Hans Journal of Nanotechnology 纳米技术, 2025, 15(2), 34-41
Published Online May 2025 in Hans. https://www.hanspub.org/journal/nat
https://doi.org/10.12677/nat.2025.152005

Hans汉斯

Ir/Co-N-C的制备及其氧双功能催化性能研究

任梅梅，刘　倩*

天津工业大学物理科学与技术学院，天津

收稿日期：2025年3月25日；录用日期：2025年5月6日；发布日期：2025年5月19日

摘　要

构建清洁低碳的能源体系已成为全球可持续发展的关键任务，在这一转型过程中，发展高效储能技术对于提升可再生能源利用效率具有战略意义。开发具有氧双功能活性(OER/ORR)的催化剂对于燃料电池、金属空气电池器件的效率是至关重要的，贵金属铱(Ir)表现出比较优异的OER性能，然而，Ir作为贵金属，储量极为稀少，致使其成本居高不下，这一现状成为阻碍其大规模商业化推广应用的严重桎梏。开发兼具高活性、高稳定性且成本可控的非贵金属催化剂已成为推动锌空气电池产业化进程的核心课题。本文利用两步退火法结合湿法浸渍制备了低载量Ir的Ir/Co-N-C。首先通过制备金属有机骨架衍生的Co-N-C，再利用浸渍法将Ir负载在Co-N-C上获得的具有双金属位点的Ir/Co-N-C，过电位为304 mV，其过电位低于商业催化剂IrO_2，且$E_{1/2}$ (半波电位)达到0.824 V，表现出良好的双功能催化活性。Ir/Co-N-C的制备还提高了贵金属的原子利用率。通过本文的研究工作为双金属位点的双功能氧电催化剂的制备具有一定的参考意义。

关键词

析氧反应，氧还原反应，低铱电催化剂，两步退火，电催化

Study on the Preparation of Ir/Co-N-C and Its Bifunctional Oxygen Catalytic Activity

Meimei Ren, Qian Liu*

School of Physical Science and Technology, Tiangong University, Tianjin

Received: Mar. 25th, 2025; accepted: May 6th, 2025; published: May 19th, 2025

Abstract

Constructing a clean and low-carbon energy system has become a crucial task for global sustainable development. In the process of this transformation, the development of efficient energy storage tech-

*通讯作者。

文章引用: 任梅梅, 刘倩. Ir/Co-N-C 的制备及其氧双功能催化性能研究[J]. 纳米技术, 2025, 15(2): 34-41.
DOI: 10.12677/nat.2025.152005

nologies is of strategic significance for improving the utilization efficiency of renewable energy. Developing catalysts with bifunctional oxygen activity (OER/ORR) is of vital importance for the efficiency of fuel cells and metal-air battery devices. The noble metal iridium (Ir) exhibits relatively excellent OER performance. However, as a noble metal, Ir has an extremely scarce reserve, leading to its persistently high cost. This situation has become a serious obstacle hindering its large-scale commercial promotion and application. Developing non-noble metal catalysts with high activity, high stability, and controllable cost has become the core issue in promoting the industrialization process of zinc-air batteries. In this paper, Ir/Co-N-C was prepared by using a two-step annealing method combined with the impregnation method. Firstly, Co-N-C derived from a metal-organic framework was prepared, and then Ir was loaded onto Co-N-C by the impregnation method to obtain Ir/Co-N-C with bimetallic sites. The overpotential of Ir/Co-N-C is 304 mV, which is lower than that of the commercial catalyst IrO_2, and its $E_1/_2$ (half-wave potential) reaches 0.824 V, showing good bifunctional catalytic activity. The preparation of Ir/Co-N-C also improves the atomic utilization rate of noble metals. The research work in this paper has certain reference significance for the preparation of bifunctional oxygen electro-catalysts with bimetallic sites.

Keywords

Oxygen Evolution Reaction, Oxygen Reduction Reaction, Low Loading Amount of Ir, Two-Step Annealing, Electrocatalysis

1. 引言

应对传统化石能源依赖与环境恶化问题，科研界正着力推进低成本、生态友好的可再生能源采集、转换及存储技术的研发[1]-[3]。在此背景下，可充电锌空气电池(ZABs)由于其理论能量密度高达 1086 $Wh \cdot kg^{-1}$，工作电压为 1.66 V。不仅安全性能卓越，成本较低，而且对环境十分友好，展现出良好的环境兼容性，因此成为新型储能体系中的重要候选技术，在电动汽车和柔性电子设备等领域展现出应用前景[4]-[8]。尽管研究持续取得突破，该体系仍面临若干技术壁垒，其实际应用仍受制于双功能空气电极的性能瓶颈[9]-[13]。由于充放电过程中涉及的氧还原(ORR)与析氧(OER)反应动力学缓慢，电池性能严重受限于空气电极上双功能催化剂的活性[14]-[16]。开发兼具优异 ORR 和 OER 催化效能的双功能电极材料，已成为提升 ZABs 综合性能的核心突破口。η_{10} (达到 OER 电流密度为 10 $mA \cdot cm^{-2}$ 的电位)和 $E_{1/2}$ (达到 ORR 极限电流密度的一半的电位)之间的电位差($\Delta E = E_{j=10} - E_{1/2}$)是评价双功能催化性能的关键参数。在可逆氧催化过程中，ΔE 值越小，损失的效率也就越小，说明催化性能越好[17]。

ORR 和 OER 由于机理复杂，通常需要不同的催化剂。对 ORR (例如 Pt/C)和 OER (例如 IrO_2，RuO_2)具有高催化活性的贵金属催化剂可以大大加速其缓慢的动力学。然而，它们不能满足可充电 ZABs 的双功能催化活性要求，因为它们仅仅只具有单一的催化活性。通常将 ORR 活性组分和 OER 活性组分混合以获得双功能催化剂。较为遗憾的是，仅仅将贵金属催化剂进行简单混合，往往无法精准达成对 ORR 和 OER 的催化选择性要求。这种混合方式所呈现出的双功能催化活性欠佳、耐久性不佳以及成本高昂等问题，成为了可充电 ZABs 在实际应用推广过程中的严重阻碍[18]-[22]。

过渡金属(TM)基材料和碳基材料作为贵金属基电催化剂的低成本替代材料，近年来得到了众多研究人员的研究关注[16] [23]-[25]。制定有效的策略(如表面功能化、结构工程、杂原子掺杂和制造缺陷)来提

高其内在活性，增加暴露的有效活性位点，对于提高其双功能活性和稳定性至关重要[26]。据报道，TM氧化物或氢氧化物是最有效的 OER 电催化剂之一，与无金属碳材料相比，具有更高的电流密度和更好的稳定性[27]。然而，它们的导电性较差，很难有效地催化 ORR。同时，作为高效的无金属替代品，可充电 ZABs 的实际应用也越来越广泛[28]。同时，具有高导电性和高比表面积的纳米结构碳基材料(如碳纳米管、多孔碳和氮掺杂石墨烯)作为 ORR 的高效无金属替代品，也引起了广泛的研究关注[29]。

在多种过渡金属元素中，以 Co 或 Fe 为中心过渡金属原子的 M-N-C 单原子电催化剂表现出优异的氧电催化活性。基于理论计算，Xu 等人发现 Co-N-C 位点表现出最好的 OER 活性和可接受的 ORR 活性，与基于其他中心金属原子的 M-N-C 位点相比，具有最好的双功能性能[30]。

在实验研究方面，人们对 Co-N-C 双功能电催化剂的研究取得了巨大的进展，特别是对单钴原子分散的先进合成路线的研究。例如，Li 等人通过退火合理设计的前驱体成功制备了 Co-N-C 电催化剂(Co-POC)，这种前驱体是由钴配位框架卟啉与石墨烯杂化而成。前驱体呈现出多尺度结构，涵盖了钴配位卟啉单元、通过共价键相连的框架骨架，以及和石墨烯模板形成的杂化结构。Sun 等人探索了一种简单的“牺牲模板”方法，从排列良好的金属有机框架(MOF)上层结构中制备出分层结构的 Co-N-C 电催化剂，其ΔE 为 0.72 V [31]。由于其双功能催化活性还有待提升，因此，我们提出了两步退火结合湿法浸渍的方法制备了 Ir/Co-N-C，其 OER 的过电位低至 304 mV，$E_{1/2}$ 为 0.824 V。

2. 实验部分

2.1. 试剂

六水合硝酸锌($Zn(NO_3)_2·6H_2O$)、六水合三氯化铁($FeCl_3·6H_2O$)、2-甲基咪唑(2-Methylimidazole)、氯铱酸($H_2IrCl_6·6H_2O$)、无水乙醇(CH_3CH_2OH)、甲醇(CH_3OH)、氢氧化钾(KOH)。实验中所用的试剂未经任何额外处理，实验用水均为去离子水。

2.2. Co-N-C 的制备

首先是将 2.62 g 2-甲基咪唑溶解于 80 mL 甲醇中获得溶液 A；而将 1.34 g 硝酸锌六水合物($Zn(NO_3)_2·6H_2O$)与 0.15 g 硝酸钴($Co(NO_3)_2·6H_2O$)溶解于 80 mL 甲醇中，制成溶液 B。随后，将溶液 A 和溶液 B 混合，所得混合物再搅拌 30 min，然后将溶液陈化 24 h。接着，将得到的沉淀物进行离心处理，并用无水乙醇洗涤数次，然后在 60℃的真空环境下干燥，将产物置于管式炉中，在氩气流中加热至 950℃，并保持 1 h，制得 Co-N-C。

2.3. Ir/Co-N-C 的制备

随后，将 20 mg 的氯铱酸($H_2IrCl_6·6H_2O$)加入到 30 ml 去离子水中获得溶液 C，将制得的 100 mg Co-N-C 在超声辅助下分散于 C 溶液中，超声处理 2 h，然后继续搅拌 2 h。之后，通过离心收集所得样品，用去离子水洗涤数次，再在 60℃的烘箱中干燥。将样品置于管式炉中，在氩气流下 350℃热解 2 h，得到 Ir/Co-N-C。

2.4. 催化剂结构和电化学性能测试

本文通过扫描电子显微镜(SEM)研究了样品的微观形貌并且通过 X 射线衍射(XRD)研究了样品的物相结构。

电化学测试均使用电化学工作站(CHI 760E)，选择三电极体系进行相关测试，以旋转圆盘电极(RDE)为工作电极，对电极和参比电极分别为石墨棒电极和 Ag/AgCl 电极，电解液为 0.1 mol/L KOH 溶液。测试中的所有电位都转化为可逆氢电极(RHE)电位，转换公式：

$$E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.964 \quad (1)$$

其中，E_{RHE} 为相对于可逆氢电极的电势(V)， $E_{Ag/AgCl}$ 为实验测得的相对于 Ag/AgCl 参比电极的电位(V)，pH 由电解液的 pH 测得。

3. 结果与讨论

从图 1(a)为 Co-N-C 的 SEM 图，发现其呈现菱形十二面体的形貌，在负载 Ir 以后保留了菱形十二面体的形貌。没有观察到明显的团簇现象，因此，能够促进更多的活性位点的暴露。

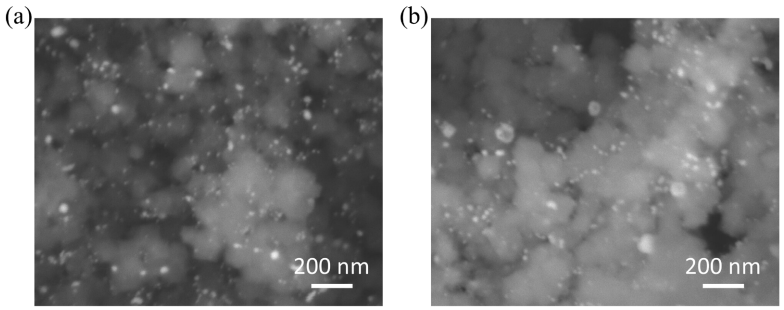

Figure 1. SEM images of (a) Co-N-C and (b) Ir/Co-N-C
图 1. (a) Co-N-C and (b) Ir/Co-N-C 的 SEM 图

为了了解 Co-N-C 和 Ir/Co-N-C 的物相结构，我们对其进行了 XRD 测试，如图 2，测试结果发现，碳峰有一定的偏移，这这可能是由于 Ir 的掺杂引起的，我们在测试结果中没有观察到明显的金属 Ir 相对应的 XRD 信号，这可能是由于 Ir 组分的其分散度高或者含量低所导致的。

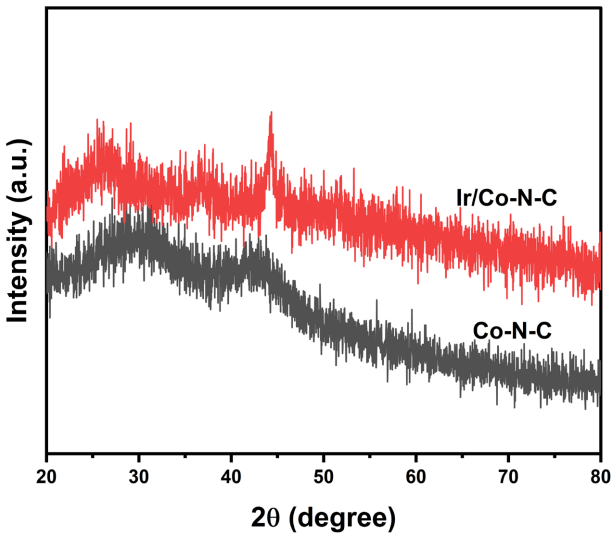

Figure 2. XRD patterns of Co-N-C and Ir/Co-N-C
图 2. Co-N-C and Ir/Co-N-C 的 XRD 图谱

为了研究催化剂的氧双功能催化活性，我们分别在 1 M KOH 和 0.1 M KOH 进行了 OER/ORR 测试，Ir/Co-N-C 过电位为 304 mV，低于 Co-N-C 的过电位(354 mV)和商业 IrO_2(390 mV) (图 3(a))，且其塔菲尔斜率为 165.53 $mV \cdot dec^{-1}$，低于商业催化剂 IrO_2(200.15 $mV \cdot dec^{-1}$) (图 3(b))。Co-N-C 的 $E_{1/2}$ 为 0.842 V，Ir/Co-N-C 的 $E_{1/2}$ 为 0.824 V (图 3(c))，其塔菲尔斜率与 ORR 活性一致(图 3(d))，表现出优异的双功能催

化活性。

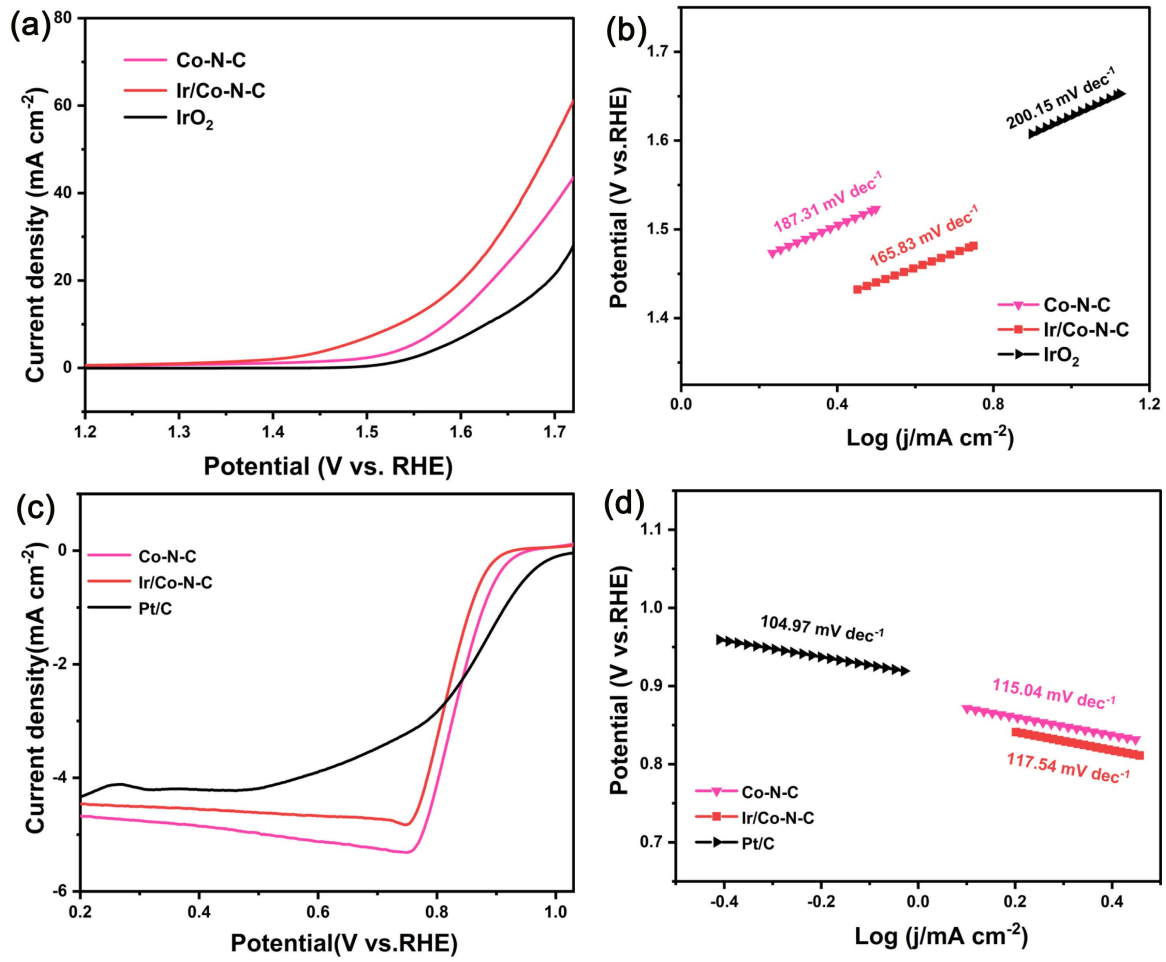

Figure 3. (a) OER polarization curves of Co-N-C, Ir/Co-N-C and IrO_2 catalysts; (b) Tafel slopes; (c) ORR polarization curves of Co-N-C, Ir/Co-N-C and Pt/C catalysts; (d) Tafel slopes

图 3. Co-N-C、Ir/Co-N-C 及 IrO_2 催化剂的 (a) OER 极化曲线；(b) 塔菲尔斜率；(c) Co-N-C、Ir/Co-N-C 及 Pt/C 催化剂的 ORR 极化曲线；(d) 塔菲尔斜率

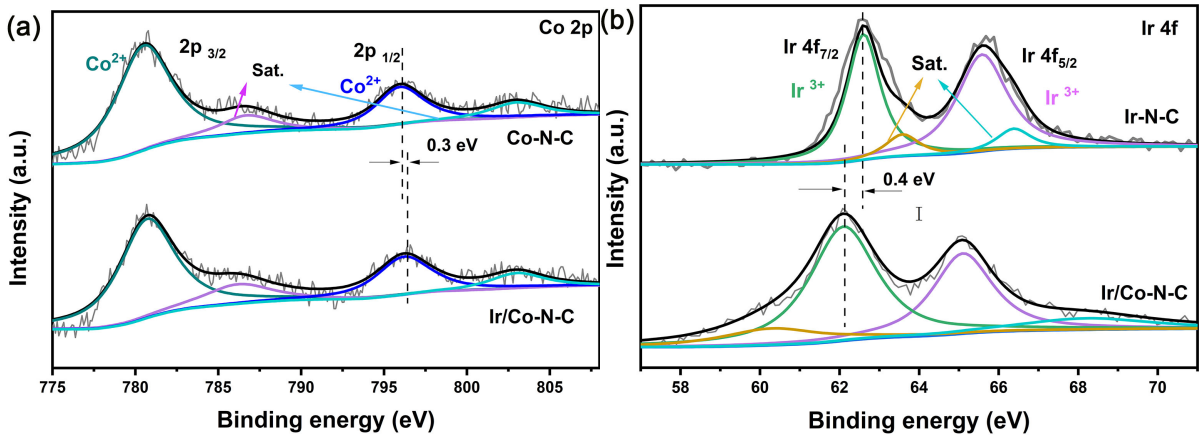

Figure 4. (a) High-resolution Co 2p spectra of Co-N-C, Ir/Co-N-C; (b) High-resolution Ir 4 spectra of Ir/Co-N-C, Ir-N-C

图 4. (a) Co-N-C，Ir/Co-N-C 的 Co 2p 高分辨率图谱；(b) Ir/Co-N-C，Ir-N-C 的 Ir 4f 高分辨率图谱

我们通过 XPS 测试能够了解 Co-N-C、Ir/Co-N-C 和 Ir-N-C 的电子结构，从图 4(a)中可以看到对比于 Co-N-C，在负载铱以后向高能级正移了 0.3 eV，而图 4(b)中 Ir/Co-N-C 对比于 Ir-N-C 向低能级负移了 0.4 eV，表明 Ir/Co-N-C 中 Ir 位点周围的电子密度增加，电子由 Co 向 Ir 转移，Ir/Co 的相互作用有利于提升 Ir 位点的氧双功能催化活性。

图 5(a)是 Co-N-C，Ir/Co-N-C 的电化学阻抗谱图，很明显，Ir/Co-N-C 具有最低的 Rct，表明它的反应动力学过程最快。具有最快的质子传输速率。

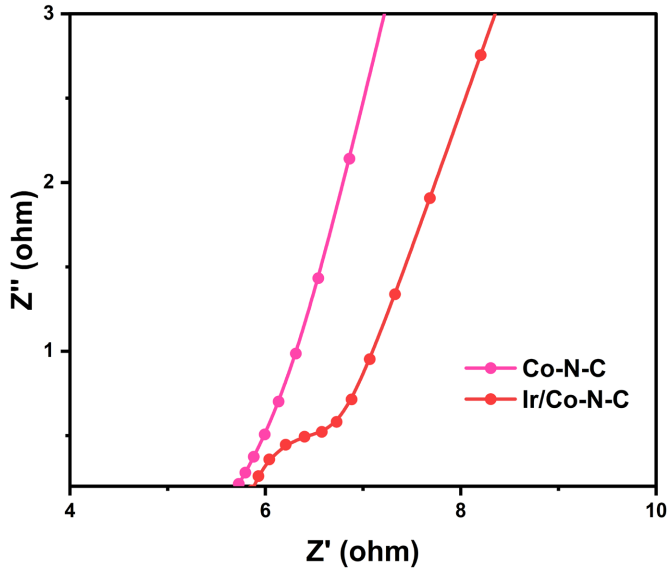

Figure 5. Electrochemical impedance spectroscopy diagrams of Co-N-C, Ir/Co-N-C
图 5. Co-N-C，Ir/Co-N-C 的电化学阻抗谱图

为了测试催化剂的过氧化氢产率和电子转移数，我们进行了 RRDE 测试，如图 6 所示，催化剂 Co-N-C 在负载铱物种前后，其催化过程都接近 4 电子过程，且双氧水产率低于都较低。

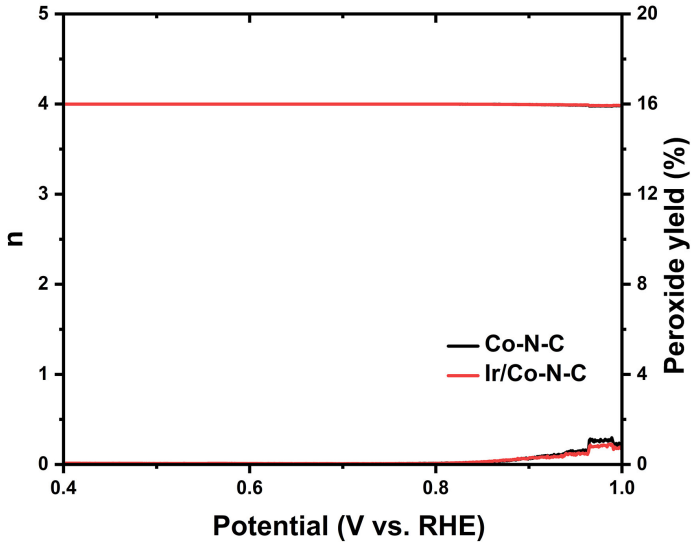

Figure 6. RRDE tests with the percentage of peroxide and electron transfer number
图 6. 旋转圆盘电极(RRDE)测试(关于)过氧化氢的百分比和电子转移数

4. 结果与讨论

综上所述，我们通过高温热解的方法制备了 Co-N-C，然后在 Co-N-C 上浸渍负载贵金属 Ir 获得了 Ir/Co-N-C。通过电化学测试表明，Ir/Co-N-C 的过电位为 304 mV，其过电位低于 Co-N-C(354 mV)和商业 IrO_2(394 mV)。Ir/Co-N-C 在提升 OER 催化活性的同时，也保留了良好的 ORR 活性($E_{1/2}$ = 0.824 V)，增加了催化剂的氧双功能催化剂活性。Ir/Co-N-C 还提升了贵金属的原子利用率，且使得催化剂的石墨化程度增加，且催化过程为四电子过程，有较低的过氧化氢产率。因此，利用两步退火结合湿法浸渍的方法制备的具有双金属位点双功能氧电催化剂 Ir/Co-N-C，其 Ir/Co 的相互作用有利于提升 Ir 位点的氧双功能催化活性。这对其它氧双功能催化剂制备具有一定借鉴作用。

参考文献

[1] Cui, H., Guo, Y., Guo, L., Wang, L., Zhou, Z. and Peng, Z. (2018) Heteroatom-Doped Carbon Materials and Their Composites as Electrocatalysts for CO_2 Reduction. *Journal of Materials Chemistry A*, **6**, 18782-18793. https://doi.org/10.1039/c8ta07430e

[2] Luo, M., Sun, W., Xu, B.B., Pan, H. and Jiang, Y. (2020) Interface Engineering of Air Electrocatalysts for Rechargeable Zinc-Air Batteries. *Advanced Energy Materials*, **11**, Article ID: 2002762. https://doi.org/10.1002/aenm.202002762

[3] Liu, D., Tong, Y., Yan, X., Liang, J. and Dou, S.X. (2019) Recent Advances in Carbon-Based Bifunctional Oxygen Catalysts for Zinc-Air Batteries. *Batteries & Supercaps*, **2**, 743-765. https://doi.org/10.1002/batt.201900052

[4] Khalid, M., Bhardwaj, P.A., Honorato, A.M.B. and Varela, H. (2020) Metallic Single-Atoms Confined in Carbon Nanomaterials for the Electrocatalysis of Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions. *Catalysis Science & Technology*, **10**, 6420-6448. https://doi.org/10.1039/d0cy01408g

[5] Wu, M., Zhang, G., Qiao, J., Chen, N., Chen, W. and Sun, S. (2019) Ultra-Long Life Rechargeable Zinc-Air Battery Based on High-Performance Trimetallic Nitride and NCNT Hybrid Bifunctional Electrocatalysts. *Nano Energy*, **61**, 86-95. https://doi.org/10.1016/j.nanoen.2019.04.031

[6] Wu, M., Tang, Q., Dong, F., Wang, Y., Li, D., Guo, Q., *et al*. (2016) The Design of Fe,N-Doped Hierarchically Porous Carbons as Highly Active and Durable Electrocatalysts for a Zn-Air Battery. *Physical Chemistry Chemical Physics*, **18**, 18665-18669. https://doi.org/10.1039/c6cp02785g

[7] Dong, F., Liu, C., Wu, M., Guo, J., Li, K. and Qiao, J. (2019) Hierarchical Porous Carbon Derived from Coal Tar Pitch Containing Discrete Co-N_x-C Active Sites for Efficient Oxygen Electrocatalysis and Rechargeable Zn-Air Batteries. *ACS Sustainable Chemistry & Engineering*, **7**, 8587-8596. https://doi.org/10.1021/acssuschemeng.9b00373

[8] Chen, T., Wu, J., Zhu, C., Liu, Z., Zhou, W., Zhu, C., *et al*. (2021) Rational Design of Iron Single Atom Anchored on Nitrogen Doped Carbon as a High-Performance Electrocatalyst for All-Solid-State Flexible Zinc-Air Batteries. *Chemical Engineering Journal*, **405**, Article ID: 125956. https://doi.org/10.1016/j.cej.2020.125956

[9] Zhao, C., Liu, J., Wang, J., Ren, D., Yu, J., Chen, X., *et al*. (2021) Zinc-Air Batteries: A δe = 0.63 V Bifunctional Oxygen Electrocatalyst Enables High-Rate and Long-Cycling Zinc-Air Batteries (Adv. Mater. 15/2021). *Advanced Materials*, **33**, Article ID: 2170117. https://doi.org/10.1002/adma.202170117

[10] Ma, L., Chen, S., Pei, Z., Huang, Y., Liang, G., Mo, F., *et al*. (2018) Single-Site Active Iron-Based Bifunctional Oxygen Catalyst for a Compressible and Rechargeable Zinc-Air Battery. *ACS Nano*, **12**, 1949-1958. https://doi.org/10.1021/acsnano.7b09064

[11] Zhou, T., Zhang, N., Wu, C. and Xie, Y. (2020) Surface/Interface Nanoengineering for Rechargeable Zn-Air Batteries. *Energy & Environmental Science*, **13**, 1132-1153. https://doi.org/10.1039/c9ee03634b

[12] Wang, M., Ji, H., Liu, S., Sun, H., Liu, J., Yan, C., *et al*. (2020) Single-Atom Scale Metal Vacancy Engineering in Heteroatom-Doped Carbon for Rechargeable Zinc-Air Battery with Reduced Overpotential. *Chemical Engineering Journal*, **393**, Article ID: 124702. https://doi.org/10.1016/j.cej.2020.124702

[13] Yang, D., Tan, H., Rui, X. and Yu, Y. (2019) Electrode Materials for Rechargeable Zinc-Ion and Zinc-Air Batteries: Current Status and Future Perspectives. *Electrochemical Energy Reviews*, **2**, 395-427. https://doi.org/10.1007/s41918-019-00035-5

[14] Zang, W., Sumboja, A., Ma, Y., Zhang, H., Wu, Y., Wu, S., *et al*. (2018) Single Co Atoms Anchored in Porous N-Doped Carbon for Efficient Zinc-Air Battery Cathodes. *ACS Catalysis*, **8**, 8961-8969. https://doi.org/10.1021/acscatal.8b02556

[15] Zhong, Y., Xu, X., Wang, W. and Shao, Z. (2018) Recent Advances in Metal-Organic Framework Derivatives as Oxygen Catalysts for Zinc-Air Batteries. *Batteries & Supercaps*, **2**, 272-289. https://doi.org/10.1002/batt.201800093

[16] Wang, X., Liao, Z., Fu, Y., Neumann, C., Turchanin, A., Nam, G., *et al*. (2020) Confined Growth of Porous Nitrogen-Doped Cobalt Oxide Nanoarrays as Bifunctional Oxygen Electrocatalysts for Rechargeable Zinc-Air Batteries. *Energy Storage Materials*, **26**, 157-164. https://doi.org/10.1016/j.ensm.2019.12.043

[17] Xia, C., Zhou, Y., He, C., Douka, A.I., Guo, W., Qi, K., *et al*. (2021) Recent Advances on Electrospun Nanomaterials for Zinc-Air Batteries. *Small Science*, **1**, Article ID: 2100010. https://doi.org/10.1002/smsc.202100010

[18] Wang, Y., Kumar, A., Ma, M., Jia, Y., Wang, Y., Zhang, Y., *et al*. (2020) Hierarchical Peony-Like Feco-Nc with Conductive Network and Highly Active Sites as Efficient Electrocatalyst for Rechargeable Zn-Air Battery. *Nano Research*, **13**, 1090-1099. https://doi.org/10.1007/s12274-020-2751-7

[19] Huang, K., Guo, S., Wang, R., Lin, S., Hussain, N., Wei, H., *et al*. (2020) Two-Dimensional MOF/MOF Derivative Arrays on Nickel Foam as Efficient Bifunctional Coupled Oxygen Electrodes. *Chinese Journal of Catalysis*, **41**, 1754-1760. https://doi.org/10.1016/s1872-2067(20)63613-0

[20] Xu, Y.Y., *et al*. (2019) 2D Nitrogen-Doped Carbon Nanotubes/Graphene Hybrid as Bifunctional Oxygen Electrocatalyst for Long-Life Rechargeable Zn-Air Batteries. *Advanced Functional Materials*, **30**, Article ID: 1906081.

[21] Chen, J., Li, H., Fan, C., Meng, Q., Tang, Y., Qiu, X., *et al*. (2020) Dual Single-Atomic Ni-N_4 and Fe-N_4 Sites Constructing Janus Hollow Graphene for Selective Oxygen Electrocatalysis. *Advanced Materials*, **32**, Article ID: 2003134. https://doi.org/10.1002/adma.202003134

[22] Zhang, K., Zhang, Y., Zhang, Q., Liang, Z., Gu, L., Guo, W., *et al*. (2020) Metal-Organic Framework-Derived Fe/Cu-Substituted Co Nanoparticles Embedded in CNTs-Grafted Carbon Polyhedron for Zn-Air Batteries. *Carbon Energy*, **2**, 283-293. https://doi.org/10.1002/cey2.35

[23] Wang, H., Tang, C. and Zhang, Q. (2018) A Review of Precious-Metal-Free Bifunctional Oxygen Electrocatalysts: Rational Design and Applications in Zn-Air Batteries. *Advanced Functional Materials*, **28**, Article ID: 1803329. https://doi.org/10.1002/adfm.201803329

[24] Dong, F., Cai, Y., Liu, C., Liu, J. and Qiao, J. (2018) Heteroatom (B, N and P) Doped Porous Graphene Foams for Efficient Oxygen Reduction Reaction Electrocatalysis. *International Journal of Hydrogen Energy*, **43**, 12661-12670. https://doi.org/10.1016/j.ijhydene.2018.04.118

[25] Li, X., Dong, F., Xu, N., Zhang, T., Li, K. and Qiao, J. (2018) Co_3O_4/MnO_2/Hierarchically Porous Carbon as Superior Bifunctional Electrodes for Liquid and All-Solid-State Rechargeable Zinc-air Batteries. *ACS Applied Materials & Interfaces*, **10**, 15591-15601. https://doi.org/10.1021/acsami.7b18684

[26] Han, X., Wu, X., Zhong, C., Deng, Y., Zhao, N. and Hu, W. (2017) $NiCo_2S_4$ Nanocrystals Anchored on Nitrogen-Doped Carbon Nanotubes as a Highly Efficient Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries. *Nano Energy*, **31**, 541-550. https://doi.org/10.1016/j.nanoen.2016.12.008

[27] Qiu, H., Du, P., Hu, K., Gao, J., Li, H., Liu, P., *et al*. (2021) Metal and Nonmetal Codoped 3D Nanoporous Graphene for Efficient Bifunctional Electrocatalysis and Rechargeable Zn-Air Batteries. *Advanced Materials*, **33**, Article ID: 2101386. https://doi.org/10.1002/adma.202101386

[28] Xia, B.Y., Yan, Y., Li, N., Wu, H.B., Lou, X.W. and Wang, X. (2016) A Metal-Organic Framework-Derived Bifunctional Oxygen Electrocatalyst. *Nature Energy*, **1**, Article No. 15006. https://doi.org/10.1038/nenergy.2015.6

[29] Wei, L., Ang, E.H., Yang, Y., Qin, Y., Zhang, Y., Ye, M., *et al*. (2020) Recent Advances of Transition Metal Based Bifunctional Electrocatalysts for Rechargeable Zinc-Air Batteries. *Journal of Power Sources*, **477**, Article ID: 228696. https://doi.org/10.1016/j.jpowsour.2020.228696

[30] Xu, H., Cheng, D., Cao, D. and Zeng, X.C. (2018) Retracted Article: A Universal Principle for a Rational Design of Single-Atom Electrocatalysts. *Nature Catalysis*, **1**, 339-348. https://doi.org/10.1038/s41929-018-0063-z

[31] Sun, X., Sun, S., Gu, S., Liang, Z., Zhang, J., Yang, Y., *et al*. (2019) High-Performance Single Atom Bifunctional Oxygen Catalysts Derived from ZIF-67 Superstructures. *Nano Energy*, **61**, 245-250. https://doi.org/10.1016/j.nanoen.2019.04.076