Copper has high abundance in the crust and its stable elemental properties, which are widely used in biomimetic materials and metallurgical devices. Copper belongs to the transition metal of the ds zone, which has a strong coordination ability and is easy to form complexes with pyridines, peptides and amides. Applicants' previous studies have found that nickel-or copper-doped precious-metal catalysts can significantly reduce costs without affecting their activity. Therefore, the design and development of excellent nickel, copper based MOFs electrocatalytic materials, change the structure of MOFs materials, adjust the composition of the catalyst, study the influence of the second metal doping on catalyst properties and structure, reveal the active center of the catalyst and the possible catalytic reaction mechanism, will deepen the understanding of MOFs nanomaterials based electrocatalytic ORR rule, and guide the development of high performance ORR catalyst.

III. Research objectives and general thinking

3.1 Green chemical process was used to control the synthesis of a series of Cu-MOFs, Ni-MOFs, Ni-MOFs, and Cu-Ni-MOFs.

3.2 Master the influence of ligand type and metal ion source on the growth, structure, morphology and composition of MOFs; clarify the growth mechanism, determine the relationship between experimental conditions and factors affecting product structure, provide support for the identification, analysis and performance mining of the system, and promote the research and development of new materials.

3.3 The physical and chemical characteristics of copper and nickel-based MOFs and the relationship between the catalytic activity and stability of oxygen reduction reaction should be clarified from the micro scale, so as to establish the structure-activity relationship of the surface interface, so as to provide theoretical basis and guiding direction for the design and synthesis of efficient and stable non-precious metal oxygen and raw materials.

IV. Key scientific issues to be addressed

4.1 Green synthesis method and growth mechanism of nanomaterials of nickel and copper-based MOFs

This project adopts electrochemical method and green solvent screening technology to accurately regulate the macro-morphology and micro-structure of MOFs; such as designing materials with good electrical conductivity and pore structure. The relationship between experimental parameters and product structure is established to control the control of nickel and copper based MOFs. The crystal growth process was analyzed by careful characterizing and quantified computation to propose the growth mechanism.

4.2 Structure activity relationship of nickel and copper-based MOFs nanomaterials in electrochemical reactions

The composition, structure of the catalyst and the correlation between the electron distribution state of nickel and copper and the electrocatalytic performance of ORR were clarified, the general law of the influence of the structure, composition and preparation process of the catalyst was revealed, and the catalytic active center of the catalyst and the possible catalytic reaction mechanism were revealed. To compare and analyze the differences in bifunctional electrocatalytic properties of MOFs with different components and structures, and to understand their catalytic performance influence on ORR reaction at the micro-scale. To understand the correlation between the physical morphology structure, surface interface chemistry, internal electronic structure and electrochemical catalytic properties, to clarify the relationship between oxygen reduction and structure activity of nickel and copper-based MOFs, and to provide theoretical basis and guiding direction for the design and optimization of efficient and stable non-precious metal bifunctional oxygen reduction electrocatalysts.

Although copper and nickel-based MOFs based nanomaterials catalysts have been synthesized in recent years, the properties of these catalysts are far from the level of practical application [22,23]. In particular, the synthesis of green chemistry and the research on the active center, catalytic mechanism and structure-activity relationship of the catalyst should be further deepened. Applicants follow the principle of low carbon chemistry, synthetic one-dimensional, two-dimensional or three-dimensional structure multi-scale nickel, copper based MOFs nano electrocatalytic materials, study its special morphology effect, surface exposure of the active site on the ability of ORR, help to reveal the MOFs material catalytic active center and catalytic reaction mechanism, deepen the understanding of ORR electrocatalytic rules, to guide the higher level of MOFs based nanomaterials ORR electrocatalytic materials development lay the theoretical basis.

V. Prospects and prospects

According to the previous research results, the future innovation and breakthrough points are summarized as follows: Firstly, following the principle of low-carbon concept, adopts electrochemical synthesis and preferred green solvent method, designs multi-scale nickel and copper-based MOFs ORR catalysts, and

systematically discusses the influence of the preparation method and process conditions on the structure and performance of the catalyst. Secondly, By regulating the morphology and structure of copper-based MOFs nanomaterials and introducing the second transition metal nickel, the internal structure of the catalyst is changed to regulate its catalytic activity, so as to realize the construction of the catalyst with excellent ORR performance. Thirdly, through quantitative calculation, revealed the structure-active relationship between the catalytic active center and the ligand of the catalyst, which provided theoretical basis and experimental basis for the development of nickel and copper-based MOFs.

References :

- [1]. Xinlong Tian, Xiao Zhao, Ya-Qiong Su, Lijuan Wang, Hongming Wang, Dai Dang, Bin Chi, Hongfang Liu, Emiel J.M. Hensen, Xiong Wen (David) Lou, Bao Yu Xia. Engineering bunched Pt-Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. **Science**, **2019**, **366(6467)**: 850-856.
- [2]. Meiling Liu, Zipeng Zhao, Xiangfeng Duan, Yu Huang. Nanoscale structure design for high-performance Pt-based orr catalysts. **Advanced Materials**, **2019**, **31 (6)**:1802234.
- [3]. Liu Yuhao, Pharr Matt, Salvatore Giovanni Antonio. A lab-on-skin: a review of flexible and stretchable electronics for wearable health monitoring. **ACS Nano**, **2017**, **11(10)**: 9614-9635.
- [4]. Ambarish Kulkarni, Samira Siahrostami, Anjali Patel, Jens K. Norskov. Understanding catalytic activity trends in the oxygen reduction reaction. **Chemical Reviews**, **2018**, **118(5)**: 2302-2312.
- [5]. Huanyu Jin, Chunxian Guo, Xin Liu, Jinlong Liu, Anthony Vasileff, Yan Jiao, Yao Zheng, Shi-Zhang Qiao. Emerging two-dimensional nanomaterials for electrocatalysis. **Chemical Reviews**, **2018**, **118 (13)**: 6337-6408.
- [6]. Ming Zhao, Xue Wang, Xuan Yang, Kyle Gilroy, Dong Qin, Younan Xia. Hollow metal nanocrystals with ultrathin, porous walls and well-controlled surface structures. **Advanced Materials**, **2018**, **30(48)**: 1801956.
- [7]. Yin Xiong, Yao Yang, Francis J. DiSalvo, Héctor D. Abruna. Pt-decorated composition-tunable Pd-Fe@Pd/C core-shell nanoparticles with enhanced electrocatalytic activity toward the oxygen reduction reaction. **Journal of the American Chemical Society**, **2018**, **140 (23)**: 7248-7255.
- [8]. Weiyue Zhao, Yuekun Ye, Wenjie Jiang, Jing Li, Haibo Tang, Jinsong Hu, Li Du, Zhiming Cui, Shijun Liao. Mesoporous carbon confined intermetallic nanoparticles as highly durable electrocatalysts for oxygen reduction reaction. **Journal of Materials Chemistry A**, **2020**, doi: 10.1039/D0TA01437K.
- [9]. Bing-Ye Song, Ming-Jia Li, Yi-Wen Yang, Ya-Ling He. Achievement of a novel porous non-noble-metal catalyst with excellent oxygen reduction reaction activity: promoting the commercialization of alkaline fuel cells. **Journal of Cleaner Production**, **2020**, **249**:119314.
- [10]. Zhifu Wu, Dai Dang, Xinlong Tian. Designing Robust Support for Pt Alloy Nanoframes with Durable Oxygen Reduction Reaction Activity[J]. **ACS Applied Materials & Interfaces**, **2019**,**3**, (9): 9117-9124.
- [11]. Priyanka Pal, Sahil Kumar, Mayanglambam Manolata Devi, Shunmugavel Saravanamurugan. Oxidation of 5-hydroxymethylfurfural to 5-formyl furan-2-carboxylic acid by non-precious transition metal oxide-based catalyst. **The Journal of Supercritical Fluids**, **2020**, **160**: 104812.
- [12]. Yudong Xue, Yunting Wang, Zhenhua Pan, Chunhui Zhang. Metal-organic frameworks derived cobalt encapsulated in porous nitrogen-doped carbon nanostructure towards highly efficient and durable oxygen reduction reaction electrocatalysis. **Journal of Power Sources**, **2020**, **451**: 227747-227756.
- [13]. Dehui Deng, Liang Yu, Xiaoqi Chen, Guoxiong Wang, Li Jin, Xiulian Pan, Jiao Deng, G. S. Sun, Xinhe Bao. Iron encapsulated within pod-like carbon nanotubes for oxygen reduction reaction. **Angewandte Chemie International Edition**, **2013**, **52(1)**: 371-375.
- [14]. Xiao Xia Wang, Sooyeon Hwang, Yung-Tin Pan, Kate Chen, Yanghua He, Stavros Karakalos, Hanguang Zhang, Jacob S. Spendelov, Dong Su, Gang Wu. Ordered Pt₃Co intermetallic nanoparticles derived from metal-organic frameworks for oxygen reduction. **Nano Letters**, **2018**, **18(7)**: 4163-4171.
- [15]. Xiaopeng Han, Xiaofei Ling, Ying Wang, Tianyi Ma, Cheng Zhong, Wenbin Hu, Yida Deng. Spatial isolation of zeolitic imidazole frameworks-derived cobalt catalysts: from nanoparticle, atomic cluster to single atom. **Angewandte Chemie International Edition**, **2019**, **58(16)**: 5359-5364.
- [16]. Zhenhua Li, Mingfei Shao, Lei Zhou, Ruikang Zhang, Cong Zhang, Min Wei, David G Evans, Xue Duan. Directed growth of metal-organic frameworks and their derived carbon-based network for efficient electrocatalytic oxygen reduction. **Advanced Materials**, **2016**, **28(12)**: 2337-2344.
- [17]. Tarun C. Narayan, Tomoyo Miyakai, Shu Seki, Mircea Dincă. High charge mobility in a tetrathiafulvalene-based microporous metal-organic framework. **Journal of the American Chemical Society**, **2012**, **134(31)**: 12932-12935.
- [18]. Monica A. Gordillo, Paola A. Benavides, Dillip K. Panda, Sourav Saha. The advent of electrically conducting double-helical metal-organic frameworks featuring butterfly-shaped electron-rich π -extended tetrathiafulvalene ligands. **ACS Applied Materials & Interfaces**, **2020**, **12 (11)**: 12955-12961.
- [19]. Weiren Cheng, Xu Zhao, Hui Su, Fumin Tang, Wei Che, Hui Zhang, Qinghua Liu. Lattice-strained metal-organic-framework arrays for bifunctional oxygen electrocatalysis. **Nature Energy**, **2019**, **4**: 115-122.
- [20]. Takaaki Tsuruoka, Koji Mantani, Ayumi Miyanaga, Tetsuhiro Matsuyama, Takashi Ohhashi, Yohei Takashima, Kensuke Akamatsu. Morphology control of metal-organic frameworks based on paddle-wheel units on ion-doped polymer substrate using an interfacial growth approach. **Langmuir**, **2016**, **32(24)**: 6068-6073.
- [21]. Hoda Mollabagher, Salman Taheri, Mohammad Majid Mojtahedi, Seyed Amirhossein Seyedmousavi. Cu-metal organic frameworks (Cu-MOF) as an environment-friendly and economical catalyst for one pot synthesis of tacrine derivatives. **RSC Advances**, **2020**, doi: 10.1039/C9RA10111J.
- [22]. Zhifu Wu, Ya-Qiong Su, Emiel J.M. Hensen, Xinlong Tian, Chenghang You, Qin Xu. Highly Stable Pt₃Ni Nanowires Tailored by Trace Au for the Oxygen Reduction Reaction. **Journal of Materials Chemistry A**, **2019**, **7**, 26402-26409
- [23]. Gaurav Khandelwal, Nirmal Prashanth Maria Joseph Raj, Sang-Jae Kim. Zeolitic imidazole framework: metal-organic framework subfamily members for triboelectric nanogenerators. **Advanced Functional Materials**, **2020**, **30 (12)** doi: 10.1002/adfm.201910162.