

Rational Design of Engineered Porous Transition Metal-based Electrocatalysts for Rechargeable Zinc-air Batteries

by

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This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

The thesis is based on published works and contains drafted work for submission. Various chapters are adapted from the following publications.

Chapter 3 this thesis includes a paper that co-authored by myself, my supervisor, Dr. Yi Jiang, Dr. Gaopeng Jiang, Tyler Or, Dr. Rui Gao, Haoze Zhang, Dr. Zhengyu Bai, Chen Ning, Dr. Yaping Deng. I am the first author of this paper. I conducted most of the experiments, data processing and analysis along with writing of the manuscript. Dr. Yaping Deng participants in the setup design for operando X-ray absorption spectroscopic measurements and X-ray absorption spectroscopy analysis.

“Ordered mesoporous Fe_2N_x electrocatalysts with regulated nitrogen vacancy for oxygen reduction reaction and Zn-air battery”, Nano Energy, 2023, 108672.

Chapter 5 of this thesis includes a paper that was co-authored by myself, my supervisor, Dr. Zhen Zhang, Dr. Gaopeng Jiang, Dr. Alireza Haghighat Mamaghani, Dr. Serubbabel Sy, Dr. Rui Gao, Dr. Yi Jiang, Dr. Yaping Deng, Dr. Zhengyu Bai, Dr. Lin Yang and Dr. Aiping Yu. I am the first author of this paper. I conducted most of the experiments, data processing and analysis along with writing of the manuscript. Dr. Zhen Zhang participants in the setup design for operando X-ray absorption spectroscopic measurements and X-ray absorption spectroscopy analysis.

“Three-dimensionally ordered mesoporous Co_3O_4 decorated with Mg as bifunctional oxygen electrocatalysts for high-performance zinc-air batteries”, Nano Energy, 2022, 107425.

Abstract

The adoption of primary zinc-air batteries (ZABs) for telecommunication and medical applications underscores their commercial viability. However, the progress of ZABs have been hindered by challenges associated with air electrodes. The substantial electrode polarizations of the Oxygen Reduction Reaction (ORR) and the Oxygen Evolution Reaction (OER) pose significant energy barriers, impeding the efficiency of charge and discharge processes. Hence, there's an urgent need to develop bifunctional electrocatalysts with superior performance, energy efficiency, and long-term stability for ZABs.

In the first work, three-dimensional interconnected and ordered mesoporous Fe_2N_x decorated on TiO_y with the introduced nitrogen vacancies was constructed ($\text{Fe}_2\text{N}_x@\text{TiO}_y$). By creating defects in ordered porous materials, the increased surface area, pore volume, and active sites boost the kinetics of the ORR. $\text{Fe}_2\text{N}_x@\text{TiO}_y$ with created nitrogen defects reveals a superior ORR performance, including a high half-wave potential (0.88 V vs reversible hydrogen electrode) and high current density (71 mA cm^{-2} at 0.8 V). The zinc-air battery assembled with $\text{Fe}_2\text{N}_x@\text{TiO}_y$ catalysts presents a high specific capacity of 809 mAh g^{-1} . Density functional theory (DFT) analysis and X-ray absorption spectroscopy further confirm that the engineering of nitrogen vacancies modulates the electronic environment of Fe and regulates the adsorption and desorption of intermediates to facilitate the ORR activity. The Fe d-band center moving toward the Fermi energy level strengthens the interaction between the adsorbate and substrate, allowing oxygen species to be favorably stabilized onto $\text{Fe}_2\text{N}_x@\text{TiO}_y$, while significantly reducing the kinetic barrier. This work serves as a guideline for developing effective defect engineering and ordered porous materials for efficient energy conversion and storage.

In the second work, among a series of ternary Cu-Ti-O electrocatalysts, a hierarchical macroporous $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst achieves a balance between structural stability and active sites exposure, showing an electron density reconfiguration in the Cu-Ti-O system. X-ray absorption fine structure analyses reveal the partial electron density reconfiguration presented among Cu, Ti, and O atoms can be the dominant reason for the peaks shift. It was demonstrated that Ti atoms tended to delocalize maximum charge by releasing it to the Cu atoms in the compositions of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, which lower the thermodynamic barrier of the total reaction, and hence contributes to a remarkable enhancement in zinc-air battery. This work offers an attractive approach to developing the nonprecious transitional metal-based ORR/OER catalysts, and zinc-air battery for the design of performance-oriented electrocatalysts for wider electrochemical energy applications.

In the last work, a unique Mg-decorated three-dimensionally ordered mesoporous (3DOM) Co_3O_4 electrocatalyst is engineered and evaluated as cathodic material for zinc-air batteries. The modulation of electronic structure and bonding configuration of Co sites through coordination with substituted Mg atoms effectively enhance the interaction with oxygen species and, therefore, the ORR/OER activity. Meanwhile, the substitution of Co^{2+} with Mg^{2+} creates abundant, more catalytically active octahedral sites (Co^{3+}) in 3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Moreover, the tailored 3D interpenetrating porous structure endows the electrocatalyst with large diffusion channels for oxygen species and highly accessible active sites. The as-prepared catalyst retains 99% and 98% of its initial ORR and OER current, respectively, after 16 h under chronoamperometric measurement. The zinc-air battery assembled with 3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ exhibits a high power density of 253 mW cm^{-2} and long-term cyclability over 236 h, outperforming the commercial noble-metal-based catalysts in terms of performance and stability.

This work offers a straightforward and promising design strategy for the development of robust bifunctional electrocatalysts toward practical applications of zinc-air batteries.

In summary, this thesis exhibits three types of transition metal-based materials with hierarchical three-dimensional porous structures applied in rechargeable zinc-air batteries. The main emphasis is focused on the synthesis and electrocatalytic activity as well as the underlying mechanisms for these materials in zinc air battery. It gives a prospect that is expected to engineer and synthesize porous transition metal-based materials for zinc-air batteries.

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Table of Contents

Examining Committee Membership	ii
Author's Declaration	iii
Statement of Contributions.....	iv
Abstract.....	v
Acknowledgments	viii
List of Figures.....	xii
List of Tables	xix
List of Abbreviations	xx
Chapter 1 Introduction.....	1
1.1 Background and Motivation	1
1.2 The fundamentals of Zn-air battery	5
1.2.1 ORR and OER	10
1.3 Transition metal-based catalysts with porous structure	18
1.3.1 Ordered porous structure	22
1.3.2 Creating vacancies.....	25
1.3.3 Ternary transition metal-based materials.....	28
1.5 Structure of thesis.....	35
Chapter 2 Characterization Techniques.....	37
2.1 Electrochemical Characterization Techniques.....	37
2.1.1 Galvanodynamic charge and discharge testing	37
2.1.2 Galvanostatic cycling testing	38
2.1.3 Electrochemical testing methods.....	39
2.2 Physical characterization.....	41

2.2.1 X-ray diffraction (XRD).....	41
2.2.2 Scanning electron microscopy (SEM).....	42
2.2.3 Transmission electron microscopy (TEM).....	43
2.2.4 X-Ray photoelectron spectroscopy (XPS)	44
2.2.5 X-ray adsorption spectroscopy.....	45
2.2.6 N ₂ adsorption desorption analysis.....	46
Chapter 3 Nitrogen-vacancy-regulated ordered mesoporous Fe₂N_x electrocatalysts for enhanced oxygen reduction reaction	48
3.1 Introduction	48
3.2 Experimental methods	50
3.2.1 Materials characterization.....	51
3.2.2 Electrochemical measurements.....	52
3.3 Results and Discussions	53
3.4 Conclusions	66
Chapter 4 Synergistic regulation of ternary Cu-Ti-O catalyst for zinc air batteries	68
4.1 Introduction	68
4.2.2 Material characterization	71
4.2.3 Electrochemical evaluation.....	71
4.3 Results and discussion.....	74
4.4 Conclusion.....	82
Chapter 5 Three-dimensionally ordered mesoporous Co₃O₄ decorated with Mg as bifunctional oxygen electrocatalysts for high-performance zinc-air batteries.....	84
5.1 Introduction	84
5.2 Experimental section.....	86
5.2.1 Synthesis of 3DOM Mg _x Co _{3-x} O ₄ and bulk Mg _x Co _{3-x} O ₄	86
5.2.2 Materials Characterization.....	88

5.2.3 Electrochemical measurements	88
5.2.4 DFT simulation details	89
5.3 Results and discussion	90
5.4 Conclusion	104
Chapter 6 Conclusions and Recommendations	106
Letters of Copyright Permission	110
References	111

List of Figures

Figure 1.1 Schematic of global energy consumption. Copyright BP Statistical Review of World Energy.....	2
Figure 1.2 a) Theoretical energy and b) Ragone plots for various metal–air batteries. ¹² Copyright 2019 Nanomaterials.	5
Figure 1.3 Schematic diagram of alkaline zinc-air battery. ¹⁶ Copyright 2020, Journal of Power Source.	7
Figure 1.4 a) illustration of the required structural properties of the O ₂ electrocatalyst. b) Evaluation of the potential difference (ΔE) during the OER and ORR. E ₁₀ : potential needed to achieve a current density (j) of 10 mA cm ⁻² during the OER, E _{1/2} : half-wave potential for the ORR, and RHE: reversible hydrogen electrode. ²⁴ Copyright 2020, APL Mater.	9
Figure 1.5 a) Schematic illustration of the ORR LSV curve. (b) Experimental and fitting ORR LSV curves for Pt/C. j_0 and n are simulated accordingly. ²⁸ Copyright 2021, Applied Catalysis B: Environmental.....	15
Figure 1.6 Modification strategies, corresponding means and electrochemical applications of TMOs. ⁴⁵ Copyright 2021, Energy Storage Materials.	20
Figure 1.7 Classification based on pore size of porous materials.....	22
Figure 1.8 Schematic for preparation of mesoporous materials by HTM. ⁵⁶ Copyright 2018, Ionics.....	24
Figure 1.9 Schematic for preparation of mesoporous materials by STM. ⁵⁶ Copyright 2018, Ionics.....	25
Figure 1.10 The role of vacancies on tuning the electrocatalytic performance. ⁴⁸ Copyright 2021, Journal of Alloys and Compounds.....	26

Figure 1.11 a) Schematic for the preparation of defective amorphous-crystalline CoO nanosheets. b-d) Density of states (DOS) of CoO and oxygen-defective CoO models. Reproduced with permission from ref ⁶⁵ e) Schematic for the preparation of FeOOH/PNGNs. The atomic structure of f) (100) surface of perfect β -FeOOH (Fe-perf), g) (100) surface of β -FeOOH with a Fe vacancy (Fe-vac), h) Fe-perf covered by graphene (Fe-perf-G), and i) Fe-vac covered by graphene (Fe-vac-G). j) The free energy variations for Fe-perf, Fe-vac, Fe-perf-G, and Fe-vac-G during the oxygen reduction processes. The red, white, gray, blue, and brown spheres denote O, H, C, N, and Fe atoms, respectively. Reproduced with permission from ref ⁶⁷ Copyright 2018, Advanced Functional Materials. 28

Figure 1.12 a) Schematic illustration of synthesis of $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{@hNCTs}$. b) Charge and discharge polarization curves; inset: a photograph of a blue LED powered by a ZAB based on the $\text{Fe}_4\text{Co}_1\text{Ni}_2\text{@hNCT}$ catalyst. c) The mechanism of a 4e^- ORR in an alkaline medium occurring on the single-site Fe atom of FeNi-N_6 . d) Gibbs free energy diagram of the ORR at 0.46 V on Fe-N_4 , FeCo-N_6 , and FeNi-N_6 , respectively. Reproduced with permission from ref⁷¹ Copyright 2022, Nanoscale e) Polarization curves of FeCo/NUCSs and Pt/C (or RuO_2) catalysts using the three-electrode system in the full OER/ORR region in O_2 -saturated 0.1 M KOH solution. f) Schematic diagram of the XRD diffractometer equipped with a two-electrode electrolysis system for in situ XRD measurement. g) In situ XRD patterns of FeCo/NUCSs collected during OER. Reproduced with permission from ref ⁷² 30

Figure 1.13 a) Adsorption configuration of OER and ORR intermediate (OOH^* , O^* , and OH^*) for cubic centered Co_9S_8 and $\text{Ni-Co}_9\text{S}_8$; b) Free energy diagram of two models at different operation potentials for the ORR and c) OER. Reproduced with permission from ref²⁸ Copyright 2021, Applied Catalysis B: Environmental c) The Gibbs free energy profiles of the four-step

oxygen reduction of Mn/Co-450 at pH= 13 and U= 0 V (b), and the oxygen evolution reaction over Co ₃ O ₄ (001) and the Co1site of Mn/Co-450 (001) at pH= 13 and U= 0.46 V. Reproduced with permission from ref ⁷⁷	32
Figure 1.14 Schematic illustration of the research goals throughout this thesis.....	34
Figure 2.1 Charge–discharge polarization curves for the rechargeable zinc air battery. ⁷⁸ Copyright 2015, John Wiley & Sons.	38
Figure 2.2 Cycle performance for the rechargeable zinc-air battery. ⁷⁸ Copyright 2015, John Wiley & Sons.....	38
Figure 2.3 The schematic of XRD mechanism and the Bragg’s Law. Copyright 2018, ©2021 Let’s Talk Academy.	41
Figure 2.4 The schematic illustration of core components and working principles of SEM. ⁷⁹ Copyright 2019, Bone Research.	43
Figure 2.5 The schematic illustration of a XPS instrument. Copyright 2021, In Handbook of Mineral Spectroscopy	44
Figure 2.6 The schematic illustration of a XAS instrument. Copyright 2010, Chem. Soc. Rev.	45
Figure 3.1 a) Synthesis route for Fe ₂ N _x @TiO _x . b-h) HADDF-STEM image and corresponding elemental mapping for Fe, N, Ti, O, C and mixture. i) Enlarged TEM image and j) HRTEM image of Fe ₂ N _x @TiO _x	56
Figure 3.2 a) XRD pattern, and b) EPR spectra of Fe ₂ N _x @TiO _y -20, Fe ₂ N _x @TiO _y -40, Fe ₂ N _x @TiO _y -60 and Fe ₂ N@TiO _y . c) N ₂ adsorption-desorption isotherms, and (d) pore size distribution plots of Fe ₂ N _x @TiO _y -20, Fe ₂ N _x @TiO _y -40, Fe ₂ N _x @TiO _y -60 and Fe ₂ N@TiO _y . XPS spectra of Fe ₂ N _x @TiO _y : (e) Fe 2p spectra, and (f) N 1s spectra.	57

Figure 3.3 a) LSV curves of $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60 and a series of counterpart catalysts in 0.1M KOH; b) corresponding Tafel plots and c) comparison of J_k at 0.8 V and $E_{1/2}$ for various reference catalysts. d) Power density plots and e) long-term durability test for $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60-based zinc-air battery and the reference catalysts-based zinc-air battery at 10 mA cm^{-2} . f) Specific capacity of $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60-based zinc-air battery and Pt/C-based zinc-air battery. 59

Figure 3.4 a) LSV curves of $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60 at different rotation speeds from 400 to 1600. and b) corresponding Koutecký–Levich plots of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials from 0.3 to 0.5 V..... 60

Figure 3.5 a) ORR chronoamperometric response at 0.6 V vs. RHE for $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60 and Pt/C. b) Open circuit plot of $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -20, $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -40, $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60 and $\text{Fe}_2\text{N}@\text{TiO}_x$ of the zinc-air batteries as air cathodes. 61

Figure 3.6 a) The calculated charge density densities and b) optimized model configuration of $\text{Fe}_2\text{N}_x@\text{TiO}_x$. c) Calculated energy barriers of $^*\text{OOH}$ transformation to $^*\text{OH}$ at active sites of $\text{Fe}_2\text{N}@\text{TiO}_y$ and $\text{Fe}_2\text{N}_x@\text{TiO}_y$. d) Projected density of states for model catalysts with surface Fe sites in $\text{Fe}_2\text{N}@\text{TiO}_x$ and $\text{Fe}_2\text{N}_x@\text{TiO}_x$. Free energy variations for ORR on e) $\text{Fe}_2\text{N}@\text{TiO}_x$ and f) $\text{Fe}_2\text{N}_x@\text{TiO}_x$ 63

Figure 3.7 a) Fe K-edge XANES spectra, Fe_2O_3 and standard Fe foil. b) Fe K-edge XANES spectra at specific area and c) Fourier-transformed (FT) curves at R space of $\text{Fe}_2\text{N}@\text{TiO}_y$, $\text{Fe}_2\text{N}_x@\text{TiO}_y$. WT for the k^3 -weighted Fe K-edge of d) Fe foil, e) $\text{Fe}_2\text{N}@\text{TiO}_y$ and f) $\text{Fe}_2\text{N}_x@\text{TiO}_y$ g) Fe_2O_3 65

Scheme 4.1 Schematic illustration for the Cu-Ti-O ternary materials electrocatalysts. 74

Figure 4.2 a) XRD pattern of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, b) N_2 adsorption–desorption isotherms and c) pore size distribution plots of $\text{Cu}_{0.4}\text{Ti}_{0.6}\text{O}_2$, $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, and $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$. d) High-

resolution XPS spectra for O 1s of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, e) for Ti 2p of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and TiO_2 , f) for Cu 2p of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, and CuO 76

Figure 4.3 a) Cu K-edge XANES spectra and) corresponding Fourier-transform k^3 -weighted EXAFS spectra for various samples. 78

Figure 4.4 a) LSV curves of different catalysts in O_2 -saturated solution with a scan rate of 5 mV s^{-1} . b) LSV curves of the $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ in O_2 -saturated 0.1 M solution at different rotation rates with a scan rate of 5 mV s^{-1} . c) K-L plot obtained from LSV curves of (b) at various potentials. d) LSV curves of different catalysts in N_2 -saturated solution with a scan rate of 5 mV s^{-1} . e) Tafel plot of the $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$ and RuO_2 catalyst. f) overpotential differences between the $E_{\text{half-wave}}$ of ORR and $E_j = 20 \text{ mA cm}^{-2}$ of OER different electrocatalysts in 0.1 M KOH 80

Figure 4.5 a) Open circuit plot; b) Galvanodynamic charge and discharge polarization curves of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and commercial Pt/C+Ir/C of the zinc-air batteries as air cathodes; c) Galvanostatic cycling stability of ZABs prepared with $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and commercial Pt/C+Ir/C electrode. d) Corresponding power density plots of two electrodes. 81

Figure 5.1 (a) Schematic illustration of the preparation procedure of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. (b) STEM image and (c-f) corresponding EDS elemental mapping, and (g-i) TEM and HRTEM image and (j) corresponding SAED pattern of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ 93

Figure 5.2 SEM images of PS beads. 93

Figure 5.3 SEM images of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ 93

Figure 5.4 (a) X-ray diffraction pattern, (b) N_2 adsorption-desorption isotherms, and (c) pore size distribution plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ catalysts. (d) XPS spectra and high-resolution spectra of (e) Mg 1s, (f) Co 2p and (g) O 1s of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ 95

Figure 5.5 (a) ORR polarization curves, (b) OER LSV curves, and (c) OER Tafel plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 , $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrocatalysts, commercial Ir/C, and Pt/C. (d) overpotential differences between the $E_{\text{half-wave}}$ of ORR and $E_j = 10 \text{ mA cm}^{-2}$ of OER for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 , $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrocatalysts in 0.1M KOH. (e) ORR chronoamperometric response at 0.6 V vs. RHE for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C. (f) OER chronoamperometric response of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Ir/C at a fixed potential of 1.6 V vs. RHE. (g) Galvanostatic discharge–charge long-term cycling test using 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and commercial “Ir/C+ Pt/C” electrodes at a constant density 10 mA cm^{-2} . (h) Charge and discharge polarization curves and (i) power density plots for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and commercial “Ir/C+ Pt/C” electrodes. 96

Figure 5.6 a) Open-circuit voltage curves of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C+Ir/C electrode. b) Energy efficiency plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C+ Ir/C electrode. 97

Figure 5.7 a) LSV curves of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ in 0.1 M KOH at different rotation rates and sweep rate of 10 mVs^{-1} ; b) K-L plots (J^{-1} versus $\omega^{-1/2}$) at different potentials. 98

Figure 5.8 a) The proposed ORR mechanism on 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. (b) Calculated energy barriers of $\ast\text{OH}$ transformation to $\ast\text{OOH}$ at active sites of 3DOM Co_3O_4 and 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Calculated free energy for (c) ORR and (d) OER on 3DOM Co_3O_4 and 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Calculated density of states (DOS) of d orbitals of surface active sites in (e) 3DOM Co_3O_4 (two Co sites) and (f) 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ (one Mg site and one Co site). The blue dashed line represents the corresponding energy level of d band center; the Fermi level is set to 0 eV. 101

Figure 5.9 a) Co K-edge XANES spectra and (b) corresponding Fourier-transform k^3 -weighted EXAFS spectra for various samples. (c) Co L-edge XANES and (d) Mg K-edge XANES spectra

of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and some reference samples. (e) Wavelet transforms for the k^3 -weighted Co K-edge EXAFS signals of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and (f) Co_3O_4 103

List of Tables

Table 3.1 Comparison of bifunctional performance and zinc-air batteries performance of $\text{Fe}_2\text{N}_x@\text{TiO}_x$ -60 with recently reported Fe-based electrocatalysts.....	62
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List of Abbreviations

Abbreviations	Intended Word/Phrases
3DOM	Three-dimensionally ordered mesoporous
ZABs	Zinc air batteries
DFT	Density functional theory
LIBs	Lithium-ion batteries
RZABs	Rechargeable zinc air batteries
ORR	Oxygen reduction reaction
OER	Oxygen evolution reaction
GDL	Gas Diffusion Layer
PTFE	Polytetrafluoroethylene
HTM	Hard templating method
STM	Soft templating method
EDS	Energy-dispersive X-ray spectroscopy
LSV	Linear sweep voltammetry
RDE	Rotating disc electrode
SCE	Saturated calomel electrode
RHE	Reversible hydrogen electrode
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

STEM	Scanning Transmission Electron Microscopy
XAS	X-ray Absorption Spectroscopy
XANES	X-ray Absorption Near Edge Structure
EXAFS	Extended X-ray absorption fine structure
BET	Brunauer–Emmett–Teller
EPR	Electron Paramagnetic Response
η	Overpotential

Chapter 1 Introduction

1.1 Background and Motivation

In the contemporary era, humanity confronts substantial challenges posed by global energy and environmental crises. The relentless pace of industrialization and population expansion has precipitated a significant depletion of fossil energy reserves, encompassing natural gas, coal, and petroleum.¹⁻³ Despite efforts to augment the utilization of renewable and environmentally sustainable resources, fossil fuels persist as the dominant component of the global energy portfolio. From 1971 to 2011, their share in the world energy supply merely decreased from 86% to 82%. Notably, coal's contribution to energy consumption declined from 39% in 1965 to 27% in 2020 (Figure 1.1). Moreover, the incessant escalation in CO₂ emissions compounds these concerns, underscoring the urgency of transitioning away from finite fossil resources to avert the perils of climate change and environmental degradation.

The urgent need to develop zero-carbon renewable energy resources is paramount in addressing today's environmental challenges. Considerable efforts have been directed towards advancing renewable alternative energy technologies, such as solar cells and rechargeable batteries. Among these options, batteries stand out as a particularly promising avenue for the conversion and storage of chemical energy. Unlike traditional energy sources, batteries offer the unique advantage of scalability, allowing for energy storage solutions ranging from large-scale applications to compact, portable devices. To date, researchers have explored various battery technologies, each offering distinct advantages in terms of feasibility and reliability. These include lead-acid batteries, lithium-ion batteries⁴ (LIBs), rechargeable zinc-air batteries.⁵

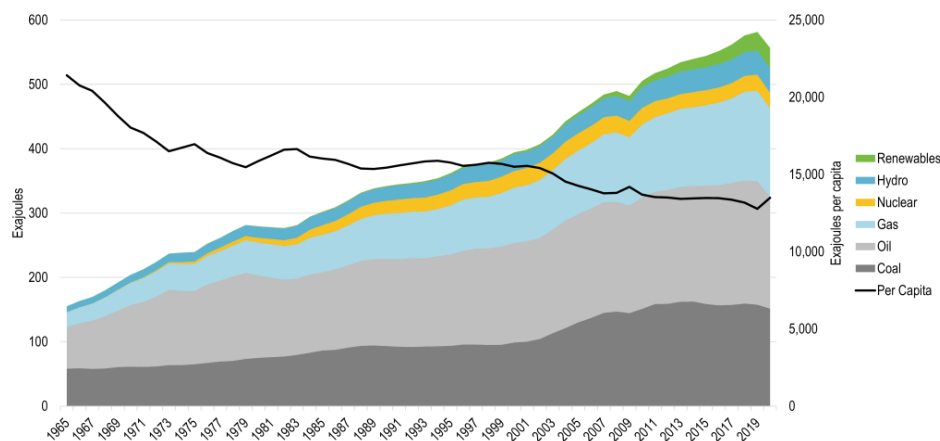


Figure 1.1 Schematic of global energy consumption. Copyright BP Statistical Review of World Energy.

(RZABs) and redox flow batteries⁶. Commercial LIBs own an energy density of 200 Wh kg^{-1} , less than 350 Wh kg^{-1} in the future, thus pure electrical vehicles perform poorly than fuel vehicles in mileage.⁷

Electrically rechargeable metal-air batteries have emerged as a compelling alternative energy harvesting and storage technology to lithium-ion batteries (LIBs). Their exceptionally high energy density has garnered widespread interest globally, positioning them as a practical solution to potentially meet the range requirements of electric vehicles (EVs). Metal-air batteries combine characteristics of both batteries and fuel cells, leveraging a metal anode, liquid electrolyte, and separator to batteries, while employing a highly porous electrode as a cathode to fuel cells. A notable feature of metal-air battery technology is its open cell structure, wherein oxygen gas molecules from the air serve as an inexhaustible fuel source at an air-breathing cathode. In contrast, LIB necessitates carrying the fuel (intercalation compounds) within the battery, limited by the battery's size. Consequently, the absence of cathode active material stored

inside the cathode reduces the total volume and weight of metal-air battery system. This reduction ultimately enhances energy densities, which can be up to 2-10 times higher than those of LIBs. Metal-air batteries can be divided into two categories by the types of electrolytes, including aqueous and nonaqueous. The anode materials can be magnesium, aluminum, sodium, lithium, zinc and so on. Hence, Aqueous electrolytes find application in less reactive metal anodes, such as Zn, Al, Mg, and Fe, offering notable advantages in safety against moisture ingress. Additionally, their utilization results in decreased material costs, owing to the affordability of water. On the other hand, non-aqueous electrolytes serve to shield active metals like Li and Na from water and moisture intrusion, with the most common application being in the Li-air system.

Metal-air batteries encounter several scientific and technological hurdles, similar to other battery technologies. The primary challenges revolve around the low utilization efficiency of the anode and sluggish kinetics of the cathode, ultimately leading to constrained practical energy density. Anode-related issues include severe passivation and corrosion, impeding further electrolyte access and diminishing active material discharge. Self-discharge and anode corrosion further degrade coulombic efficiency and shorten battery shelf life. One approach to counteract deterioration involves operating metal-air cells with a reserve structure, segregating key components until activation. Concerning the cathode, intrinsic slow reactions, high overpotentials, and poor reversibility of oxygen chemistry pose significant obstacles. Cathode reactions involve complex processes, with underlying mechanisms often elusive. Consequently, the air electrode profoundly influences metal-air battery performance, despite its inherent complexity, expense, and bulkiness. While utilizing oxygen from ambient air holds promise, the air electrode remains the most intricate component of metal-air batteries. To unlock the full

potential of metal-air batteries, elucidating basic oxygen chemistry and developing highly efficient air electrodes are paramount. Extensive efforts are dedicated to investigating cathode reaction mechanisms, developing efficient bifunctional catalytic materials for oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER), and rationalizing electrode structures to facilitate mass/charge transport and interface interaction. These endeavors are crucial for advancing metal-air battery technology and overcoming existing challenges.

Metal-air batteries have garnered significant attention due to their high energy density, allowing for the utilization of oxygen as a reactant while storing the positive electrode outside before discharge. Typically, these batteries consist of a metal anode, such as K, Mg, Al, Zn, Li, and Na, along with an electrolyte, a separator, and an air electrode.⁸⁻¹⁰ Metal-air batteries exhibit impressive energy densities and rely on freely available atmospheric oxygen, contributing to reduced battery weight. Extensive studies have been conducted in this field since the invention of the first primary ZAB in 1878.¹¹ Alkali metal-air batteries boast high voltage values, with examples including 2.96 V for Li-air, 2.33 V for Na-air, and 2.48 V for K-air batteries, respectively. Various metal-air batteries, including lithium-air batteries, offer theoretical energy densities and Ragone plots, shown in Figure 1.2a and b. However, lithium-air batteries, despite their strong candidacy due to the highest theoretical specific energy (5928 Wh kg⁻¹), are limited by inherent instability when exposed to air and aqueous electrolytes. Magnesium and aluminum-air batteries exhibit compatibility with aqueous electrolytes and energy densities comparable to lithium-air batteries. However, their low reduction potential results in rapid self-discharge and poor coulombic charging efficiency. Furthermore, alkali metals have low mass densities, leading to volume energy densities of Li-air (6104 Wh L⁻¹), Na-air (2634 Wh L⁻¹), and K-air (1513 Wh

L⁻¹) batteries, as well as other metal-air batteries, lower than that of zinc-air batteries, which boast a density of 9653 Wh L⁻¹.¹²

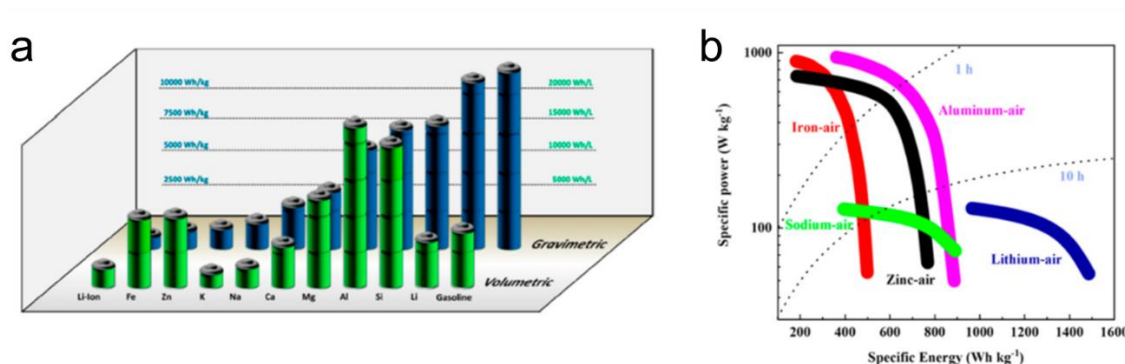


Figure 1.2 a) Theoretical energy and b) Ragone plots for various metal–air batteries.¹³

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1.2 The fundamentals of Zn-air battery

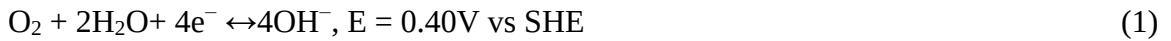
In the early 1960s, research on rechargeable zinc-air batteries (RZABs) commenced, yet a commercial breakthrough has remained elusive due to inferior overall energy efficiency and poor cyclability. These challenges are primarily attributed to difficulties in managing both the cathode and anode components.^{14–16} Zinc metal, abundant on Earth and highly resistant to corrosion in alkaline solutions, serves as a key component in zinc-air batteries (ZABs). This novel device demonstrates notable advantages, including high safety and low cost.

Zn–air batteries exhibit a high theoretical energy density of 1218 Wh kg⁻¹, approximately five times greater than that of current lithium-ion batteries (LIBs). While Zn-air batteries may exhibit inferior gravimetric energy density compared to Li-air batteries, their practical volumetric energy density surpasses that of Li-air batteries due to the significantly higher atomic density of zinc metal. Volumetric energy densities are particularly crucial in specific energy applications such as electric passenger vehicles, where space for battery installation is limited. Consequently,

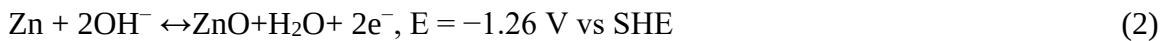
Zn-air batteries are increasingly regarded as the most viable alternative energy technology to replace current LIBs for future long-range electric passenger vehicle applications.

Typically, a rechargeable zinc-air battery (Figure 1.3) composed of zinc electrode, a separator, the alkaline electrolyte, and an air electrode with gas diffusion layer. The electrons released from the zinc electrode by an external load to the air electrode, and the zinc cations are generated from the zinc electrode. Simultaneously, the oxygen transfers to the air electrode and oxygen reduction reaction (ORR) occurs to produce hydroxide ions. The hydroxide ions move from air electrode into the zinc electrode, to produce zincate ($\text{Zn}(\text{OH})_4^{2-}$) ions and further decomposing into ZnO. The overall reaction of the zinc-air battery is shown as (3), and the charging reaction (1) has the ability of storing electricity, while zinc deposited at the zinc electrode (reaction 2) to occur oxygen evolution reaction (OER).

The air electrode reaction:



The zinc electrode reaction:



The overall reaction:



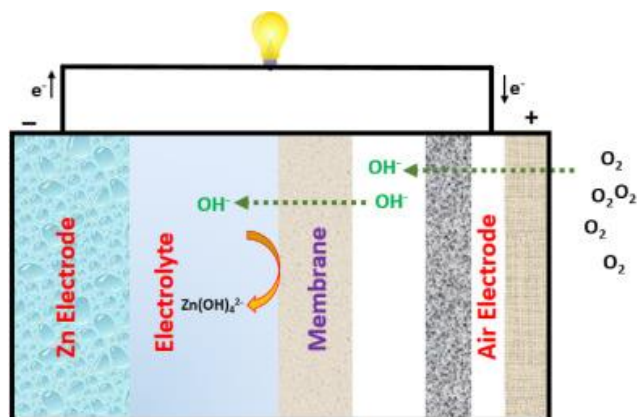


Figure 1.3 Schematic diagram of alkaline zinc-air battery.¹⁷ Copyright 2020, Elsevier.

When the anode and cathode reactions are combined, the overall theoretical battery voltage, typically referred to as the "open-circuit voltage (OCV)" of the Zn-air battery, becomes 1.66 V, where $E_{\text{battery}} = E_{\text{cathode}} - E_{\text{anode}}$. While the theoretical equilibrium potential of the rechargeable Zn-air battery stands at 1.66 V, the practical discharging voltage typically hovers around 1.2 V, significantly lower than the theoretical value. Moreover, the charging voltage commonly exceeds 2 V, indicating considerable energy loss attributed to what is termed "overpotential". This phenomenon arises from activation, ohmic, and concentration losses stemming from various resistive reactions occurring during battery operation.

At the air-breathing electrode, both the Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) are crucial reactions in this system. Their inherently slow reaction kinetics, stemming from high activation barriers, significantly impede overall battery performance, including energy density, power density, rechargeability, and energy efficiency. Consequently, extensive scientific research efforts have been dedicated to optimizing battery components such as the zinc anode, electrolyte, and catalyst-coated air-electrode to mitigate significant voltage losses during battery discharge and charge cycles. However, given that the

overpotentials associated with the zinc electrode and electrolyte are comparatively lower than those related to the air-electrode, particularly at the three-phase interface, the majority of studies have concentrated on the development of efficient electrochemical catalyst materials and air-breathing electrode designs.

During charge and discharge processes, oxygen reduction reaction and oxygen evolution reaction on air electrodes lead to the conversion of O_2 to OH^- . However, the intrinsic sluggish kinetics of both reactions, ORR and OER, necessitate high overpotential due to their four-electron transferring processes and complicated mechanisms. Consequently, for practical Zinc-Air Batteries (ZABs), the most critical issue is the large voltage gap (ΔE) between the charge and discharge processes, primarily attributable to high overpotentials at the air electrode.^{18, 19} Therefore, ORR and OER at the cathode serve as the rate-limiting steps for ZAB reactions. To address this issue, significant efforts have been dedicated to the development of advanced oxygen catalysts.²⁰⁻²² However, a bottleneck exists in that ORR and OER necessitate different catalytically active sites. Furthermore, while some suitable catalysts have been identified with numerous exposed active sites, many cannot withstand the varied reductive–oxidative environments encountered during charge and discharge cycles.^{11, 23} Hence, there is a pressing need to develop suitable oxygen electrocatalysts capable of facilitating both ORR and OER for Rechargeable Zinc-Air Batteries (RZABs).

The air electrode plays a vital role among all components in enhancing the electrical performance of a zinc-air battery (ZAB). Typically, an air electrode comprises a gas diffusion layer (GDL), O_2 catalyst, and conductive substrate. A well-designed air electrode facilitates the mass and charge transport of ZABs, ensuring high roundtrip efficiency and high-power output. During the discharge process, the gas–liquid–solid triple-phase region of the air electrode is

where the oxygen reduction reaction occurs. To meet requirements, the air electrode should possess a porous structure that enables efficient diffusion of air while maintaining a balanced hydrophobicity and hydrophilicity. This balance helps to mitigate evaporation loss of the electrolyte, thus contributing to prolonged battery performance.^{22, 24}

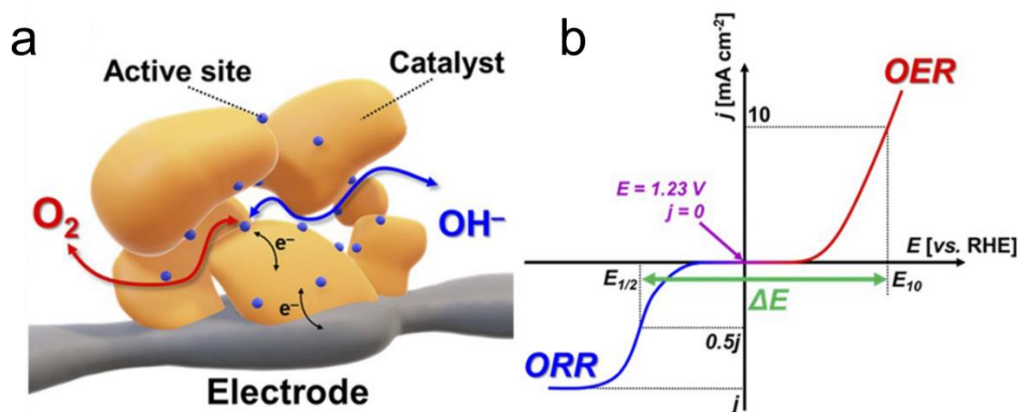


Figure 1.4 a) illustration of the required structural properties of the O_2 electrocatalyst. b) Evaluation of the potential difference (ΔE) during the OER and ORR. E_{10} : potential needed to achieve a current density (j) of 10 mA cm^{-2} during the OER, $E_{1/2}$: half-wave potential for the ORR, and RHE: reversible hydrogen electrode.²⁵ Copyright 2020, AIP Publishing.

Simultaneously, the gas diffusion layer (GDL) serves a crucial role in facilitating oxygen diffusion between air and electrolyte to prevent leakage and electrolyte flooding.²⁶ The GDL must strike a balance, being somewhat wettable yet slightly hydrophobic, with smaller pore sizes to facilitate efficient gas transfer within the system while minimizing exposure to the external environment. Achieving a hydrophobic GDL can be attained by impregnating it with superhydrophobic agents such as polytetrafluoroethylene (PTFE).²⁷ This PTFE-membrane-like coating serves as a wet-proofing agent and regulates the permeation of CO_2 into the electrolyte. Despite being thin, the GDL presents a high surface area and porosity to facilitate efficient gas

diffusion. Moreover, it is essential for the GDL to be electrically conductive to enable charge transfer and electrochemically durable to withstand rapid oxidation and exposure to alkaline electrolytes, thereby safeguarding the electrode from corrosion.

The oxygen catalyst plays a critical role in Zinc-Air Batteries (ZABs), requiring high electrical conductivity to facilitate electron transfer efficiently. Additionally, these electrocatalysts should possess dual active sites for both the oxygen reduction reaction and oxygen evolution reaction, or a single bifunctional active site that benefits both reactions. As depicted in Figure 1.4a, the ideal electrocatalyst should exhibit the necessary structure to optimize performance. Several parameters can be used to evaluate the performance of ZABs, including round-trip efficiency, voltage gap, and energy/power density. Round-trip efficiency measures the energy utilization efficiency of a ZAB, calculated by dividing the voltage of charge and discharge processes at constant current density. Low round-trip efficiency can pose a significant obstacle for ZAB, making it crucial to reduce overpotentials for both ORR and OER to address this issue. As illustrated in Figure 1.4b, the potential difference (ΔE) between the potential of 10 mA cm^{-2} during OER (E_{10}) and the half-wave potential ($E_{1/2}$) during ORR can characterize the bifunctional activity of the catalyst. The overall overpotential for both ORR and OER is commonly measured by the potential difference between the half-wave potential ($E_{1/2}$) from ORR and the OER potential at 10 mA cm^{-2} (E_{10}), with lower overpotentials indicating superior electrocatalytic activity.

1.2.1 ORR and OER

During the discharge process of a zinc-air battery, oxygen reduction reaction occurs at the cathode as oxygen is continuously attracted. Typically, two main pathways facilitate ORR in

alkaline electrolyte. In the first pathway, bidentate oxygen molecules are absorbed on the active sites (*) and then undergo a four-electron pathway to produce OH⁻, which is considered a superior pathway for ORR performance. This direct four-electron pathway is as following:



Another pathway is a two-electron pathway, including the O₂ molecules absorbed on the top of the active sites to generate the H₂O₂ intermediate. This pathway means the ORR performance is relatively weak, shown following:



As extensively documented, the oxygen reduction reaction can occur through either a four-electron (4e) pathway or a two-electron (2e) pathway on metal surfaces. The specific ORR pathways and mechanisms can vary depending on the catalytic materials utilized. Additionally, the ORR is known to be structure-sensitive, meaning that different configurations of oxygen adsorption exist on the active sites of the catalyst, influenced by factors such as crystallographic structure and binding energy. In the context of oxygen adsorption configurations, two primary modes are observed. In the "end-on" configuration, only one oxygen atom is coordinated perpendicularly to the surface, favoring a 2e pathway with peroxide generation. Conversely, the "parallel" coordination involves two oxygen atoms adsorbed on the surface, promoting O₂

dissociation and facilitating the direct 4e ORR pathway without peroxide formation. Moreover, the 2e oxygen reduction may lead to further reduction of peroxide or a chemical disproportionation process, forming a serial 2×2e pathway. These complexities underscore the intricate nature of the ORR, with its pathways and mechanisms intricately intertwined with the catalytic materials and surface interactions.

Both the aforementioned four-electron (4e) and two-electron (2e) reaction schemes may occur simultaneously and compete with each other. Recent experimental studies and mathematical modeling have revealed the existence of dual-path ORR mechanisms comprising both direct 4e and series 2×2e pathways on carbon-supported Pt nanoparticles. In high potential intervals, the direct path dominates, while at low potential, the reduction switches to the peroxide-mediated path. Additionally, transport effects such as desorption and re-adsorption of intermediates play a crucial role in the kinetics and pathway-selectivity of the ORR. Non-covalent interactions between hydrated alkaline-metal cations and adsorbed species on active sites also significantly affect the ORR characteristics. The actual surface reactions may be obscured due to limitations of analysis techniques, suggesting the existence of potentially more underlying pathways. Furthermore, if the serial reduction or chemical decomposition of intermediate species proceeds rapidly, the generated peroxide may be simultaneously reduced to hydroxide, leading to an apparent 4e reduction reaction. For instance, previous studies have demonstrated that manganese oxides exhibit high catalytic activity toward peroxide decomposition and/or reduction, resulting in a detected ORR with apparent quasi-4e transfer. Consequently, determining an explicit ORR mechanism may pose a challenging task in many cases.

In the case of metal oxides, the surface charge distribution differs from that of pure metals. Stoichiometric oxides' surface cations are not fully coordinated with oxygen, and their anion coordination is completed by water molecules in aqueous solutions. When a surface cation undergoes reduction, it is charge-compensated by the protonation of a surface oxygen ligand. Consequently, a four-step catalytic mechanism has been proposed for the oxygen reduction reaction (ORR) pathway on transition-metal oxide surfaces.



For different catalysts and different environments, the pathways can be varied. There are other complementary pathways for ORR:

(i) in acid media, a “direct” four-electron reduction to produce H_2O ;

(ii) a “series” pathways including two-electron and four-electron pathway;

(iii) a mechanism includes the diffusion of species from a “series” path into a “direct” path is possible;

(iv) an “associative” pathway combined with the adsorption of molecular O_2 and direct proton/electron transfer to it and to OOH , breaking into O and OH .

(v) a dissociative pathway involves the splitting of the O–O bond in O₂ and the hydrogenation of atomic O to OH and to H₂O.

Numerous experiments have been conducted on oxygen reduction reaction catalysts to evaluate their performance using a three-electrode system.²⁸ The linear sweep voltammetry (LSV) tests are pivotal in this evaluation, where the current density is recorded as a function of the working electrode potential. Typically, LSV curves (Figure 1.5a and b) exhibit three distinct regions, each corresponding to different electrocatalytic processes. The high potential grey area delineates a region where overpotential is constrained by crossing the energy barrier, thereby influencing catalytic performance. This segment is termed the surface reaction-controlled region, where surface reaction kinetics are the primary limiting factor for the reaction's activity. In the blue region, the dissolution rate of oxygen on the electrode is rapid, resulting in the current remaining constant as overpotential increases. This phenomenon characterizes the diffusion-controlled region. The orange region, situated between the surface reaction-controlled and diffusion-controlled regions, is known as the mixed controlled region. In this region, ORR is co-dominated by both surface reaction and mass diffusion, with $E_{1/2}$ serving as a metric to evaluate the activity of the electrocatalysts.

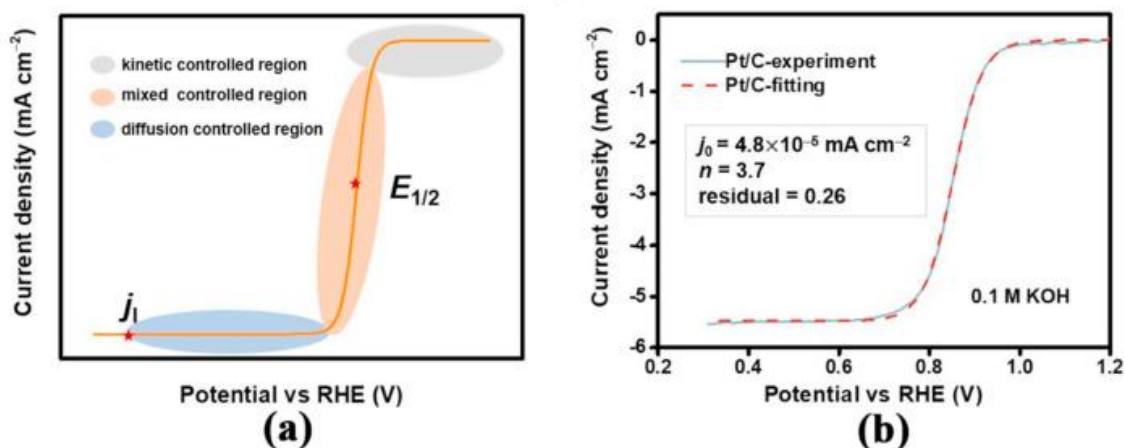


Figure 1.5 a) Schematic illustration of the ORR LSV curve. (b) Experimental and fitting ORR LSV curves for Pt/C. j_0 and n are simulated accordingly.²⁹ Copyright 2021, Elsevier.

The module design of these systems may seem complex, but the underlying concepts are relatively straightforward. They all operate as two-electrode systems, with the cathode involving either the hydrogen evolution reaction (HER) or the oxygen reduction reaction (ORR), while the anode facilitates the oxygen evolution reaction (OER) or oxidizes certain chemical fuels. However, a significant hindrance preventing these systems from achieving practical utility thus far is the sluggish kinetics, characterized by high overpotential, associated with the oxygen evolution reaction. OER involves a four-electron-proton coupled reaction, whereas HER is only a two-electron transfer reaction. Consequently, it's evident that OER demands higher energy (manifested as higher overpotential) to overcome the kinetic barrier required for its occurrence. The OER can indeed be viewed as the counterpart to both the ORR and HER processes. During the charging of a Zn-air battery, OH^- ions undergo oxidation, contrasting with the reduction of O_2 that occurs during the battery's discharge. Similarly, in electrolyzers, oxygen gas is evolved at the anode, in contrast to the evolution of hydrogen gas at the cathode. This symmetry underscores the dual nature of electrochemical reactions and their roles in various energy storage

and conversion systems. In the case of the oxygen evolution reaction, this is the half reaction of the water splitting reaction as following.



The preference for alkaline electrolysis over acidic water splitting has intensified due to the scarcity and costliness of acid-insoluble OER catalysts with adequate activity. Consequently, alkaline electrolysis has emerged as a leading contender for large-scale hydrogen production. Thus, there is a pressing need to develop precious-metal-free electrocatalysts that exhibit robust activity for both OER and HER in highly alkaline environments. In the overall process, OER occurs at the anode while HER takes place at the cathode of the electrolyzer. Particularly in alkaline media with a pH of 14, the corresponding reactions at the anode and cathode are as follows:

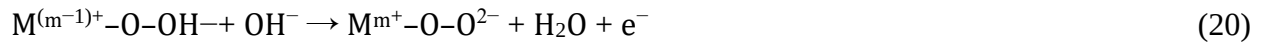


OER is the reverse and charging process of ORR at the cathode of the zinc-air battery. The mechanism of OER is the opposite of the four-electron pathway for ORR. RuO_2 and IrO_2 are currently been widely used as commercial catalysts, but the high cost and poor stability are the big challenges for real application. Due to the high potential range of OER compared with ORR, the catalyst would suffer strong polarization, which may cause amorphization of the material and leading to unstable activity. Therefore, transition metal porous materials are highly considered to be the promising catalyst. The proposed mechanism in alkaline solution is following:





As the above proposed OER mechanism, under alkaline solution, it can be understood that electrolytic OER is a heterogeneous reaction. The bonding interaction with intermediates, like MOH, MO and MOOH, are critical for the whole electrocatalytic ability. As outlined above, the pathways and mechanisms of OER are notably intricate. Unlike bare metals, oxygen is typically evolved from an oxide phase, leading to diverse reaction mechanisms dependent on the electrode materials with distinct site geometries of metal cations. The multi-valence characteristic of transition metal ions is crucial for catalyzing OER, as the reaction arises from the interaction between metal ions and oxygen intermediates like O*, OH*, and OOH*, accompanied by changes in their valence states. The site geometry of transition metal cations influences the adsorption energy of oxygen species, thereby dictating OER kinetics. The OER in alkaline electrolyte proceeds as presented below:



While electrolyzers offer a promising method for generating high-purity oxygen and hydrogen, their practical application for mass production of gases is hindered by the sharply uphill reactions of oxygen evolution reaction and hydrogen evolution reaction, which exhibit large overpotentials. Commercially available electrolysis systems typically operate at cell

voltages of 1.8–2.0 V, significantly higher than the theoretical value of 1.23 V. Consequently, active electrocatalysts for both anodic OER and cathodic HER are crucial to minimize water-splitting overpotentials, enhancing process efficiency and achieving rapid kinetics for practical applications.

Among the wide array of available electrocatalysts, platinum (Pt)-group metals demonstrate exceptional electrocatalytic HER performance, characterized by extremely high exchange current density. However, OER in alkaline media is a more complex process due to the involvement of multiple steps. The most effective catalysts for OER typically comprise less abundant and expensive Ir- and Ru-based compounds. Yet, to ensure sustainable oxygen and hydrogen production, the replacement of low-abundance, expensive, and particularly unstable noble metal-based catalysts like Pt, Ir, and Ru with cost-effective and environmentally benign alternatives are highly desirable. Therefore, the design and development of efficient OER and HER catalysts utilizing earth-abundant elements, particularly non-precious transition metals, present an attractive avenue. Further details regarding the advancement of these electrocatalysts will be discussed in the following section.

1.3 Transition metal-based catalysts with porous structure

Electrocatalysts have the ability to increase the rate of chemical reactions and accelerating the transformation of electrons and intermediates without being consumed in the whole reaction.(Figure 1.6) ³⁰ Noble metal-based materials normally exhibit advanced activity and stability, for instance, ruthenium (Ru)/iridium (Ir) oxide for oxygen evolution reaction, and

platinum (Pt) based materials for oxygen reduction reaction.³¹ While the high price and low abundance on the earth are the limitations of the scalable application of these technologies.

The design and synthesis of transition metal-based materials have been extensively studied for the enhancement of renewable emerging crucial technologies. Transition metal-based materials with special electronic structure own numerous merits as follows, variable valence states, tending to oxygen reduction reaction. They have losable unpaired single electrons and unfilled valence layer 3d orbitals, like Mn or Fe-based catalysts, helpful to increase the performances of the catalysts.³²⁻³⁴ Transition metal-based materials process plentiful advantages including high stability, environmentally friendly, and high intrinsic activity, making them the most promising materials. But there are some limitations, such as low cationic-protonic diffusion, small specific area, poor intrinsic electrical conductivity and low specific capacitances compared to theoretic materials.^{35, 36}

Nowadays, engineered transition metal-based derived materials are the most promising non-precious catalysts for energy conversion and storage.³⁷ These materials have been studied for decades due to their unique structure and uniform coordination environments: i) ordered hollow structure, with suitable size of mesopores, high active surface beneficial for transporting intermediates to enhance the electronic conductivity^{38, 39}; ii) cationic metal doping, doping with foreign metal cation, like Fe, Co, etc^{40, 41}; iii) defects engineering, vacancies as active sites, to stabilize the reactants and intermediates^{42, 43} vi) ternary system with synergetic effects, to lower the kinetic by modifying the chemical bonding for advanced ORR and OER.^{44, 45}

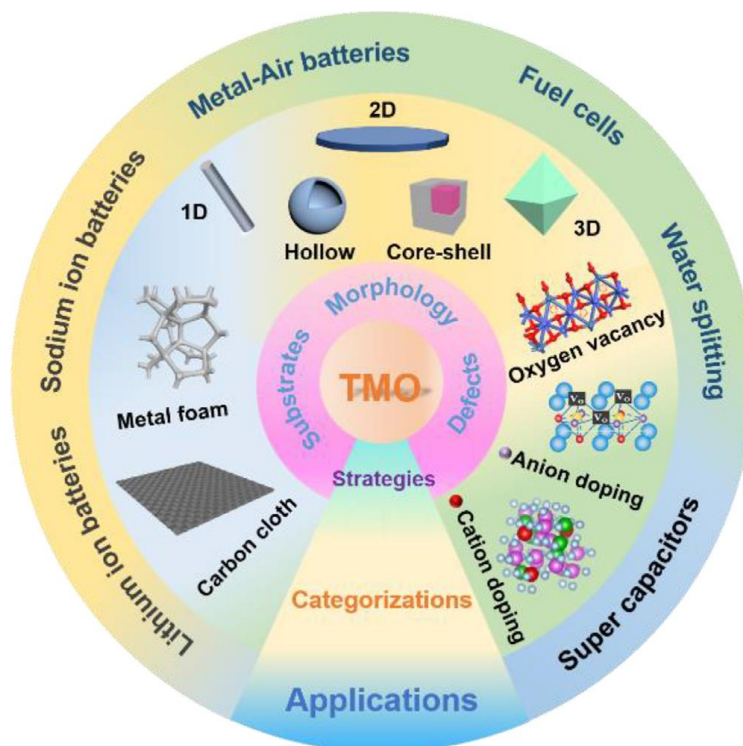


Figure 1.6 Modification strategies, corresponding means and electrochemical applications of TMOs.⁴⁶ Copyright 2021, Elsevier.

Up to date, transition metal-based materials with a single ORR/OER activity have been widely developed.^{47, 48} However, due to the different mechanisms of two reaction for zinc-air batteries, it is hard to meet the requirements for preparing bifunctional transition metal-based materials toward for both ORR and OER. Thus, countless efforts have been devoted to exploring catalysts that could meet the requirements. Unfortunately, catalysts show either excellent ORR or OER performance, but not able to represent well for both processes. ORR and OER have different demands for active sites, so it is crucial to conduct the surface engineering of the catalysts to boost the intrinsic activity for the two processes. In addition, the theoretical overpotential triggered by the scaling relationship can also be considered a problem for the

catalysts.⁴⁹ It reminds us the development of an idea bifunctional catalysts to minimize the overpotentials of both ORR and OER is a big obstacle.

In spite of the progress and achievements of ORR, OER in transition metal-based materials, to further improve the performance of zinc-air batteries, the seek for effective bi-functional oxygen catalysts is still in high demands.⁵⁰ For the zinc-air batteries, ORR and OER are two significant redox reactions, and it is difficult to find a non-precious catalyst that exhibited both ORR and OER activities. To date, mesoporous materials have been widely researched attributed to their high specific surface, narrow pore size distribution, and various applications in energy conversion and storage.^{51, 52} With the hierarchical mesopores, it exposes more active sites and provides charge transfer channels to boost the intrinsic ORR and OER activity and stability.^{53, 54}

As a consequence, in this study, several electrocatalysts have been engineered to facilitate ORR and OER performances. For the first proposal, to deeply understand the mechanism of ORR, a renewable engineered Fe₂N decorated on TiO_y with the creation of nitrogen vacancies hybrid has been constructed. DFT analysis and X-ray absorption spectroscopy can confirm that the engineering of nitrogen vacancies changes the adsorption and desorption of intermediates as well as alter the electronic environment of Fe to facilitate the ORR activity. Secondly, a series of ternary Cu-Ti-O ordered porous electrocatalysts have been synthesized to achieve the tradeoff between structure stability and exposure of active sites. X-ray absorption fine structure analyses reveal the electron density reconfiguration in the Cu-Ti-O system. Finally, the efficient three-dimensionally ordered mesoporous Co₃O₄ decorated with Mg as a bifunctional electrocatalyst for zinc-air battery has been developed. With the substitution of Mg, the altered electronic structure and bonding configuration of Co₃O₄ enhance both ORR and OER activities.

1.3.1 Ordered porous structure

The ordered porous transition metal-based materials have garnered significant attention over the years due to their unique properties in electrical devices. These materials, classified by the International Union of Pure and Applied Chemistry (IUPAC) into three types based on pore size—micropores (less than 2 nm), mesopores (between 2 nm and 50 nm), and macropores (more than 50 nm)—have demonstrated excellent performance in energy conversion and storage. Their narrow pore size, high surface area, and uniform pore structure contribute to their efficacy in these applications. Mesoporous materials, in particular, with their large pore volumes, offer the ability to accommodate guest species, facilitating expansion and strain relaxation during energy conversion and storage reactions. Additionally, the extensive surface area of these materials provides numerous active interaction sites for surface processes such as adsorption, desorption, and catalysis. This makes them highly desirable for various energy-related applications.^{55, 56}

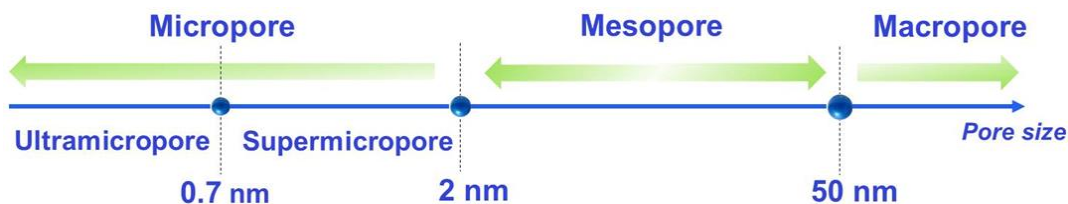


Figure 1.7 Classification based on pore size of porous materials.

Cellular materials can be broadly categorized into two types: stochastic and periodic materials. Stochastic materials exhibit random pore distributions, characterized by varying degrees of short-range order and pore size distribution. On the other hand, periodic structures feature a repeating base cell in two dimensions (e.g., honeycomb) or three dimensions (e.g., trusses). Each category possesses distinct mechanical properties, relative densities, and production costs. Synthesis methods play a significant role in determining pore and ligament

sizes, ranging from macroscale to nanoscale dimensions. Both stochastic and periodic materials can be fabricated using a diverse range of base metals, including aluminum and titanium, and can feature closed or open porosity. The differentiation between closed and open porosity is crucial, with the latter implying fluid permeability and typically lower density.

When assessing the mechanical properties of stochastic and periodic structures, it's evident that, for a given relative density, ordered porous structures exhibit superior load-bearing properties compared to their stochastic counterparts. This is because periodic networks are typically stretch-dominated materials when loaded, whereas random networks are bending-dominated. Additionally, closed-cell materials usually have an increased relative modulus for a given relative density, making them more desirable for load-bearing applications. Key advantages of using open porous structures for practical applications include mass reduction and the large accessible surface area. This is particularly important for catalysis or applications requiring cooling, since both the rate of product formation and heat transfer increase with the available surface area.

Mesoporous materials have been the subject of extensive study due to their distinctive structure and chemical properties. In the quest to fabricate ordered mesoporous materials, the template method stands out as an effective approach for controlling particle size, structure, and morphology compared to conventional methods. The choice of template is pivotal in achieving desired structures, and various specific methods are employed in the preparation process:

The Hard Templating Method (HTM) involves utilizing a colloidal crystal template typically composed of silica or polymer spheres. Unlike other natural hard templates such as plant components, viruses, and skeletons, this template exhibits high periodicity in three dimensions. Figure 1.8 illustrates the HTM process, which can be outlined in the following steps:

first, preparing the template; second, immersing the pore system into the guest precursor; and finally, removing the template to leave behind a skeleton with air holes at the original sphere sites. Typically, the spheres are removed via etching, heating treatment, or dissolution in suitable solvents.

The HTM to prepare the mesoporous nanostructure has vast merits as following: (i) the smallest features for mesoporous materials have low diameters; (ii) various templates for choosing to prepare mesoporous materials; (iii) mesoporous nanostructures with crystalline skeletons can be fabricated by thermal treatment with high temperature but still maintain original structure; (iv) this method is adapted to different material due to the combination of surfactants and inorganic species.

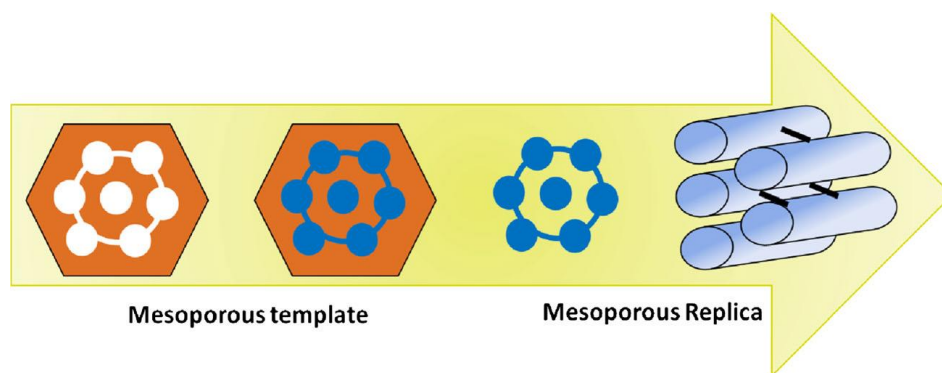


Figure 1.8 Schematic for preparation of mesoporous materials by HTM. ⁵⁷ Copyright 2018, Elsevier.

The soft templating method (STM) differs from HTM in that it doesn't rely on a rigid structure. Instead, during the STM process, various forces such as static electricity, chemical bonding, and intermolecular and intramolecular interactions drive the formation of aggregated structures with specific features. Through precipitation, electrochemical methods, and other

synthetic approaches, inorganic species are deposited onto the surface or within the interior of these aggregated structures, resulting in mesoporous materials with defined shapes and sizes (Figure 1.9). STM offers several advantages, including simplicity, good repeatability, and the elimination of the need to remove metal oxides. These qualities have led to the widespread use of STM in preparing mesoporous materials for various advanced applications.^{58, 59}

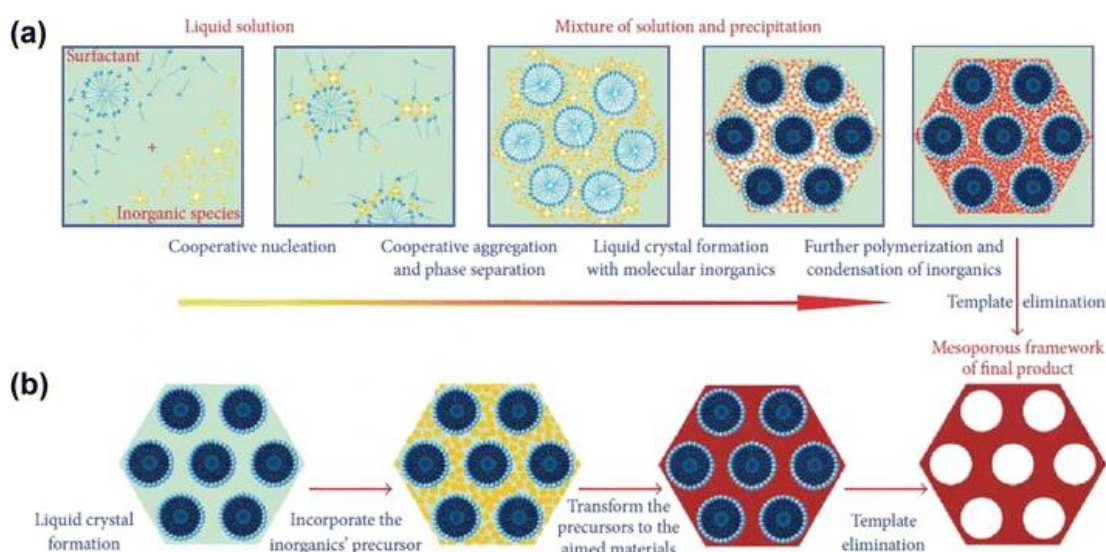


Figure 1.9 Schematic for preparation of mesoporous materials by STM.⁵⁷ Copyright 2018, Elsevier.

1.3.2 Creating vacancies

Defect engineering has emerged as a crucial strategy for enhancing the electrochemical activity in electronic devices. Vacancies, in particular, play a pivotal role as electron donors, thereby influencing the electronic structure and facilitating the transport of electrons and ions. Moreover, the presence of vacancies can promote phase transitions at the interface of the electrolyte and electrode by modulating surface thermodynamics and preserving electrode surface integrity.^{60, 61} To achieve superior performance, employing various strategies to create vacancies can adjust the morphology, size, and composition of catalysts. Due to their disordered

atomic arrangement, many materials have been deliberately designed with vacancies. The introduction of vacancies offers several advantages, including: i) tuning the electronic structure; ii) regulating active sites by increasing density and optimizing their distribution; and iii) enhancing electrical conductivity. (Figure 1.10)

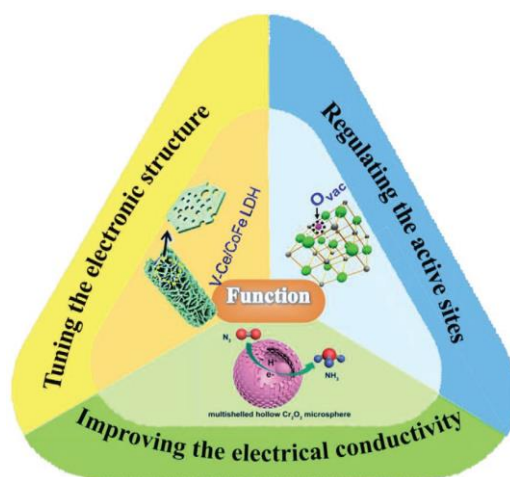


Figure 1.10 The role of vacancies on tuning the electrocatalytic performance. ⁶² Copyright 2021, Elsevier

Introducing vacancies into transition-metal-based materials can be a feasible approach to enhance ORR activities by altering crystal structure, electronic properties, and surface chemistry.⁶³ For instance, vacancies in transition-metal oxides can introduce electron holes and redox couples, leading to changes in structure and surface chemistry. This modulation can affect the adsorption of oxygen and the desorption of intermediates and products during the ORR process.⁶⁴ Tian and coworkers have a rational design and synthesis of Co (II) oxide (CoO) with high performance on ORR and OER activities.⁶⁵ Through a facile and controllable vacuum-calcination strategy, $\text{Co}(\text{OH})_2$ was transformed into defective amorphous-crystalline CoO nanosheets (Figure 1.11a). Density functional theory (DFT) calculations were subsequently conducted to elucidate the influence of oxygen vacancies on the electronic structure and catalytic

activity of the catalyst. As depicted in Figure 1.11b, pristine CoO exhibits a wide bandgap and poor conductivity akin to a semiconductor, hindering electron transfer. However, Figure 1.11c illustrates that the introduction of a single oxygen vacancy in the subsurface of CoO results in the emergence of new electronic states within the bandgap. Additionally, Figure 1.11d demonstrates that a surface oxygen vacancy leads to electronic states above the Fermi level for both spin components, enhancing conductivity and reducing energy barriers for electron donation to the surface substrate, consequently accelerating reaction kinetics.

For another aspect, metal vacancies can also bring about the improvement ascribed to various electrons and orbital distributions.⁶⁶ Li and coworkers prepare a stable and effective architecture hybrid with porous nitrogen-doped graphene encapsulated β -FeOOH nanoparticles β -(FeOOH/PNGNs) toward ORR. (Figure 1.11e).⁶⁷ As depicted in Figures 1.11f-i, the β -FeOOH/PNGNs are synthesized via a straightforward process involving freeze-drying and carbonization procedures with NaCl templates. The micropore graphene shells covering the structure facilitate mass transfer and charge transport, effectively shielding the active sites from direct immersion in electrolytes. The presence of Fe vacancies induces FeO_6 active sites in β -FeOOH/PNGNs, significantly reducing the thermodynamic barrier of the overall reaction and thereby greatly enhancing ORR activity. The porous nitrogen-doped 3D graphene networks encapsulating β -FeOOH have been successfully synthesized. This catalyst demonstrates advanced ORR performance, exhibiting high onset potential and half-wave potential comparable to Pt/C. These findings underscore the development of a stable, efficient, practical, and cost-effective ORR electrocatalyst based on β -FeOOH/PNGNs, while also providing insights into the

mechanism of the catalytic oxygen reduction reaction.

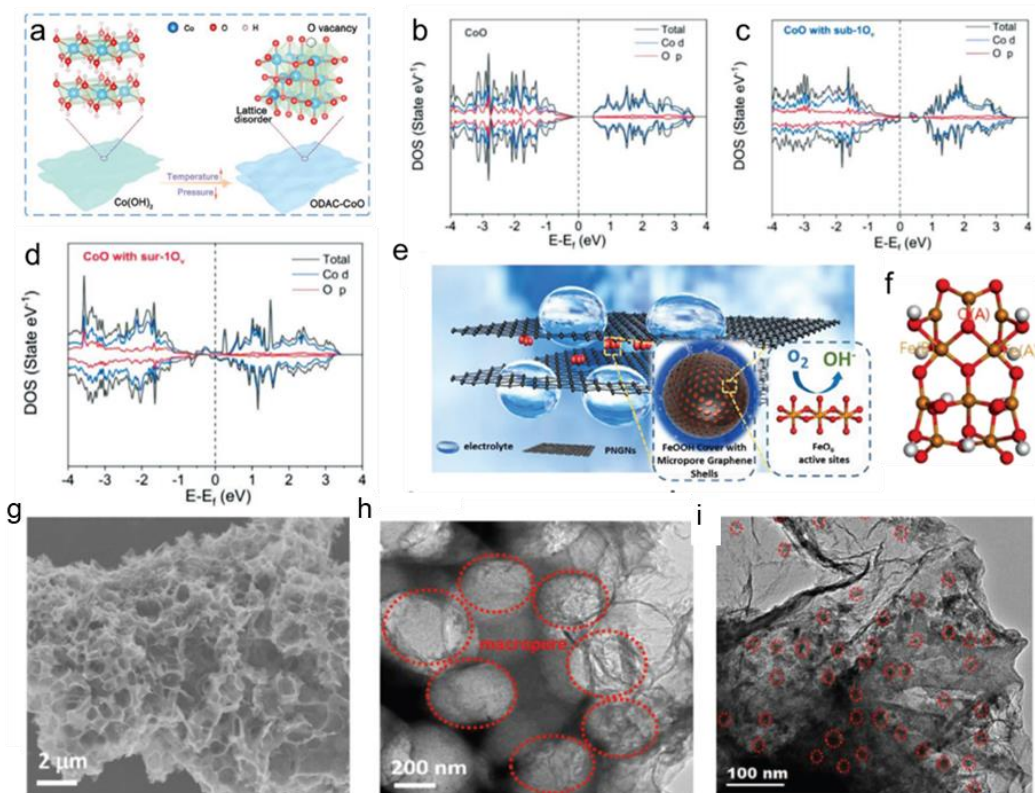


Figure 1.11 a) Schematic for the preparation of defective amorphous-crystalline CoO nanosheets. b-d) Density of states (DOS) of CoO and oxygen-defective CoO models. Reproduced with permission from ref ⁶⁵ e) Schematic for the preparation of FeOOH/PNGNs. The atomic structure of f) (100) surface of perfect β -FeOOH (Fe-perf), g) typical SEM image, h and i) TEM images. Reproduced with permission from ref ⁶⁷ Copyright 2018, Wiley-VCH.

1.3.3 Ternary transition metal-based materials

Recently, ternary transition metal-based materials have emerged as ideal candidates for bifunctional catalysts capable of facilitating both the oxygen reduction reaction and the oxygen evolution reaction.^{66, 68, 69} Due to the incorporation of multiple metal species, ternary transition metal-based materials offer advantages over single transition metal-based materials, including an

abundance of active sites and enhanced stability. Within the ternary system, bimetallic or trimetallic sites play a crucial role in effectively controlling the adsorption of intermediates, thereby promoting the diffusion of O₂ and electrolytes during both the oxygen reduction reaction and the oxygen evolution reaction.⁷⁰ The diverse coordination modes also contribute to alterations in physical properties, leading to the formation of different crystal structures such as octahedral structures, layer structures, chain structures, and so forth.

Tang and coworkers fabricate 3d Transition-metal nitrogen-carbon nanocomposites (T-N-C, T = Fe, Co, Ni, etc.) with highly active M-N_x sites applied in zinc-air batteries.⁷¹ 3D transition-metal nitrogen-carbon nanocomposites (T-N-C, where T = Fe, Co, Ni, etc.) featuring highly active M-N_x sites have garnered significant attention in rechargeable zinc-air battery research. These composites, with four N or C atoms in the same plane, form single or double atom catalysts characterized by atomic dispersion and direct coordination. They demonstrate excellent ORR activity owing to their maximum atomic utilization efficiency and exposed active centers. Novel bifunctional electrocatalysts composed of M-N-C single atoms and transition metal nanoparticles (NPs) doped in hollow nitrogen-doped carbon tubes (Fe₄Co₁Ni₂@hNCT) have been developed. Benefitting from the synergistic effect of M-N-C single atoms and alloy NPs, the Fe₄Co₁Ni₂@hNCT catalyst exhibits excellent OER activity (with a low overpotential of 258 mV at 10 mA cm⁻² in 1.0 M KOH solution) and ORR activity (with a half-wave potential of 0.83 V) (Figure 1.12a). A rechargeable Zn-air battery was assembled using metallic Zn foil as the anode. The open circuit potential of the battery assembled with Fe₄Co₁Ni₂@hNCTs as the air cathode catalyst was 1.454 V, as depicted in Figure 1.12b. Charge and discharge polarization curves illustrated in Figure 1.12c demonstrate that the battery based on Fe₄Co₁Ni₂@hNCTs exhibits superior charge and discharge characteristics compared to the Pt/C + IrO₂ reference,

especially at relatively high current densities. In Figure 1.12d, the $\text{Fe}_4\text{Co}_1\text{Ni}_2@\text{hNCTs}$ -based ZAB exhibits a peak power density of 125.6 mW cm^{-2} , surpassing that of commercial Pt/C + IrO_2 catalysts (94 mW cm^{-2}).

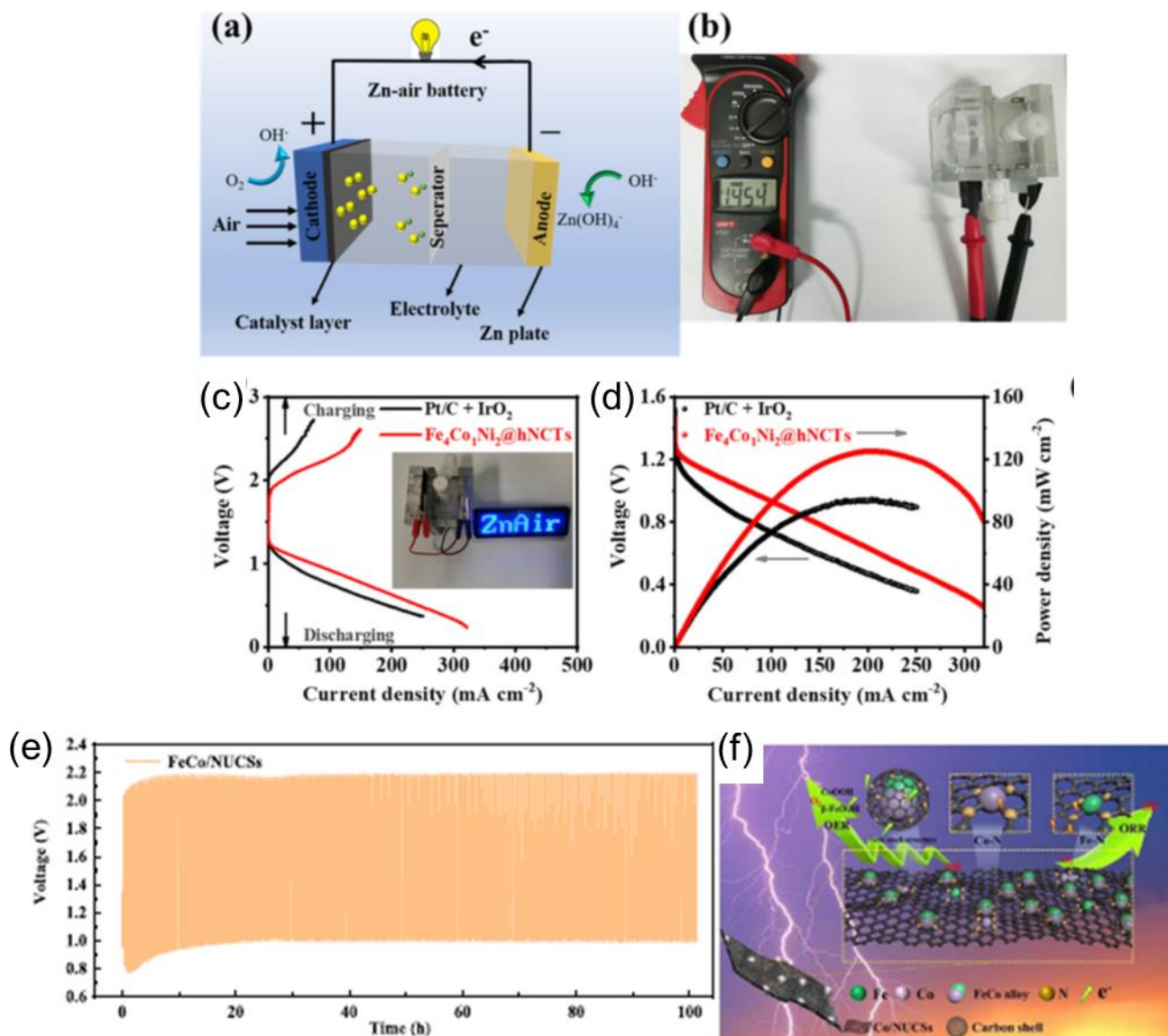


Figure 1.12 a) Schematic illustration of a rechargeable Zn–air battery configuration. b) Open circuit voltage of the Zn–air battery with $\text{Fe}_4\text{Co}_1\text{Ni}_2@\text{hNCTs}$ serving as an air cathode. c) Charge and discharge polarization curves; inset: a photograph of a blue LED powered by a ZAB based on the $\text{Fe}_4\text{Co}_1\text{Ni}_2@\text{hNCTs}$ catalyst. d) Discharge polarization curves and the

corresponding power density plots. Reproduced with permission from ref⁷¹ Copyright 2022, Nanoscale e) Galvanostatic charge-discharge curve of FeCo/NUCSs-based rechargeable ZAB f) ORR/OER mechanisms on FeCo/NUCSs. Reproduced with permission from ref⁷²

N atoms can alter the charge distribution of the carbon layer and bond with metals like Fe and Co to create catalytically active sites. Xu and colleagues suggest a core-shell alloy structure consisting of FeCo nanoparticles embedded within a carbon matrix anchored on nitrogen-doped porous carbon nanosheets (FeCo/NUCSs), fabricated through a self-growth strategy (Figure 1.12e inset).⁷² FeCo/NUCSs, with a specific surface area of $140 \text{ m}^2 \text{ g}^{-1}$, demonstrate a promising half-wave potential ($E_{1/2} = 0.89 \text{ V}$) and excellent methanol tolerance for ORR. The intricate OER mechanism on FeCo/NUCSs is further investigated using in situ XRD to elucidate the crystalline structural changes in the catalyst during OER. Throughout the OER process, new diffractions corresponding to β -FeOOH and γ -CoOOH emerge, indicating that FeOOH/CoOOH species originating from partial Fe^0/Co^0 (FeCo alloy) are the primary active sites for OER. To gain deeper insights into the structural advantages of the core (alloy)-shell (carbon) embedded in NUCSs, ZAB employing FeCo/NUCSs is subjected to a 102-hour (274 cycles) durability test at 10 mA cm^{-2} (Figure 1.12e). As illustrated in Figure 1.12f, Fe- N_x and Co- N_x coexist on FeCo alloy particles embedded in porous NUCSs, synergistically enhancing the ORR activity.

1.3.4 Atoms substitution

For an ideal bifunctional electrocatalyst in a zinc-air battery, it should exhibit excellent performance for both the oxygen reduction reaction and the oxygen evolution reaction. Porous transition metal-based materials are often considered promising candidates due to their ability to catalyze both ORR and OER effectively.^{73, 74} However, there is still ample room for enhancing

the performance of these materials compared to state-of-the-art noble metal-based catalysts. Doping the original materials with foreign atoms can alter the electron configuration of neighboring atoms, creating more active sites and facilitating the adsorption of reactants or intermediates. Additionally, introducing foreign atoms can improve electronic conductivity and stability. Previous studies suggest that incorporating foreign metals into transition metal-based materials is a viable approach to enhancing both ORR and OER activities, for example, Ni-doped CoO nanosheets,⁷⁵ Mg doped perovskite LaNiO_3 ,⁷⁶ Co-doped NiO .³⁴

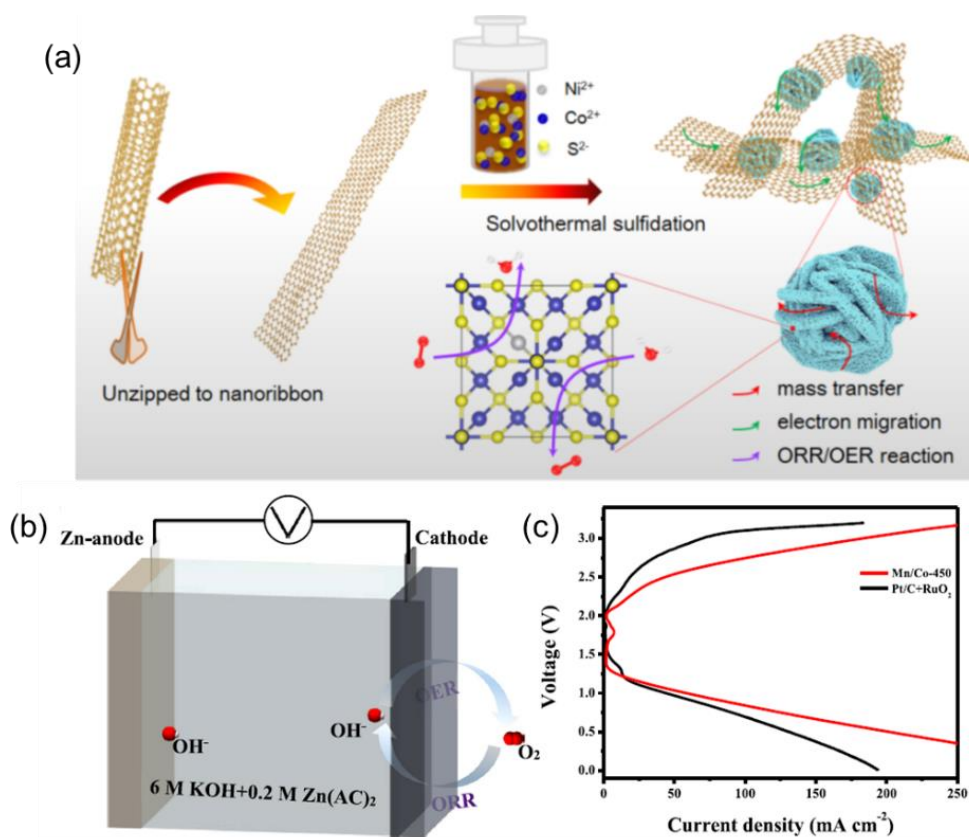


Figure 1.13 a) Schematic illustration of the synthetic procedure of hierarchical structured Ni-Co₉S₈/rGN nanocomposites. Reproduced with permission from ref²⁹ Copyright 2021, Applied Catalysis B: Environmental b) A schematic illustration of a rechargeable zinc-air battery c)

charge and discharge polarization curves of Mn/Co-450 and Pt/C+RuO₂ OER. Reproduced with permission from ref⁷⁷

When discussing the mechanism, the introduction of foreign metals can adjust the different metal 3d orbitals, thereby altering the electronic structures. This adjustment leads to an improved absorption of Gibbs free energy towards intermediates, resulting in enhanced electrical activity. For instance, Wang and colleagues utilized nickel atoms to dope Co₉S₈ spheres, producing spindle-type nanorods with excellent OER/ORR activities and long-term stabilities.²⁹ The hierarchical porous structured Ni-Co₉S₈/rGN was obtained through a straightforward solvothermal approach (Figure 1.13a). Here, the graphene nanoribbon, serving as an electronic conductor, was derived from the exfoliation of MWCNTs. This hydrophilic composite exhibits a hierarchical structure with uniform coverage of graphene nanoribbons and an open porous architecture, effectively reducing the ion diffusion pathway and enhancing the electron transfer rate.

Huang and coworkers prepared a Manganese-incorporated Co₃O₄ (denoted as MCO) catalyst for zinc-air batteries with high power density and long-term stability.⁷⁷ A series of Mn-incorporated spinel Co₃O₄ catalysts were synthesized through the pyrolysis of Mn@ZIF-67 precipitates, and their electrocatalytic performances and physicochemical properties were assessed through electrochemical testing and various characterization techniques. Mn doping induced crystalline distortion in the Co₃O₄ lattice, resulting in smaller crystallite size, increased abundance of Co²⁺, and significant oxygen vacancies. In the zinc-air battery (ZAB) setup, a polished zinc plate served as the anode, while a solution mixture of 6.0 M KOH-0.2 M Zn (CH₃COO)₂ acted as the electrolyte. The air cathode comprised a carbon paper coated with catalyst ink, as shown in Fig. 1.13b. Fig. 1.13c illustrates the charge and discharge polarization

curves of the rechargeable zinc-air battery using Mn/Co-450 and Pt/C+RuO₂ as cathodes. It can be observed that the battery employing the Mn/Co-450 catalyst exhibited higher discharge voltage and lower charge voltage compared to that utilizing Pt/C+RuO₂ at the same current density, thus confirming the excellent bifunctional electrocatalytic potential of the Mn/Co-450 catalyst.

1.4 Research objective

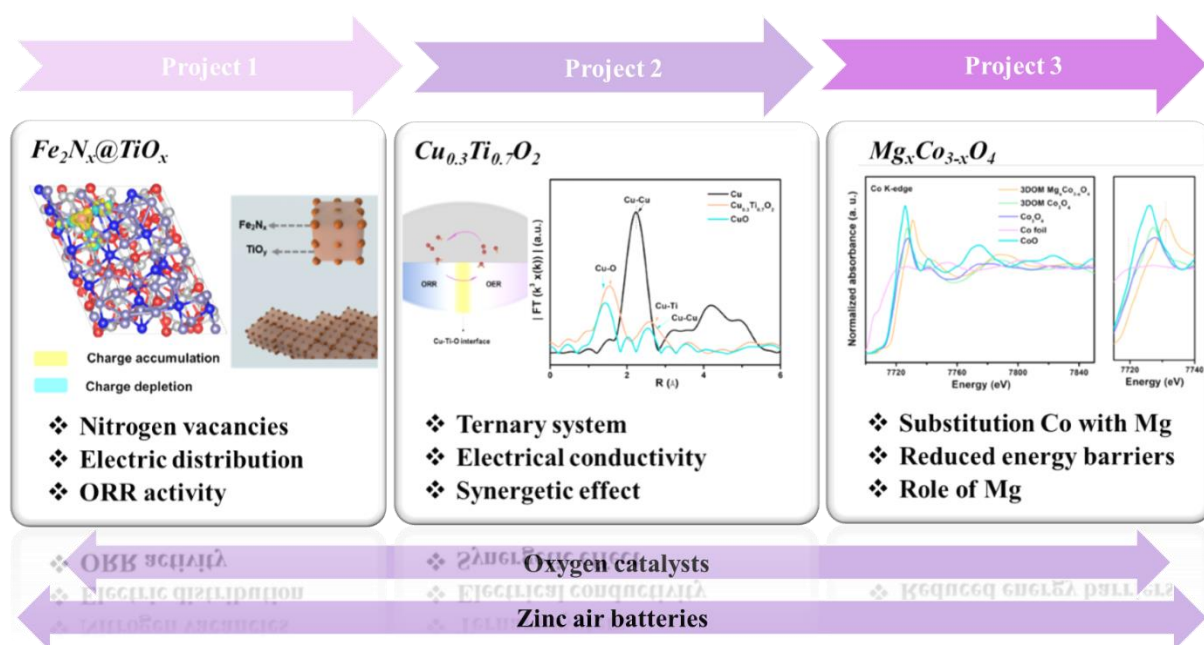


Figure 1.14 Schematic illustration of the research goals throughout this thesis.

As shown in Figure 1.14, the objective of this thesis is to develop the appropriate electrocatalysts for zinc-air batteries. The rational catalyst design and strategies are adopted to reach this goal, combined with various characterization techniques to verify the feasibility. The specific methodologies of the thesis are as follows:

- Rational design and preparation of the hierarchical three dimensional ordered porous transition metal-based materials;
- utilize characterization techniques and energy conversion

and storage system to evaluate the activation and stability of these electrocatalysts; iii) explore the specific mechanism for the energy conversion and storage systems and the change electronic configuration for the materials after surface engineering; iv) conclude the merits and demerits of the engineered electrocatalysts to improve the future application.

1.5 Structure of thesis

The thesis composed of seven chapters followed:

Chapter 1 presents an introduction of this thesis, explaining the fundamental of ZABs, and basic mechanisms of ORR and OER. It also includes the main motivation and research objectives of this thesis.

Chapter 2 introduces characterizations and electrochemical measurement techniques adopted in this thesis.

For chapter 3, the $\text{Fe}_2\text{N}_x@\text{TiO}_x$ with highly effective nitrogen vacancies has been prepared to boost ORR activity. Under NH_3 atmosphere, the nitrogen defects were created. It is rare to investigate Fe_2N partially induced with nitrogen vacancies. The created N vacancies effectively manipulate the activity of ORR by modifying the electronic distribution.

Chapter 4 shows a ternary Cu-Ti-O catalyst was constructed with 3D ordered porous structure as bifunctional electrocatalysts. Ti atoms tended to delocalize maximum charge by releasing it to the Cu atoms in the compositions of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, which lower the thermodynamic barrier of the total reaction, and hence contribute to a remarkable enhancement in zinc air battery.

Chapter 5 propose the catalyst of three-dimensionally ordered mesoporous Co_3O_4 decorated with Mg as bifunctional oxygen electrocatalysts for high-performance zinc-air

batteries. The interconnected macropores and mesopores in the 3DOM structure shorten the diffusion lengths of ions and electrons, enhancing the ORR/OER reaction kinetics.

Chapter 6 summarize the main results and expectations of the future work in transition metal-based materials.

Chapter 2 Characterization Techniques

In this chapter, the general characterization techniques used in this thesis will be introduced to gain morphological and physicochemical properties of the electrocatalysts. The materials preparation procedures and the detail techniques will be described in the section of Experimental methods of following three chapters.

2.1 Electrochemical Characterization Techniques

2.1.1 Galvanodynamic charge and discharge testing

The galvanodynamic technique enables the investigation of charge and discharge behaviors of catalysts evaluated in Zn-air batteries. This method involves gradually increasing negative currents (for battery discharge) and positive currents (for battery charge) from 0 A up to a desired value, with a set current rate (A/s), while monitoring changes in the battery's operational voltage. As shown in Figure 2.1, the operational voltage responses are plotted against the applied current, resulting in discharge and charge polarization curves. The voltage gap between the polarization curves for discharge or charge and the initially measured open-circuit voltage (OCV) at zero current indicates total voltage losses, known as discharge or charge overpotential, respectively. These overpotentials are primarily associated with oxygen electrocatalytic reactions such as ORR and OER occurring at the catalyst-coated air electrode, attributed to significant activation energy barriers for electron transfer from the electrode to the electrolyte during oxygen redox reactions. In addition to obtaining overpotentials from galvanodynamic polarization curves, the power density of the Zn-air battery can be determined by plotting the applied current density against the value obtained by multiplying the discharge voltage by the applied current density. At sufficiently high applied current densities (usually depending on the catalyst and current density), a peak power density can be observed at a specific current density. The polarization curves obtained from this technique are utilized to identify

overpotentials associated with electrocatalytic oxygen redox reactions and resistances primarily related to activation and ohmic polarization phenomena during Zn-air battery operation.

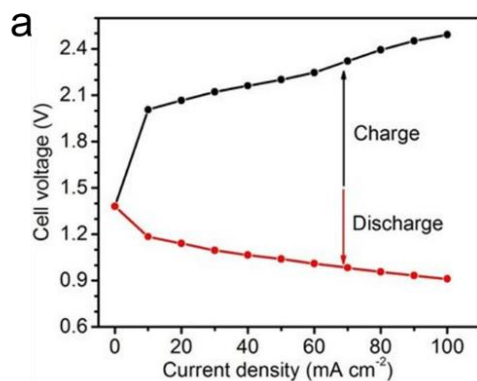


Figure 2.1 Charge–discharge polarization curves for the rechargeable zinc air battery.⁷⁸ Copyright 2015, Wiley-VCH.

2.1.2 Galvanostatic cycling testing

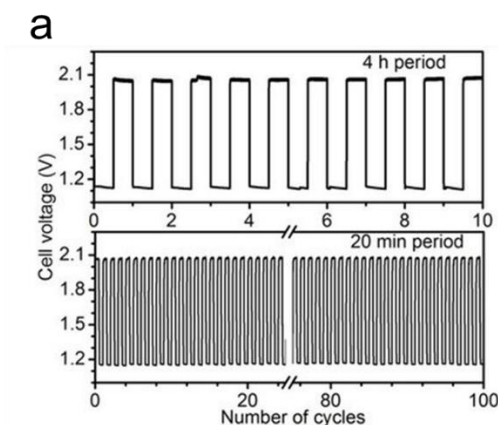


Figure 2.2 Cycle performance for the rechargeable zinc-air battery.⁷⁸ Copyright 2015, Wiley-VCH.

Galvanostatic cycling tests were performed with the catalyst to evaluate the long-term operation of the ZAB. The performance of a battery is determined as a function of its charge and discharge conditions, which are generally a given rate and a potential range. Cycle tests provide

information about the battery such as its internal chemistry, capacity, number of usable cycles, and lifetime. The cycling performance at a specific areal current density can be obtained by recording charge and discharge curves under a fixed time interval. (Figure 2.2) The rechargeability of the battery can be evaluated by a pulse cycling in short intervals, whereas extended cycling determines the more practical cycling capabilities of the battery. Galvanostatic cycling was performed using a battery tester (LAND-CT2001A) to assess the electrochemical performance of the Zn-air battery by applying a constant current, measuring charge/discharge voltage, and evaluating cycle life. In a typical fabrication process, sample powders were dispersed in a 0.2 wt% Nafion solution to form an electrocatalyst ink, which was then sprayed onto a carbon paper serving as the gas diffusion layer (GDL). The mass loading of the electrocatalyst was fixed at 1 mg cm^{-2} in this study. Subsequently, this GDL, acting as the air cathode, was assembled with a polished zinc plate serving as the anode to construct the Zn-air battery. A 6M KOH solution containing 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$ served as the electrolyte. Stainless steel mesh and copper foil were used as the current collectors at the cathode and anode sides, respectively. By recording charge and discharge profiles at fixed time intervals (e.g., 2-hour cycle period), the cycling performance at a specific areal current density was obtained. In addition to setting the galvanostatic current, a cut-off voltage was typically applied to prevent overcharging of the Zn-air battery. Two sets of parameters are commonly considered as criteria for performance comparison: the discharge-charge voltage gap and cycling number. The former can also be expressed as energy efficiency (i.e., the ratio between discharge and charge voltage), which is related to the activity of the electrocatalyst, while the latter reflects the durability of the battery under operation.

2.1.3 Electrochemical testing methods

Typically, a rotating disc electrode (RDE) is composed of a glassy carbon disk electrode embedded in an insulating Teflon outer layer, where the developed catalysts are solely coated on

the smooth surface of glassy carbon. Rotating the electrode generates a flow of electrolytes, triggered by convection, by allowing mass transport of active species such as hydroxide ions. LSV polarization curves were executed via RDE tests scanning from 0.1V to -1.1 V at a rotating speed of 400, 625, 900, 1225, and 1600 rpm for ORR with the scan rate of 10 mV s⁻¹. This three-electrode system contains a saturated calomel electrode (SCE), a graphite rod, and glassy carbon electrode (GC) as counter electrode, reference electrode and working electrode respectively. All the data can be calibrated to the reversible hydrogen electrode (RHE) by the Nernst equation. In this thesis, an RDE half-cell equipment was employed to investigate both the ORR and OER catalytic activity of the prepared materials.

From the ORR polarization curves obtained at the different rotation speeds, it is possible to study the reaction kinetics and mechanisms of the developed catalyst via a Koutecky Levich (K L) equation.

$$\frac{1}{j} = \frac{1}{j_l} + \frac{1}{j_k} = \frac{1}{B\omega^{0.5}} + \frac{1}{j_k}$$

$$B = 0.62nFC_0(D_0)^{2/3}V^{-1/6}$$

$$j_k = nFKC_0$$

Where n is the electron transfer number, j stands for the measured current density, B presents the slope of K-L plots, ω is the rotation rate of the disk electrode, j_l and j_k are the diffusion-limiting and kinetic current densities, F is the Faraday constant (96485 C mol⁻¹), C_0 presents the bulk concentration of O₂ which is 1.2 × 10⁻⁶ mol cm⁻³ in 0.1 M KOH, D_0 stands for the O₂ diffusion coefficient (1.9 × 10⁻⁵ cm² s⁻¹), V is the kinematic viscosity of the solution (0.01

$\text{cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant. The same electrochemical condition was used for testing of OER with the rotation speed of 1600 rpm.

2.2 Physical characterization

2.2.1 X-ray diffraction (XRD)

X-ray diffraction is a technique that is used to characterize the crystal structure of samples. The basic concept is that electromagnetic waves such as X-rays, can be diffracted by the crystal structure to form an interference pattern. The intensities of these patterns can be detected and correlated to structure and order of the atoms are in the sample. Bragg's law is used to relate the scattering angle to the lattice spacing and is given in the following widely known equation:

$$2d \sin\theta = n\lambda$$

where d is the lattice spacing, θ is the incident angle of the X-ray, n is any whole integer and λ is the wavelength of the X-rays. Figure 2.3 depicts the experimental setup and the spatial relationship between the lattice spacing and scattering angle.

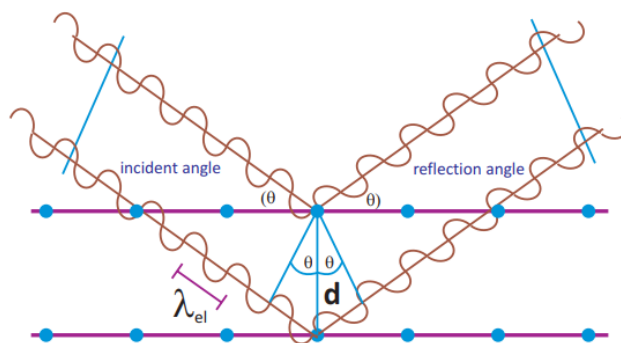


Figure 2.3 The schematic of XRD mechanism and the Bragg's Law. Copyright 2018, ©2021 Let's Talk Academy.

2.2.2 Scanning electron microscopy (SEM)

SEM is an important imaging tool to investigate and identify the morphology and topological features of materials in micro and nanoscale. As shown by Figure 2.4, it involves illuminating the sample with an electron beam, and projecting images based on collected secondary or backscattered electrons. After measuring these signals with detectors, a signal is sent to the computer which creates a real time image displaying the morphology of the sample. In this thesis, SEM will be used to investigate the morphology of the synthesized materials. Interactions between incident electrons and atoms on the sample surface (and a limited sub-surface volume) generate various signals. These include backscattered electrons (BSEs) and secondary electrons (SEs) that relay compositional and topographical information. Secondary electrons have very low energies on the order of 50 eV, which limits their mean free path in solid matter. Consequently, SEs can only escape from the top few nanometers of the surface of a sample. The signal from secondary electrons tends to be highly localized at the point of impact of the primary electron beam, making it possible to collect images of the sample surface with a resolution of below 1 nm. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. Since they have much higher energy than SEs, they emerge from deeper locations within the specimen and, consequently, the resolution of BSE images is less than SE images. However, BSE are often used in analytical SEM, along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution, but not the identity, of different elements in the sample. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. The energy or wavelength of these

characteristic X-rays can be measured by Energy-dispersive X-ray spectroscopy or Wavelength-dispersive X-ray spectroscopy and used to identify and measure the abundance of elements in the sample and map their distribution.

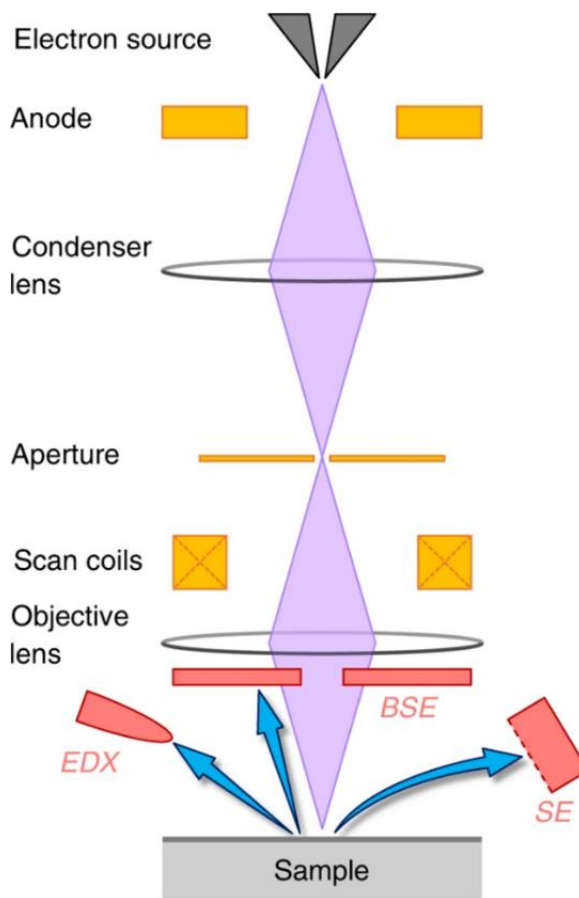


Figure 2.4 The schematic illustration of core components and working principles of SEM.⁷⁹

Copyright 2019, Springer Nature.

2.2.3 Transmission electron microscopy (TEM)

TEM is widely used in imaging nanostructures, atomic arrangements, and crystal orientation. Electrons are ejected from the electron gun (cathode) which is composed of a high voltage applied to tungsten wire. The ground or the anode directs electron flow through a hole in the anode's body and the electron is further passed through and focused by electromagnetic

condenser lenses. TEM allows direct visualization of samples' morphology on the nanometer scale. High resolution TEM imaging even shows atomic level morphology. In TEM, a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. Based on electron diffraction theory, the signals from the collected diffracted electrons can be processed to produce a high-resolution image of the sample.

2.2.4 X-Ray photoelectron spectroscopy (XPS)

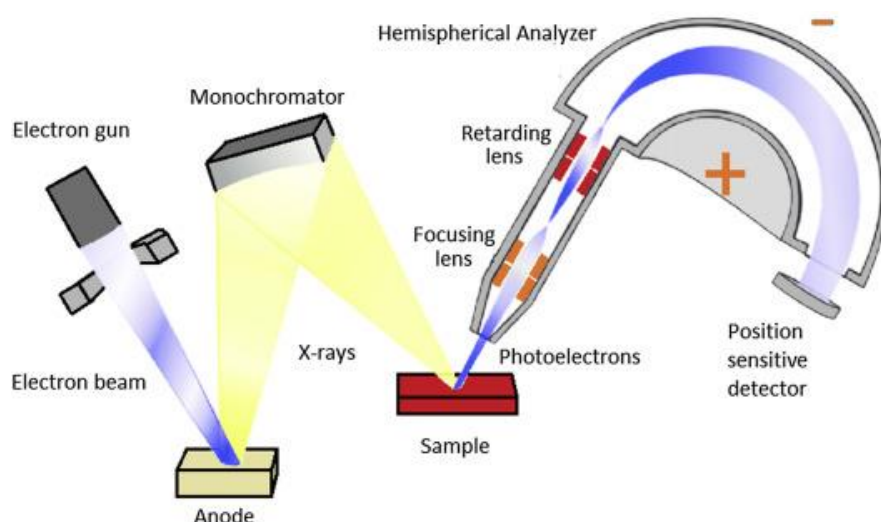


Figure 2.5 The schematic illustration of a XPS instrument. Copyright 2021, In Handbook of Mineral Spectroscopy

XPS is a surface characterization tool that allows investigation of the elemental composition, chemical and electronic states of an element on samples (Figure 2.5). In principle, the sample is exposed to X rays with a specific energy. When an atom or molecule absorbs an X-ray photon, an electron can be ejected. The kinetic energy (KE) of the electron depends upon the photon energy ($h\nu$) and the binding energy (BE) of the electron (i.e., the energy required to remove the electron from the surface). By measuring the kinetic energy of the emitted electrons, it is possible to determine which elements are near a material's surface, their chemical states and

the binding energy of the electron. The binding energy depends upon a number of factors, including the following: The element from which the electron is emitted. The orbital from which the electron is ejected. The chemical environment of the atom from which the electron was emitted.

2.2.5 X-ray adsorption spectroscopy

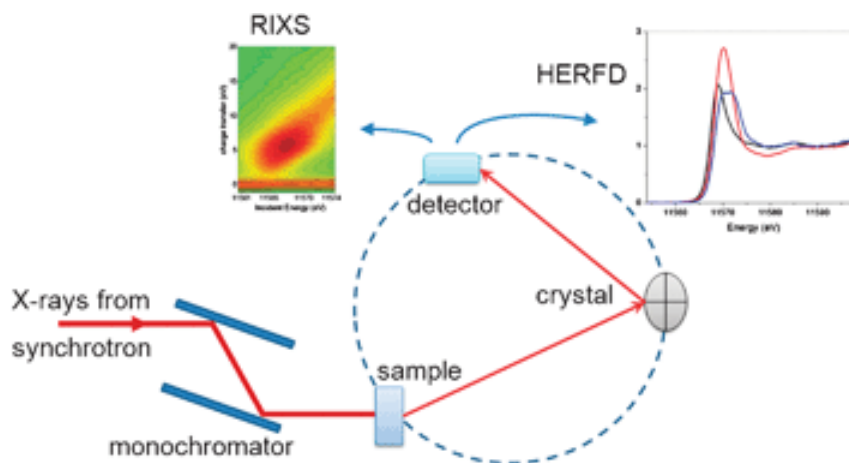


Figure 2.6 The schematic illustration of a XAS instrument. Copyright 2010, Royal Society of Chemistry.

X-ray absorption spectroscopy (XAS) can be considered as one of the most popular techniques to determine the structure of materials without long-range order (Figure 2.6). The spectrum can be divided into three regions, namely the pre-edge, the X-ray absorption near edge structure (XANES), and the extended X-ray absorption fine structure (EXAFS). The shape of XANES spectra gives the electronic structure and the local geometry around the atom that absorbs the X-ray radiation. EXAFS spectroscopy provides the coordination geometry, such as bond length (with an accuracy of about 0.01 Å), the number of neighboring atoms, which indicates the size and shape of the nanoparticles. In an XAS experiment, an electron from a core level is excited through the absorption of a photon of the incoming X-rays. The excited electron

is pushed above the Fermi level and obtains a kinetic energy equal to the difference in the energy of the incoming X-ray and the bonding energy of the excited electron. As the energy of the incoming X-rays increases, excitation occurs, causing a sharp increase in the absorption signal. This energy is referred to as the absorption edge. X-ray Absorption Near-Edge Structure (XANES): This region, as mentioned earlier, is located just above the absorption edge. It provides information about the electronic transitions and the unoccupied electronic states of the absorbing atoms. Extended X-ray Absorption Fine Structure (EXAFS): This region is located further above the absorption edge and contains oscillations resulting from the backscattering of photoelectrons by neighboring atoms. EXAFS provides details about the distances, coordination numbers, and disorder in the local atomic environment of the absorbing atoms. By analyzing both the XANES and EXAFS regions of the spectrum, researchers can obtain detailed insights into the structure and bonding characteristics of materials. XAFS is employed in various scientific fields, including chemistry, physics, materials science, catalysis, and environmental science, among others. It is commonly utilized at synchrotron radiation facilities, where intense and tunable X-ray beams are available for detailed spectroscopic investigations.

2.2.6 N₂ adsorption desorption analysis

Brunauer-Emmett-Teller (BET) analysis is a valuable technique for determining the specific surface area and porous characteristics of materials. The theory behind BET aims to elucidate the physical adsorption and desorption phenomena of gas molecules onto a solid surface. Inert gases such as nitrogen (N₂), argon (Ar), and carbon dioxide (CO₂) are commonly used as adsorbates to prevent any chemical reactions with the material surface being analyzed. The BET theory is applicable to systems of multilayer adsorption, extending the principles of Langmuir theory for monolayer molecular adsorption. Key hypotheses of the BET theory include

the assumption of physical adsorption of gas molecules on a solid in layers infinitely at saturation pressure, and the consideration of interactions solely between adjacent layers of gas molecules. In the specific research field of hierarchically porous electrocatalyst development, BET analysis is highly beneficial for investigating the high specific surface area and large porosity of materials. This is crucial as electrocatalytic processes such as oxygen reduction and oxygen evolution reactions primarily occur at the surface. Data analysis involves classifying the shape of adsorption/desorption isotherms into several types based on the porous nature of materials, facilitating the determination of surface and porous characteristics. Enhancing the specific surface area and porosity of electrocatalysts through material design and engineering is a primary objective of this research. This approach exposes more electrocatalytic active sites to reactants such as gaseous oxygen (O_2) from the environment and hydroxide ions (OH^-) in the electrolyte, essential for ORR and OER. Therefore, the design and engineering of nanostructured materials with hierarchical architectures and large specific surface areas are crucial for enhancing the activity and durability of electrocatalysts.

Chapter 3 Nitrogen-vacancy-regulated ordered mesoporous Fe₂N_x electrocatalysts for enhanced oxygen reduction reaction

3.1 Introduction

The oxygen reduction reaction (ORR) is a significant process for renewable energy conversion devices, including rechargeable metal-air batteries and fuel cells. However, the sluggish kinetic is the dominating issue, attributed to the multiple proton and four electron-transferring steps.⁸⁰⁻⁸² Currently, noble-metal based catalysts like platinum are highly effective for ORR, but the high price and scarcity limit their extensive applications. As a consequence, the design and engineering of platinum group metal-free (PGM-free) electrocatalysts is urgently required to reduce the cost.⁸³⁻⁸⁵ There has been numerous work on PGM-free electrocatalysts, containing transition metal oxides,^{86, 87} nitrides^{88, 89}, carbonous materials,^{70, 90} and sulfides^{91, 92}, which are able to enhance the catalytic ability on account of their strong chemical interaction and exceptional electrical conductivity and catalytic activity.^{19, 93, 94} Among these alternatives, transition metal nitrides (TMNs) have shown promise due to their mechanical robustness and strong corrosion resistance.^{49, 95} With the introduction of nitride atoms, the electronic environment of the original metal can be altered, which causes the increase of the density of state (DOS) and triggers the donating of the electron for metal nitrides, boosting the catalytic ability.

^{96 97}

Although there are many merits in energy conversion shown by TMNs, numerous challenges still exist. TMNs own obvious disadvantage as to the chemical inertness to maintain stable performances during electrochemical catalysis, which in turn degrades electrocatalytically active sites.⁹⁰ Vacancies play a critical role in tuning the electrochemical properties of the

catalysts and have been extensively investigated in nanomaterials. With the creation of vacancies, the atoms could be moved into other positions or removed from the original crystal lattice. Therefore, by inducing vacancies, the active sites can be regulated and electrochemical performance of the catalyst can be adjusted and increased.^{65, 98} Modifying TMNs with nitrogen vacancies is a feasible way to establish efficient M-N_x sites and to alter the coordination environment of active sites.^{23, 81}

Herein, we successfully constructed a unique three dimensional interconnected and ordered mesoporous Fe₂N_x with tailored nitrogen vacancies decorated on TiO_y (Fe₂N_x@TiO_y) for efficient and durable ORR. With the introduction of nitrogen defects, the electronic structure and coordination environment of Fe active center are effectively regulated, improving the oxygen electrocatalytic kinetics. DFT computation analysis reveals that the induced nitrogen vacancies upshift the d band level of Fe active sites closer to Fermi level, which leads to valence electron depletion and increases the binding energy, facilitating O₂ absorption on the catalyst to accelerate the ORR activity. Meanwhile, the ΔG value of potential determining step (PDS) for Fe₂N_x@TiO_y is significantly reduced, implying the presence of nitrogen induces an environment of electron deficiency, improving the acceptance of *OH to facilitate the catalytic reactions. Moreover, the 3D titania structure provides accessible surface areas and a stable interconnected skeleton for transport of various intermediates during the electric catalytical processes, facilitating ORR kinetics. As expected, Fe₂N_x@TiO_x shows outstanding ORR performance and serves as an effective cathode for zinc-air batteries, revealing the great potential in electrochemical energy storage and conversion systems and beyond.

3.2 Experimental methods

Synthesis of $\text{Fe}_2\text{N}_x@\text{TiO}_y$. All chemicals were purchased from Sigma-Aldrich Canada and employed without any further purification. Typically, for the synthesis of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60, it was derived from a hard template method, where polystyrene spheres beads are used as the template. Monodisperse polystyrene (PS) beads were synthesized using an emulsion polymerization reaction. First, distilled de-ionized (DDI) water was boiled for several minutes to remove oxygen. This water was used for the remainder of the synthesis procedure. In a three-neck flask, 2.5 g of polyvinylpyrrolidone (PVP) was dissolved in 200 mL of DDI water. Simultaneously, 0.2 g of potassium persulfate was dissolved in 40 mL of DDI water. The PVP solution was heated to 70°C using an oil bath under continuous stirring, while maintaining an inert environment with nitrogen gas. After 10 minutes, 24 mL of styrene monomer was added to the PVP solution, and the mixture was stirred for an additional 15 minutes. Next, the potassium persulfate solution was added dropwise (~1 drop per second) to the monomer solution using a separatory funnel. This mixture was stirred for 24 hours to form the final colloidal PS solution, which appeared milky white. The concentration of the prepared PS solution was then adjusted to 30 mg/mL for further use.⁹⁹ 5 mmol Ferric chloride hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] was dissolved into the mixture of ethanol (5 mL), 5 mmol titanium butoxide [$\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$] and 1mmol hydrochloric acid [HCl]. Then the obtained PS beads were added into above solution, which afterwards was placed at room temperature for 24 h. Afterwards, the light yellow skeleton were under filtration process washed by ethanol several times and dried at 40 °C overnight. Finally, the $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 was obtained by calcinating dried yellow solids through a heating process, from 300 °C and maintaining for 1 h, heating up to 540 °C and keeping for 1 h, then increasing the temperature to 800 °C and staying for 1 h to get the expected sample. The

calcination process was under Ar flowing and switched to NH_3 at 800 °C for 60 min to obtain $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60, for 40 min to obtain $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -40 and for 20 min to obtain $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -20 respectively.

Synthesis of $\text{Fe}_2\text{N}@\text{TiO}_x$. 5 mmol Ferric chloride hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] was mixed in the solution composed of 5 mL ethanol, 5 mmol titanium butoxide and 3 mmol oleamide [$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CONH}_2$] and 1 mmol hydrochloric acid. Socking PS beads into the mixture for 24 h, followed by filtration process using ethanol to wash the sample and dried at 40 °C for 8 h. The obtained polystyrene fragment then was under heat treatment at 800 °C for 1 h with Ar flowing to get $\text{Fe}_2\text{N}@\text{TiO}_x$.

3.2.1 Materials characterization

The transmission electron microscope images were obtained by a JEM 2010F microscope operated at 200 kV. Along with energy-dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED) pattern to seek the morphology and energy-dispersive spectrum elemental mappings of materials. XRD (Rigaku Mini-flex 600 X-ray Diffractometer) was employed to assess crystalline structure and phase purity. X-ray photoelectron spectroscopy (XPS) measurements were conducted a Thermal Scientific K-Alpha XPS spectrometer. Electron paramagnetic resonance (EPR) signals were recorded with a Bruker ESR A300 spectrometer at 100 K. N_2 adsorption–desorption measurements on a Brunauer-Emmett-Teller surface area analyzer (Quantachrome Instruments QuadraSorb SI4) were used to explore the pore structure and a Barrett-Joyner- Halenda (BJH) model was exploited to analyze pore size distribution. The X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine structure (EXAFS) at Fe K-edge was acquired in fluorescence mode at Canadian Light Source, Canada. All the XANES and EXAFS data were analyzed by Athena program.

3.2.2 Electrochemical measurements

A three-electrode system was utilized to carry out the electrochemical performances by an electrochemical workstation (Biologic VSP 300). This three-electrode system contains saturated calomel electrode (SCE), a graphite rod and glassy carbon electrode (GC) as reference electrode, counter electrode and working electrode respectively. All the data can be calibrated to the reversible hydrogen electrode (RHE) by Nernst equation. The catalyst ink was composed of the mixture of 4 mg catalysts in 1 mL ethanol with 0.15 wt.% Nafion dispersion, followed by sonicated for 1 h to acquire homogeneous ink. Then 20 μL suspension was dropped onto the GC electrode surface with the loading of 0.4 mg cm^{-2} . 0.1 M KOH solution was used in all measurements along with O_2 bubbling in ORR measurements. LSV polarization curves were executed via RDE tests scanning from 0.1 V to -1.1 V at a rotating speed of 400, 625, 900, 1225 and 1600 rpm for ORR with the scan rate of 10 mV s^{-1} . The zinc-air battery tests of samples were carried out by a multichannel potentiostation (Princeton Applied Research, VersaSTAT MC). The home-made zinc-air battery includes cathode, mesoporous membrane and zinc plate as anode and was conducted in the electrolyte composed of 6.0M KOH solution with 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$. Amount of catalyst was sprayed on carbon paper as cathode with the loading of 1 mg cm^{-2} . For the galvanostatic cycling stability test, an additional 2.5 mg of commercial RuO_2 was added to the ink to prepare the cathode.

3.2.3 DFT simulation details

All the spin-polarized computations were performed by using Vienna ab initio simulation package (VASP).^{100, 101} The ion-electron interactions were described by the projector augmented wave method¹⁰² and the general gradient approximation in the Perdew–Burke–Ernzerhof (PBE) form was used.^{103, 104} During the structure relaxation, the convergence criterion was set to 0.03

eV/Å and 10^{-5} eV for the residual force and energy, respectively. The model for $\text{Fe}_2\text{N}@ \text{TiO}_x$ we used was shown in Figure 1a and $\text{Fe}_2\text{N}@ \text{TiO}_y$ with N vacancy ($\text{Fe}_2\text{N}_x@ \text{TiO}_y$) was simulated by removing one surface N atom (Figure 1b). Brillouin zones were sampled by Monkhorst-Pack $2 \times 2 \times 1$ and $4 \times 4 \times 1$ k-point grids for structure relaxation and electronic structure calculation, respectively. To avoid the interaction between two periodic units, a vacuum space over 15 Å was employed.

The free energy change (ΔG) of each elementary reaction was calculated based on the computational hydrogen electrode (CHE) model¹⁰⁵:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$$

where ΔE , E_{ZPE} , T and S is the reaction energy difference, zero-point energies, temperature and entropy, respectively.

3.3 Results and Discussions

Fig. 3.1a displays the schematic of the construction procedure for the $\text{Fe}_2\text{N}_x@ \text{TiO}_y$ composite. Polystyrene spheres (PS) were assembled, stacked, and then immersed in Fe precursor solution. After calcination at high temperature under NH_3 atmosphere, the template was removed and the target ordered porous skeleton was obtained. The scanning transmission electron microscopy (STEM) image indicates that compact and ordered spheres were generated, with the average diameter around 186 nm (Figure 3.1b). It is distinct that pores own continuous channels which could interreact with surface to facilitates mass transfer and exposes active sites. Energy-dispersive spectroscopy (EDS) mappings (Figure 3.1c-h) reveals the uniform elemental distribution of Fe, N, Ti, O, and C over the ordered mesoporous framework. As shown in Fig. 1i,

it is clear that each sphere is composed of small particles, certifying Fe_2N_x nanoparticles uniformly embedded on the porous TiO_y supporting network. The high-resolution TEM (HRTEM) image (Figure 3.1j) displays the lattice fringes with the interplanar spacings of 0.28 and 0.39 nm, which correspond to the orthorhombic lattice plane of (200) and (221) for the Fe_2N_x nanoparticles, respectively.¹⁰⁶ By combination of titania skeleton and Fe_2N_x nanoparticles growth, it is a feasible way to fabricate unique hierarchical 3D mesoporous structure to make sure each pore linked together. TiO_y plays a crucial role in the $\text{Fe}_2\text{N}_x@\text{TiO}_y$ catalyst to maintain the unique 3D structure and to enlarge the transfer of the intermediates during the catalytic process. With the induce of TiO_y , the 3D skeleton with hierarchical porous architecture can facilitate the adsorption/desorption process, resulting in an excellent fast discharge behavior. In this context, porous TiO_y structures have attracted special interest in zinc-air batteries ascribe to the special properties, including high specific area, corrosion-resistive and narrow pore size distribution.

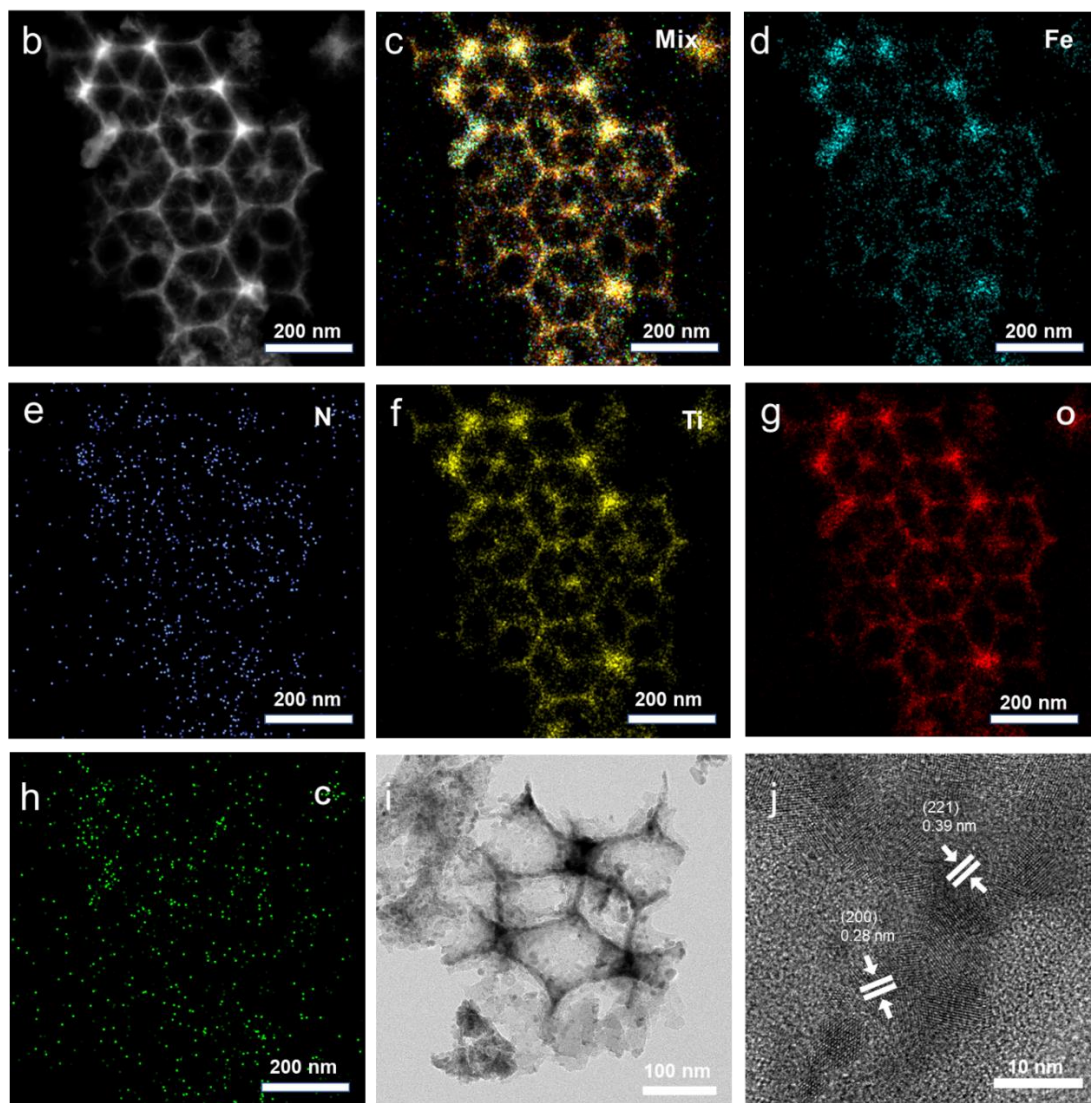
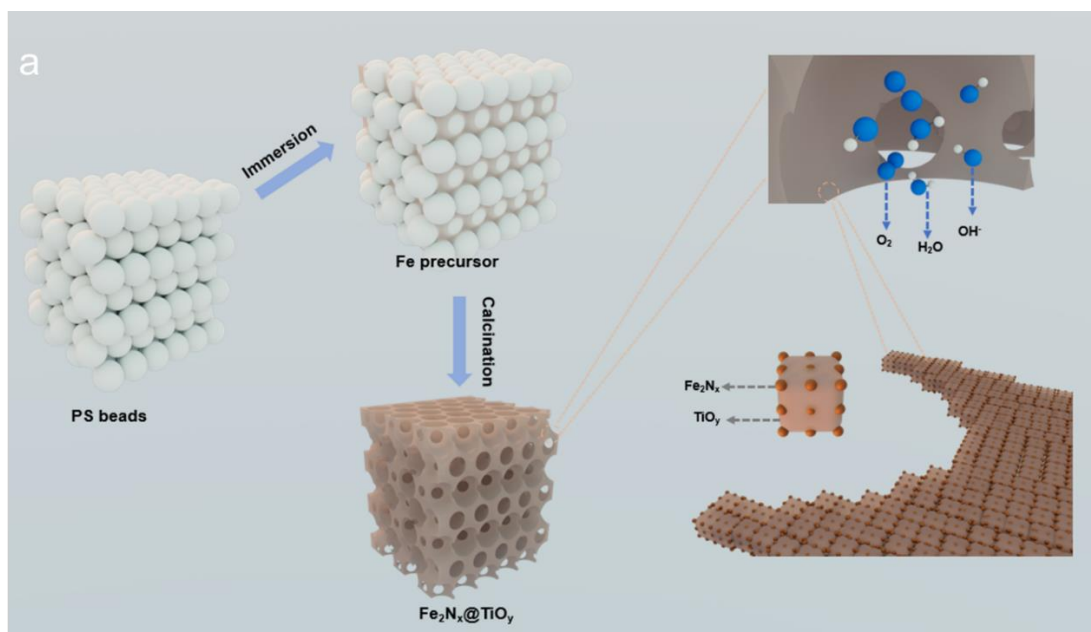


Figure 3.1 a) Synthesis route for $\text{Fe}_2\text{N}_x@\text{TiO}_y$. b-h) HADDF-STEM image and corresponding elemental mapping for Fe, N, Ti, O, C and mixture. i) Enlarged TEM image and j) HRTEM image of $\text{Fe}_2\text{N}_x@\text{TiO}_y$.

The crystalline structure of the catalysts can also be verified by X-ray diffraction (XRD) patterns of Fe_2N_x and Fe_2N . As shown in Figure 3.2a, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ is composed of Fe_2N_x , TiO and TiO_2 corresponding to TEM results. Due to the unique orthorhombic structure with interstitial sites, Fe_2N is able to enhance the electrical conductivity, chemical stability, and improve electrocatalytic activity.¹⁰⁷ The partial amplified pattern reveals that the peak at $\sim 42.7^\circ$, responding to (121) plane of Fe_2N , exhibiting a slight shift toward higher angles in $\text{Fe}_2\text{N}_x@\text{TiO}_y$, which can be attributed to the formation of nitrogen vacancies with annealing under NH_3 atmosphere, causing the lattice contraction.¹⁰⁸ Electron paramagnetic resonance (EPR) measurement (Figure 3.2b) was conducted to further confirm the presence of nitrogen vacancies. The unpaired electrons in materials were detected with an apparent EPR signal at $g=2.0074$ observed in $\text{Fe}_2\text{N}_x@\text{TiO}_y$.¹⁰⁹ The EPR signals of unpaired electrons in $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 increased significantly compared with $\text{Fe}_2\text{N}@\text{TiO}_y$, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -20, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -40. The structure of different catalysts under different time of NH_3 calcination procedure have been investigated to explore the effect of nitrogen vacancies. N_2 adsorption-desorption measurements were conducted to assess the surface area and pore texture of the materials. As shown in Figure 3.2c,

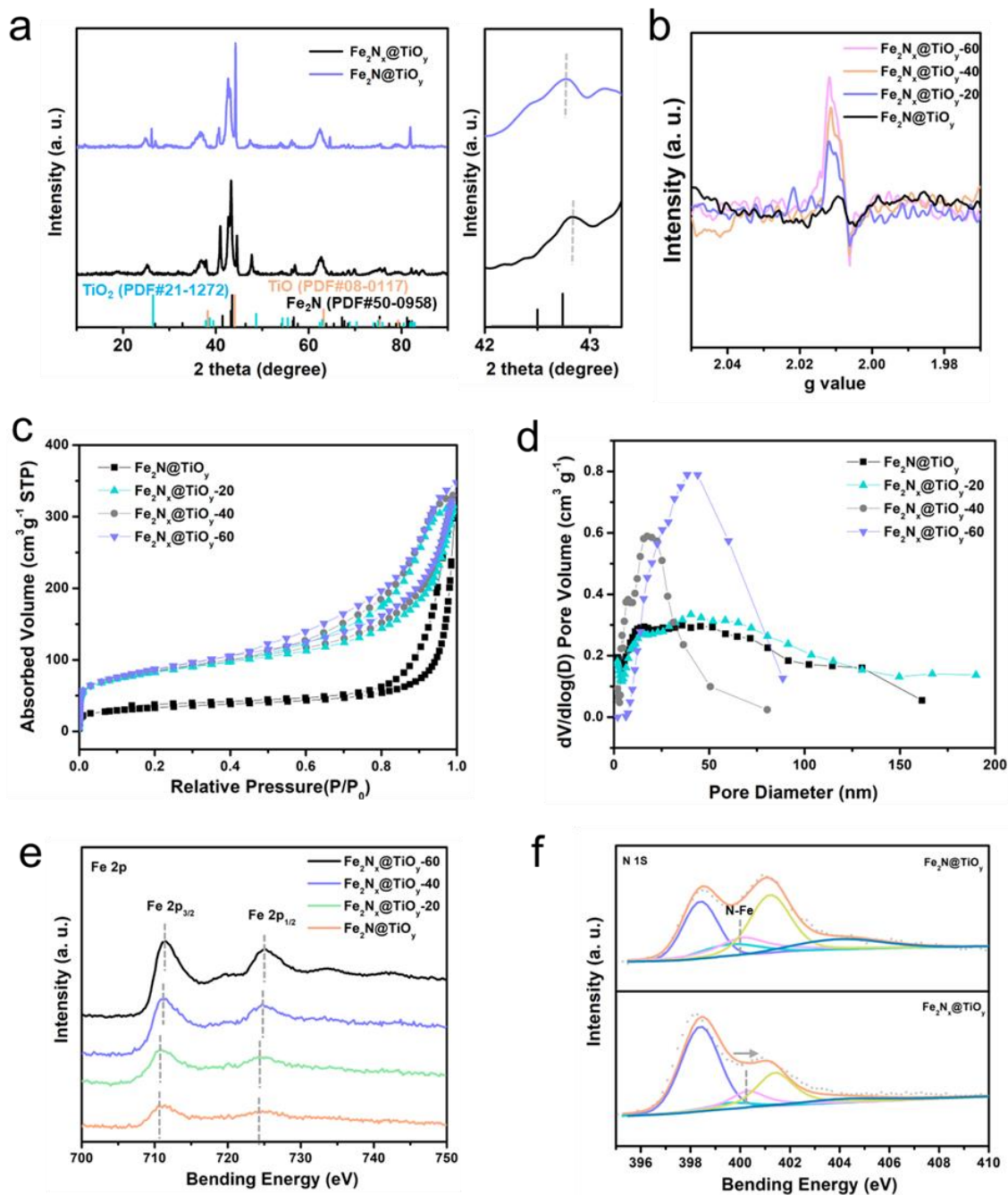


Figure 3.2 a) XRD pattern, and b) EPR spectra of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -20, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -40, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 and $\text{Fe}_2\text{N}@\text{TiO}_y$. c) N_2 adsorption-desorption isotherms, and (d) pore size distribution plots of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -20, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -40, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 and $\text{Fe}_2\text{N}@\text{TiO}_y$. XPS spectra of $\text{Fe}_2\text{N}_x@\text{TiO}_y$: (e) Fe 2p spectra, and (f) N 1s spectra.

the specific surface area of $\text{Fe}_2\text{N@TiO}_y$, $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-20}$, $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-40}$ and $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-60}$ under different NH_3 flowing are $297.9 \text{ m}^2 \text{ g}^{-1}$, $315.2 \text{ m}^2 \text{ g}^{-1}$, $329.9 \text{ m}^2 \text{ g}^{-1}$ and $347.6 \text{ m}^2 \text{ g}^{-1}$, respectively. The surface areas for the series of composites are very close, but slightly enhanced with the increase of time of NH_3 flow, revealing more nitrogen defects formed to reduce the overall density and bring more center vacancies, while promoting the formation of porous texture.

⁷² The pore size distribution curve of $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-60}$ (Figure 3.2d) is relatively narrow on 42 nm, suggesting massive mesopores in the material. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of $\text{Fe}_2\text{N}_x\text{@TiO}_y$ -based samples and all main elements are shown in Figure 3.2e. The Fe 2p peaks in $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-60}$ slightly shifts to higher binding energy compared with $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-40}$, $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-20}$ and $\text{Fe}_2\text{N@TiO}_y$. The other composites also negatively shift compared with other materials under decreased or without NH_3 annealing, indicating declined valence state of Fe after NH_3 heat treatment. ¹¹⁰ N 1s spectra shown in Figure 3.2f can be assigned to pyridinic N at 398.2, Fe–N at 399.3, pyrrolic N at 400.5, graphitic N at 401.2, and oxidized N at 403.5 eV. ¹⁶ For $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-60}$, the Fe-N peak shifts a bit to higher binding energy due to the creation of nitrogen vacancies. With engineered defects, the extra electrons can be relocated at reaction center to boost the oxygen reduction reaction. ^{111, 112}

The electrical performances of the engineered catalysts were evaluated by ORR linear sweep voltammetry (LSV) curves obtained by rotating disk electrode (RDE) in 0.1 M KOH solution with saturated oxygen. The LSV curves shown by Figure 3.3a, $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-60}$ demonstrates superior ORR performance compared with $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-40}$, $\text{Fe}_2\text{N}_x\text{@TiO}_y\text{-20}$, $\text{Fe}_2\text{N@TiO}_y$ as well as commercial Pt/C. To investigate the catalytic kinetic of catalysts, the

Tafel slopes of all catalysts derived from LSV curves are exhibited. Among them, $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 presents the smallest Tafel slope (50 mV dec^{-1}) compared to Pt/C and other reference

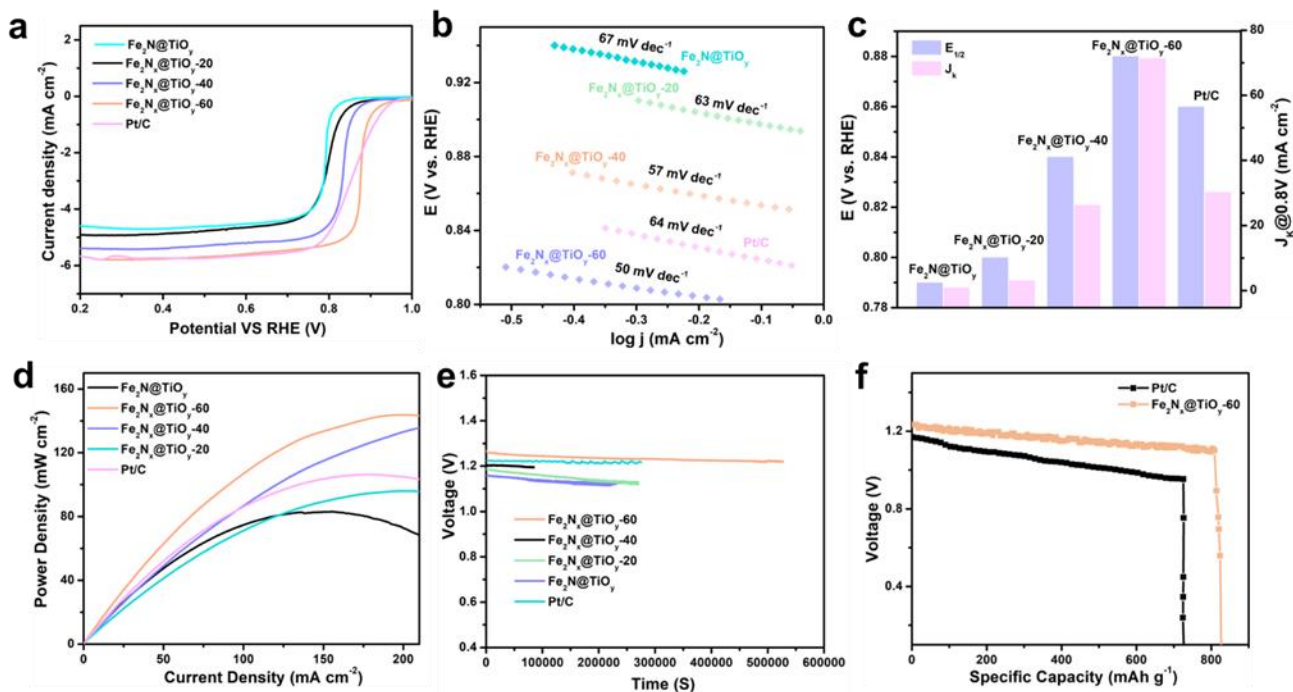


Figure 3.3 a) LSV curves of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60 and a series of counterpart catalysts in 0.1M KOH; b) corresponding Tafel plots and c) comparison of J_k at 0.8 V and $E_{1/2}$ for various reference catalysts. d) Power density plots and e) long-term durability test for $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60-based zinc-air battery and the reference catalysts-based zinc-air battery at 10 mA cm^{-2} . f) Specific capacity of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ -60-based zinc-air battery and Pt/C-based zinc-air battery.

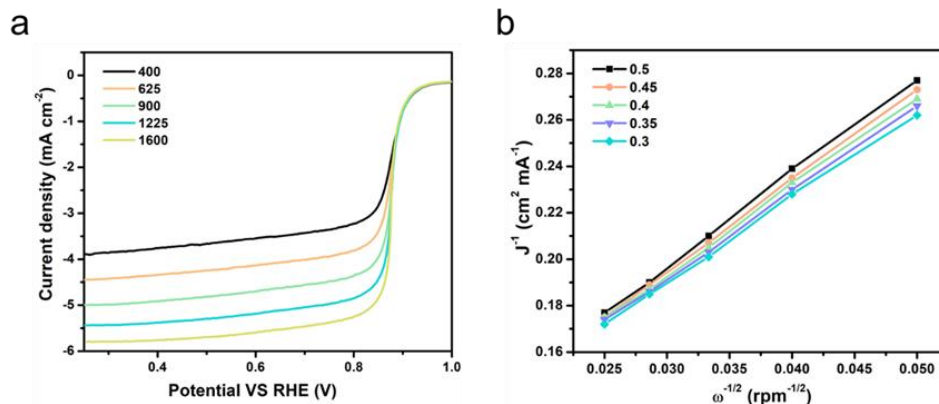


Figure 3.4 a) LSV curves of Fe₂N_x@TiO_y-60 at different rotation speeds from 400 to 1600. and b) corresponding Koutecký–Levich plots of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials from 0.3 to 0.5 V.

catalysts, implying the fastest kinetic process (Figure 3.3b). The Koutecký–Levich (K–L) plots (Figure 3.4a and b) suggest that Fe₂N_x@TiO_y-60 owns an average electron transfer number (n) of 3.99, illustrating efficient four-electron transfer process. In Figure 3.3c, it is reflected that Fe₂N@TiO_y reveals poor catalytic activity with a half wave potential ($E_{1/2}$) of 0.79 V vs. RHE and a kinetic current density (J_k) of 0.97 mA cm⁻². By contrast, the nitrogen-defective catalysts including Fe₂N_x@TiO_y-20 ($E_{1/2}$ = 0.80 V, J_k = 3.315 mA cm⁻²) and Fe₂N_x@TiO_y-40 ($E_{1/2}$ = 0.84 V, J_k = 26.31 mA cm⁻²) exhibit enhanced ORR activity; especially Fe₂N_x@TiO_y-60 delivers the highest $E_{1/2}$ (0.88 V) and J_k (71.34 mA cm⁻²), even higher than those of Pt/C ($E_{1/2}$ = 0.86 V, J_k = 30.30 mA cm⁻²). The outstanding performance of Fe₂N_x engineered with nitrogen vacancies indicates that nitrogen defects can facilitate the ORR kinetic process. The chronoamperometric (CA) technology was carried out to test the durability of Fe₂N_x@TiO_y-60 compared with commercial Pt/C (Figure 3.5a). Pt/C fails to maintain the ORR current and has 22% decrease,

while $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ presents better durability and retain 99% of the initial current. To further demonstrate the potential application of the obtained catalysts, $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ and the series of samples were employed as cathodes in zinc-air batteries. When the gas diffusion layer was loaded with $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ catalyst, the open circuit voltage is 1.48 V, which is the largest value compared to $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-40}$ (1.46 V), $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-20}$ (1.45 V), $\text{Fe}_2\text{N}@\text{TiO}_y$ (1.43 V) and Pt/C (1.42 V) (Figure 3.5b). Additionally, as shown by Figure 3.3d, $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ demonstrates the highest power density of 143.7 mW cm^{-2} compared to commercial Pt/C (108.2 mW cm^{-2}) and other reference catalysts. As shown in Figure 3.3f, $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ shows a higher specific capacity of 808.6 mAh g^{-1} compared to Pt/C 725.2 mAh g^{-1} . Moreover, as shown by Figure 3.3e, the $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ cathode has excellent long-term stability when discharging over 146 h at 10 mA cm^{-2} , with nearly negligible decrease. The current work has been made a detailed comparison of ORR and zinc-air battery performances (Table 3.1), which implies that $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ as cathode is superior than most of the reported advanced catalysts, indicating this catalyst can be promising candidate for energy storage and conversion.

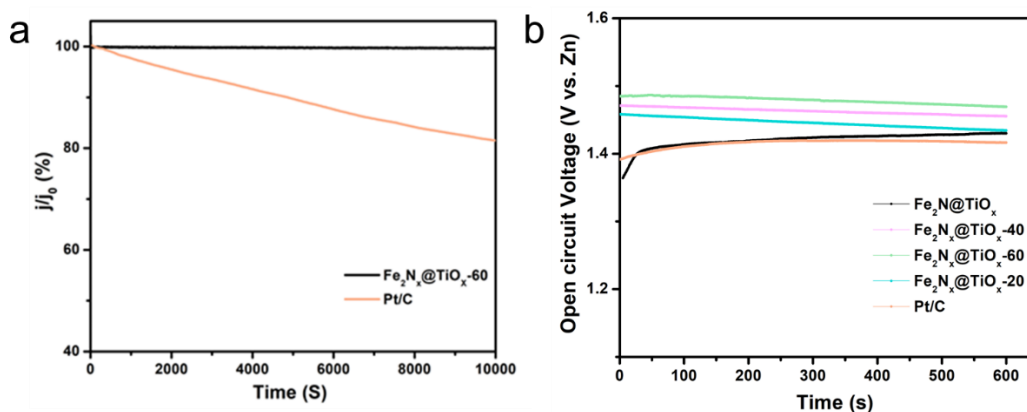


Figure 3.5 a) ORR chronoamperometric response at 0.6 V vs. RHE for $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ and Pt/C. b) Open circuit plot of $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-20}$, $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-40}$, $\text{Fe}_2\text{N}_x@\text{TiO}_y\text{-60}$ and $\text{Fe}_2\text{N}@\text{TiO}_y$ of the zinc-air batteries as air cathodes.

Table 3.1 Comparison of bifunctional performance and zinc-air batteries performance of Fe₂N_x@TiO_y-60 with recently reported Fe-based electrocatalysts.

Catalyst	ORR: $E_{half-wave}$ (V)	OER: $E_{j=10\text{ mA/cm}^2}$ (V)	Cyclability (h)	Power density (mW/ cm ²)	Ref.
Fe ₂ N _x @TiO _y -60	0.88	N. A.	27	143.7	This work
Fe-N _x -C	0.91	N. A.	250	96.4	113
Cu@Fe-N-C	0.892	N. A.	1.4	92	114
FeCo@MNC	0.86	1.48	24	115	70
Fe-N-C/N-OMC	0.93	N. A.	47	113	115
SA-Fe-3DOMC	0.901	N. A.	N. A.	140	116
FeN _x /C-700-20	0.9	N. A.	84	27	1
FeS/Fe ₃ C@NS-C-900	0.78	1.50	865	90.9	117
FeNP@Fe-N-C	0.84	1.57	30	106.5	118
Fe,N-CNS	0.88	1.84	10	128.7	119

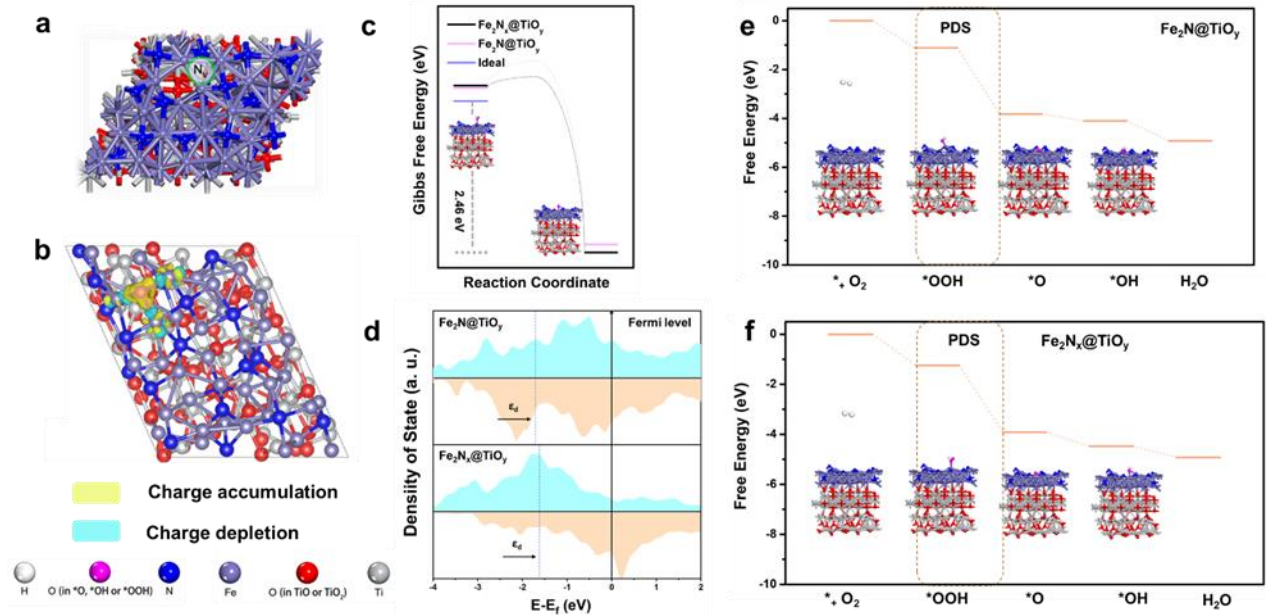


Figure 3.6 a) The calculated charge density and b) optimized model configuration of $\text{Fe}_2\text{N}_x@\text{TiO}_y$. c) Calculated energy barriers of $^*\text{OOH}$ transformation to $^*\text{OH}$ at active sites of $\text{Fe}_2\text{N}@\text{TiO}_y$ and $\text{Fe}_2\text{N}_x@\text{TiO}_y$. d) Projected density of states for model catalysts with surface Fe sites in $\text{Fe}_2\text{N}@\text{TiO}_y$ and $\text{Fe}_2\text{N}_x@\text{TiO}_y$. Free energy variations for ORR on e) $\text{Fe}_2\text{N}@\text{TiO}_y$ and f) $\text{Fe}_2\text{N}_x@\text{TiO}_y$.

To investigate the nature of the enhanced ORR kinetics and four-electron transfer mechanism with the construction of nitrogen defects in $\text{Fe}_2\text{N}@\text{TiO}_y$, DFT calculations were further carried out. The charge density configuration of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ is shown in Figure 3.6a, and it is clear that with the presence of defects, the electron density accumulates around O atoms and is depleted around Fe atoms, verifying that charge is transferred from Fe to O atoms. The model for $\text{Fe}_2\text{N}_x@\text{TiO}_y$ with nitrogen vacancy ($\text{Fe}_2\text{N}_x@\text{TiO}_y$) is constructed by removing one surface N atom as exhibited in Fig. 3.6b. The ultimate dream for the ORR is to engineer a catalyst with no overpotential, and the ideal energy separation of 2.46 eV between $^*\text{OOH}$ and $^*\text{OH}$. As shown by Fig. 3.6c, the value of $\text{Fe}_2\text{N}_x@\text{TiO}_y$ is closer than which of $\text{Fe}_2\text{N}@\text{TiO}_y$,

implying creation of nitrogen vacancies can reduce the energy barriers, thus facilitating the kinetics reduction.^{120, 121} Furthermore, the density of state (DOS) analysis (Figure 3.6d) of Fe site indicates that with the formation of nitrogen defects, the calculated d-band center (ϵ_d) of Fe in $\text{Fe}_2\text{N}_x@\text{TiO}_y$ is -1.61 eV, closer to Fermi level compared to that of $\text{Fe}_2\text{N}@\text{TiO}_y$ (-1.71 eV). The d-band center moving toward the Fermi energy level along with increased DOS signify the interaction between adsorbate and substrate turns to be stronger.^{122 123} In Figure 3.6e and f, the calculated Gibbs free energy plots of ORR for $\text{Fe}_2\text{N}@\text{TiO}_y$ and $\text{Fe}_2\text{N}_x@\text{TiO}_y$ are shown and compared. The second elementary reaction is the potential determining step (PDS) for $\text{Fe}_2\text{N}@\text{TiO}_y$ or $\text{Fe}_2\text{N}_x@\text{TiO}_y$, respectively. The ΔG value of PDS for $\text{Fe}_2\text{N}_x@\text{TiO}_y$ is (-0.44 eV) lower than that for $\text{Fe}_2\text{N}@\text{TiO}_y$ (-0.28 eV), illustrating that the presence of nitrogen vacancies increases the adsorption of *OOH, therefore lowering the energy barrier to enhance ORR activity. The theoretical simulations are consistent with the experimental studies that $\text{Fe}_2\text{N}_x@\text{TiO}_y$ with tailored nitrogen vacancies possesses improved ORR activity compared to $\text{Fe}_2\text{N}@\text{TiO}_y$.

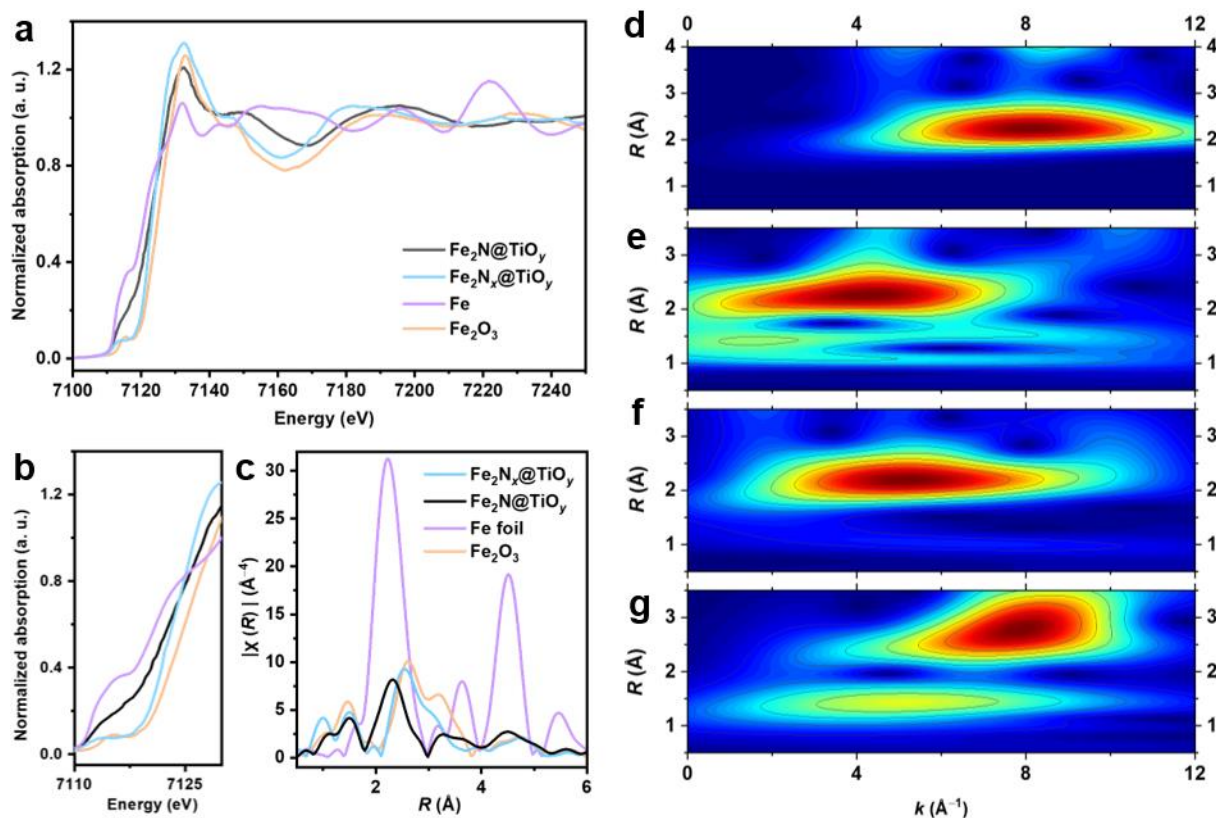


Figure 3.7 a) Fe K-edge XANES spectra, Fe_2O_3 and standard Fe foil. b) Fe K-edge XANES spectra at specific area and c) corresponding Fourier-transform k^3 -weighted EXAFS spectra for various samples. Fourier-transformed (FT) curves at R space of $\text{Fe}_2\text{N@TiO}_y$, $\text{Fe}_2\text{N}_x\text{@TiO}_y$. WT for the k^3 -weighted Fe K-edge of d) Fe foil, e) $\text{Fe}_2\text{N@TiO}_y$ and f) $\text{Fe}_2\text{N}_x\text{@TiO}_y$ g) Fe_2O_3 .

In order to further determine the chemical coordination environment of materials, X-ray absorption spectroscopy (XAS) was utilized. As shown in Figure 3.7a and b, the Fe K-edge X-ray absorption near-edge fine structure spectroscopy (XANES) result exhibits that the absorption edge position of $\text{Fe}_2\text{N@TiO}_y$ and $\text{Fe}_2\text{N}_x\text{@TiO}_y$ is higher than Fe foil and lower than Fe_2O_3 . This indicates that the valence state of Fe in $\text{Fe}_2\text{N@TiO}_y$ and $\text{Fe}_2\text{N}_x\text{@TiO}_y$ is between 0 and +3. Moreover, the absorption edge of $\text{Fe}_2\text{N}_x\text{@TiO}_y$ shifts toward higher energy compared to

Fe₂N@TiO_y, indicating that the existence of nitrogen vacancies alters the electronic structure of Fe.¹¹¹ According to the extended Fourier transform X-ray absorption fine structure (EXAFS) spectra (Figure 3.7c), it can be noticed that Fe₂N@TiO_y and Fe₂N_x@TiO_y have the peak at around 1.5 Å and 2.3 Å, which can be assigned to Fe-N and Fe-Fe coordination, respectively. Fe-Fe of Fe₂N@TiO_y and Fe₂N_x@TiO_y shift toward positive position, suggesting Fe is in nitride form, which further confirms that the coordination distance is enhanced with introduction of defects leading to slight structure distortion.^{88, 124} The wavelet transform (WT) study (Figure 3.7d-g) was conducted to present a preeminent resolution in K space and R space by distinction the backscattering atoms.¹²⁵ As shown on Figure 3.7f, the maximum intensity of WT contour plot for Fe₂N_x@TiO_y at around 4.2 Å⁻¹, attributed to Fe-N contribution.¹²⁶ Therefore, the tailored nitrogen vacancies effectively modulate the electronic configuration and coordination environment of Fe active site, enhancing the binding capability with oxygen species and hence promoting the ORR catalytic activity.

3.4 Conclusions

Using a hard template method, we synthesized a unique ordered porous Fe₂N_x embedded on TiO_x with tailored nitrogen vacancies. DFT calculations and XAS suggest that the energy barrier for adsorption and desorption of intermediates decreases on account of inducing nitrogen vacancies. After inducing of nitrogen vacancies, the Fe-Fe coordination altered with slight structure distortion to reduce energy barrier and boost electric performance. Fe₂N_x@TiO_y manifests superior ORR performance involving a kinetic current density of 71.34 mA cm⁻² at 0.8 V and half wave potential of 0.88 V. The zinc-air battery assembled with Fe₂N_x@TiO_y shows excellent durability when discharging over 146 h at 10 mA cm⁻². The 3D ordered porous structure and Fe₂N_x nanoparticles make great contributions to increase the ORR and zinc-air

battery performances. This work identifies the potential of defect engineering for catalytic ORR, providing new insights for constructing novel materials for efficient energy conversion and storage.

Chapter 4 Synergistic regulation of ternary Cu-Ti-O catalyst for zinc air batteries

4.1 Introduction

The ever-increasing global energy demand coupled with heightened awareness of climate change has catalyzed an accelerated shift from fossil fuels to clean renewable energy sources. Recognizing the finite nature of fossil fuel reserves on earth, it becomes apparent that the energy landscape will become increasingly volatile in the foreseeable future. Despite the levelized cost of renewable energy sources nearing or even surpassing that of fossil fuels, their intermittent nature presents a significant hurdle to their widespread adoption in the global energy matrix. Given these challenges, the imperative to develop innovative energy storage systems has never been more pressing.^{80, 127} Rechargeable zinc-air batteries present themselves as a sustainable and renewable solution due to their reasonable cost, high-energy density, and abundant resources.^{49, 128} However, the inherent slow kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) pose challenges to the practical implementation of zinc-air batteries. While Pt/C stands as the benchmark catalyst for ORR, its performance in OER is limited. Similarly, IrO₂, a standard for OER, exhibits poor ORR performance.^{129, 130 131} Hence, the development of efficient bifunctional catalysts devoid of precious metals, active, and stable for both ORR and OER, becomes pivotal.

Transition metal-based materials have been extensively researched as alternative bifunctional catalysts owing to their cost-effectiveness. They facilitate the efficient transmission of OH⁻/O₂ species across the active surface, especially in alkaline electrolytes, enhancing ORR/OER.^{132, 133} Among these materials, Cu-based catalysts stand out as promising candidates for practical zinc-air batteries.^{134, 135} However, challenges persist due to a lack of adequate active

sites, resulting in relatively poor stability and hindering their practical applicability. Although binary Cu-based materials like Cu_2O ¹³⁶, Cu_3P ¹³⁷, CuS ⁴⁹ have been studied as electrocatalysts for OER, finding catalysts that perform exceptionally well for both ORR and OER remains rare. Thus, the fabrication of a bifunctional catalyst with increased active sites for enhanced ORR and OER activities, along with improved stability for zinc-air batteries, remains a significant challenge. Research has demonstrated that Cu_2O or CuO active sites exhibit excellent catalytic activities and stability.^{136, 138} Incorporating Ti atoms to create a ternary system with bimetallic or trimetallic active sites has shown potential in increasing the number of active sites and enhancing bifunctional activities.

Hence, our objective is to fabricate ternary nanoparticles to meet the demanding requirements of bifunctional catalysis, simultaneously improving ORR/OER activity in alkaline solutions. In this endeavor, we have developed a structure embedding Ti in Cu, featuring a hierarchical interconnected mesoporous structure aimed at enhancing ORR and OER performances. Primarily, this ternary system induces cations such as Cu^+ and Cu^{2+} in the catalyst, bolstering electrical conductivity. Because of the electron density around Cu atoms, and the depletion of electron density happened for Ti 2p, which makes interaction between Ti and Cu/O of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst turns to be stronger. Additionally, the synergistic effect of altering partial electron density among Cu, Ti, and O through XANES analyses due to the introduction of Ti atoms creates more active sites. With the insertion of Ti atoms, the electronic structure and oxidation states of Cu active center can be adjusted to reduce the energy barrier and facilitate the absorption and diffusion of reactants in the catalytic process. Finally, the unique 3DOM framework structure offers the possibility of loading of metal oxides, thus leading to 3DOM materials as catalysts exhibit excellent catalytic performance. The hierarchical 3DOM structure

of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ provides a vast specific surface area, expediting ion (OH^-) infiltration and continuous electron transfer during the charge and discharge process.

4.2 Experimental Section

Synthesis of 3DOM $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$. All chemicals are purchased from Sigma-Aldrich Canada and used without any further purification. Polystyrene (PS) beads were employed as hard template for the preparation of 3DOM $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$. The PS beads were synthesized by polyvinylpyrrolidone (PVP), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and styrene. Using boiled distilled de-ionized (DDI) water to dissolve 2.5 g polyvinylpyrrolidone and placed in a three-neck flask. Adding 0.2 g potassium persulfate into the 40 mL DDI water. The PVP solution was under oil bath at 70 °C with continuously stirring and N_2 gas purging to create an inert environment for 10 min. Afterwards, 24 mL styrene monomer was dissolved in the PVP solution under stirring for 15 min. Finally, adding potassium persulfate solution to the monomer solution drop wise by the separatory funnel. Then the solution was under stirring for 24h to create colloidal PS solution appearing milky white.¹⁹ Copper acetate hexahydrate, titanium (IV) butoxide, and HCl were added to 30 mL of ethanol to create the metal precursor, which was subjected to ultrasonication for 30 minutes. The total metal mole ratio was maintained at 2M, calculated as the mole of metals per volume of solvent. A specific number of PS beads were then introduced into the metal precursor at various ratios and allowed to react at room temperature for 24 hours. Subsequently, excess precursor was removed via vacuum filtration, and the resulting skeleton was air-dried overnight under ambient conditions. The dried products were finally calcinated in air at 650 °C for 3 hours, with a heating rate of 1 °C/min, to eliminate the PS beads and retain the mesoporous skeleton. The resulting products, featuring four different Cu and Ti ratios as $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.4}\text{Ti}_{0.6}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$ and $\text{Cu}_{0.9}\text{Ti}_{0.1}\text{O}_2$, respectively. For the synthesis of 3DOM TiO_2 , Cu

was omitted from the metal precursor, while the remainder of the procedure remained consistent with that of 3DOM Cu_xTi_{1-x}O₂.

4.2.2 Material characterization

3DOM Cu_{0.3}Ti_{0.7}O was characterized by the transmission electron microscope (TEM; JEOL, JEM-2010 F, 200 kV) with energy-dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED) pattern to investigate the morphology and element composition. X-ray diffraction (XRD) (Rigaku Miniflex 600 X-ray Diffractometer) and X-ray photoelectron spectroscopy (XPS) (Thermal Scientific K-Alpha XPS spectrometer) were used to explore crystallographic information and chemical states of elements in catalysts. N₂ adsorption analysis was employed via Folio Micromeritics ASAP 2020 to evaluate surface area and nitrogen adsorption and desorption isothermal plots. X-ray absorption near-edge spectroscopy (XANES) of Cu K-edge and extended X-ray absorption fine structure (EXAFS) of Cu K-edge were carried out at the SXRMB at Canadian Light Source.

4.2.3 Electrochemical evaluation

The electrochemical tests were performed on electrochemical workstation (Biologic VSP 300) at ambient temperature, involving a three-electrode system, where glassy carbon electrode as working electrode, graphite rod as counter electrode and saturated calomel electrode (SCE) was used as reference electrode. By Nernst equation, all the data can be calibrated to the reversible hydrogen electrode (RHE). For ORR, 0.1 M KOH solution with O₂ saturated was used. Rotating disk electrode (RDE) test were conducted at different rotation rate (400, 625, 900, 1225, 1600, 2025 rpm) in a scan rate of 5 mV/s. Koutecky-Levich equation can be used to calculate the electron transfer number and kinetics for ORR.

$$\frac{1}{j} = \frac{1}{j_l} + \frac{1}{j_k} = \frac{1}{B\omega^{0.5}} + \frac{1}{j_k}$$

$$B = 0.62nFC_0(D_0)^{2/3}V^{-1/6}$$

$$j_k = nFKC_0$$

Where n is the electron transfer number, j stands for the measured current density, B presents the slope of K-L plots, ω is the rotation rate of the disk electrode, j_l and j_k are the diffusion-limiting and kinetic current densities, F is the Faraday constant (96485 C mol^{-1}), C_0 presents the bulk concentration of O_2 which is $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ in 0.1 M KOH , D_0 stands for the O_2 diffusion coefficient ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), V is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant.

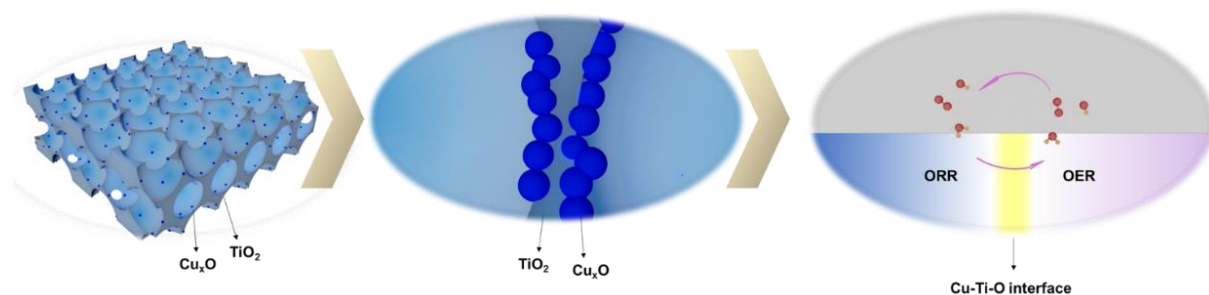
A conventional three-electrode configuration was employed, comprising a glassy carbon (GC) electrode as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) serving as the reference electrode, to assess the electrochemical performance of the catalysts at room temperature. The electrocatalytic activities for ORR and OER were evaluated using a rotating disc electrode (RDE) half-cell technique and cyclic voltammetry (CV), respectively. A CHI Electrochemical Station (Model 760D) was utilized for performance evaluation. The tests were conducted over the voltage range of 0 to -1.0 V vs. SCE at a rotation speed of 1600 rpm for ORR and 0 to 1.0 V vs. SCE at 1600 rpm for OER. The scan rate for both electrochemical tests was maintained at 10 mV s^{-1} . Accelerated degradation testing (ADT) involved performing CV in the OER potential region of 1-2 V vs. RHE with a scan rate of 50 mV s^{-1} . The potential versus SCE was converted to potential versus RHE at room temperature using the formula $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.0591\text{pH}$. Before conducting ORR and OER measurements, the electrolyte underwent purging with pure oxygen

and nitrogen gas for 30 minutes, respectively. ORR polarization curves in the oxygen-saturated electrolyte were adjusted by subtracting background curves obtained in the nitrogen-saturated electrolyte to eliminate capacitive currents during the ORR tests. All measurements were performed in a 0.1 M KOH solution. The measured overpotentials (η) for ORR and OER were determined relative to the standard oxygen reduction potential ($E^0 = 1.23$ V vs. RHE), where $\eta_{\text{ORR}} = 1.23$ V – measured ORR potential (vs. RHE) and $\eta_{\text{OER}} = \text{measured OER potential (vs. RHE)} - 1.23$ V. Before testing, the GC electrode (diameter: 5 mm) was polished using alumina suspension (particle size: 0.05 μm) on a smooth polishing cloth. Catalyst ink was prepared by mixing 4 mg of the catalyst and Vulcan Carbon (XC-72) in a 1:1 mass ratio in 1 mL of isopropanol (IPA) pre-treated with Nafion solution (0.3 wt.%), followed by ultrasonication for 30 minutes to achieve a homogeneous ink. Then, 20 μL of the prepared ink was dropped onto the GC surface using a micropipette and dried under ambient conditions, resulting in a catalyst loading of 0.2 mg cm^{-2} . As reference materials, precious metal catalysts consisting of platinum carbon (Pt/C, 28.8 wt.% Pt), iridium carbon (Ir/C, 20 wt.% Ir), and palladium carbon (Pd/C, 20 wt.% Pd) were used without blending with Vulcan Carbon to showcase the relative catalytic efficiency and practicality of bifunctionally active and stable 3DOM $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

An air electrode was fabricated by spray-coating the catalyst ink solution onto a gas diffusion layer (Ion Power Inc., SGL Carbon 35 BC) using an airbrush, covering an active area of 0.785 cm^2 (with a catalyst loading of 1 mg cm^{-2}). The catalyst ink was prepared by mixing the catalyst and Vulcan Carbon in Nafion-containing (5 wt. %) isopropanol (IPA) with a weight ratio of 1:1, followed by ultrasonication for 1 hour to achieve a homogeneously dispersed ink solution. Similar to the half-cell evaluations, commercial carbon-supported precious metal catalysts (Pt/C and Ir/C) were used to prepare reference air electrodes using the same method but

without the addition of Vulcan Carbon. For the anode, separator, and electrolyte, a zinc plate (OnlineMetals, Zinc Sheet EN 988), a microporous polypropylene membrane (Celgard 5550), and a 6.0 M KOH solution with 0.2 M zinc acetate were employed, respectively. Stainless steel meshes served as current collectors for both the anode and cathode sides. Galvanodynamic discharge and charge experiments were conducted using a multichannel potentiostat (Princeton Applied Research, VersaSTAT MC). Discharge and charge profiles were obtained over a wide range of currents (current density: 0 to $\sim 60 \text{ mA cm}^{-2}$).

4.3 Results and discussion



Scheme 4.1 Schematic illustration for the Cu-Ti-O ternary materials electrocatalysts.

The Cu-Ti-O ternary materials were obtained by a hard template method followed by a pyrolysis process, shown as Scheme 4.1. Briefly, the PS beads are soaked into the Cu and Ti precursor to make sure two elements immobilized on the PS template, followed by pyrolysis treatment in air environment and to obtain the products. The scanning transmission electron microscopy (STEM) images (Figure 3.1a and b) display the Cu-Ti-O materials present mesoporous skeleton structure with a diameter of 120 nm. Elemental maps with electron energy loss spectroscopy (EELS) were employed to reveal the composition of the 3DOM $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ material having the composition of Cu, Ti, O and C (Figure 4.1c-h) elements uniformly distributed on the architecture to expose more active sites, thus boosting ORR and OER

performances. The high-resolution transmission electron microscopy (HRTEM) performs the d-spacing corresponding to (101) plane of TiO_2 and (111) of CuO .

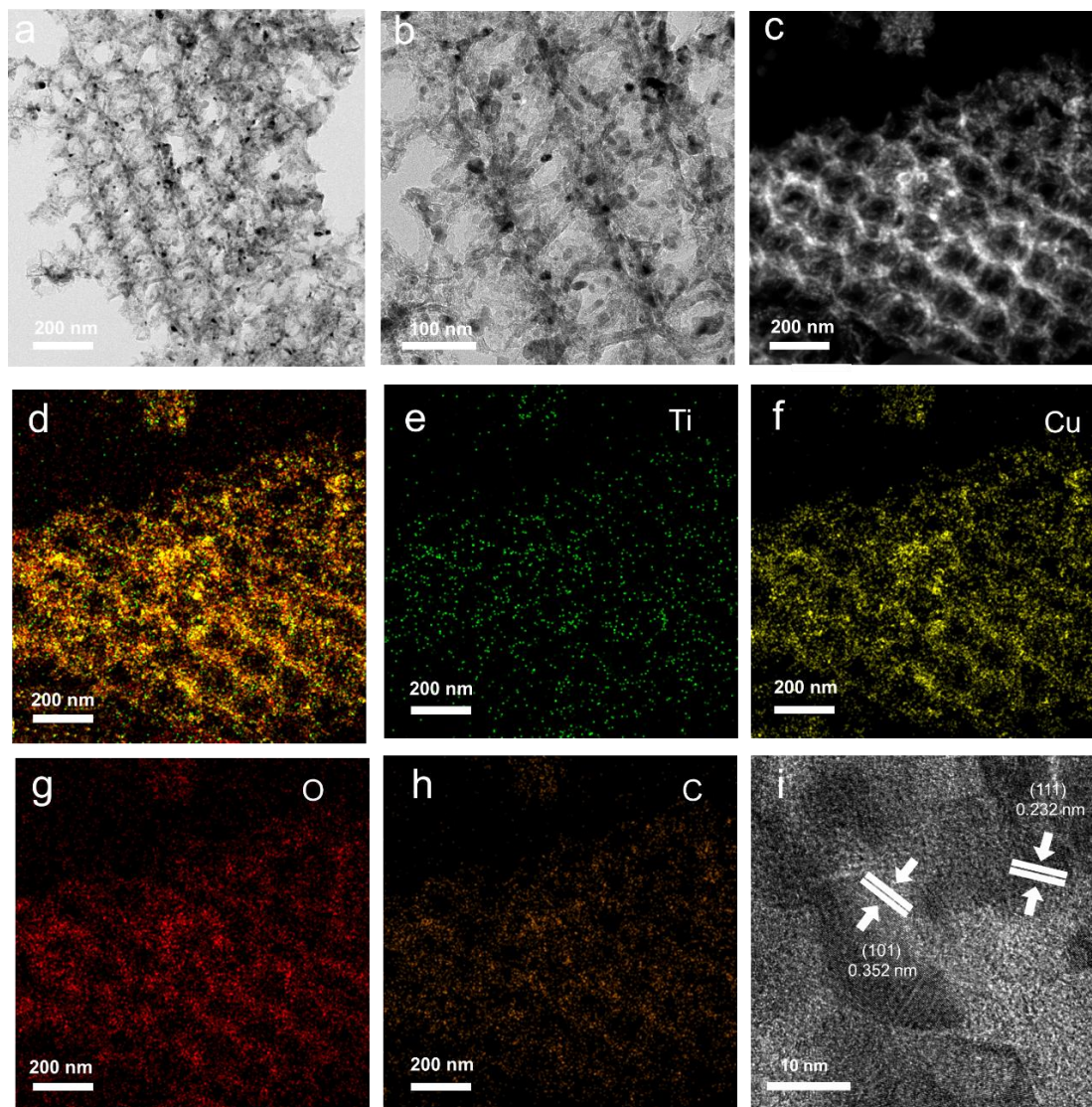


Figure 4.1 a and b) STEM images, c-h) corresponding element mappings, i) HRTEM image of 3DOM $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

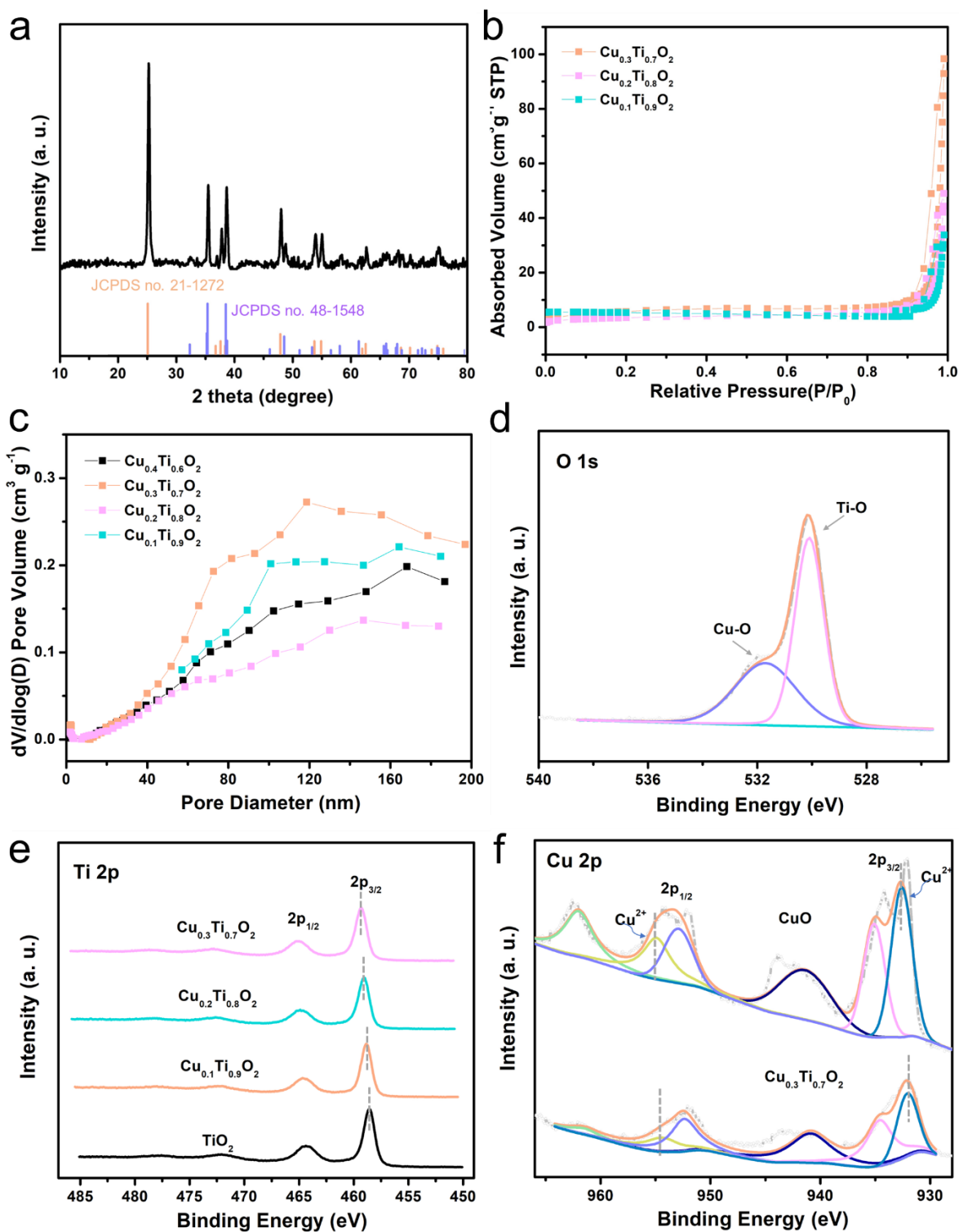


Figure 4.2 a) XRD pattern of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, b) N_2 adsorption-desorption isotherms and c) pore size distribution plots of $\text{Cu}_{0.4}\text{Ti}_{0.6}\text{O}_2$, $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, and $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$. d) High-

resolution XPS spectra for O 1s of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, e) for Ti 2p of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and TiO_2 , f) for Cu 2p of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, and CuO .

The XRD pattern of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is shown in Figure 4.2a, which demonstrates the existence of Cu, Ti, and O and the interaction of Cu and Ti atoms as amorphous structures. In the Cu-Ti-O ternary system, the diffraction peaks centered at around $2\theta = 35.5, 38.7$ and 48.7° associated with CuO (PDF#48-1548) (111) (111) (202). The diffraction peaks located at around $2\theta = 25.3, 38.6$ and 48.0° corresponding to TiO_2 (PDF#21-1272) (101) (112) (200), which confirms the existences of CuO and TiO_2 in Cu-Ti-O ternary material, agreed with HRTEM analysis. To explore the specific surface area of the samples, nitrogen (N_2) adsorption–desorption isotherms were adopted. Different ratios of $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$ ternary materials had been fabricated to investigate the effect of Ti on CuO structure. (Figure 4.2b) The $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ ternary sample displays a specific surface area of $38.72 \text{ m}^2\text{g}^{-1}$, which is larger than $20.24 \text{ m}^2\text{g}^{-1}$ for $\text{Cu}_{0.4}\text{Ti}_{0.6}\text{O}_2$, and $15.45 \text{ m}^2\text{g}^{-1}$ for $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, $11.86 \text{ m}^2\text{g}^{-1}$ for $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$. The pore size distribution plots of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ material determined by the Barret–Joyner–Halenda (BJH) method was close to 112 nm, presenting a macroporous structure, and the lowest average pore size compared to other materials showed. These results further confirm the hierarchical structure of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ ternary catalyst.

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the composition and valence states of the series of ternary materials. The deconvoluted XPS spectrum of the O 1s (Figure 4.2d) region displays component bands at binding energy positions 530.1 and 531.7 eV, which can be assigned to the oxygen bonded to titanium (Ti–O), and Cu (Cu–O), respectively.¹³⁹
¹⁴⁰ The peaks of Ti 2p (Figure 4.2e) for Cu-Ti-O ternary materials have revealed the tendency into higher energy as the increase of Cu-Ti ratio. The Cu 2p_{1/2} peaks centered at 954.9 and 952.9

eV and Cu 2p_{1/2} peaks located at 935.1 and 932.6 eV in high-resolution Cu 2p spectra could be ascribed to Cu⁺ and Cu²⁺.³⁷ Meanwhile, it is observed that the peaks for Cu 2p perform a negative shift in bonding energy as the ratio of Cu and Ti in the ternary materials decrease. To be noted, the bonding between two metals can cause electron transfer from one metal to another one by bimetal bond then leading to higher or lower binding energy to alter the peak shift.¹¹⁰ Thus, this result suggests that the strongest interaction between Ti and Cu/O of Cu_{0.3}Ti_{0.7}O₂ catalyst, due to the electron density around Cu atoms, and the depletion of electron density happened for Ti 2p.¹⁴¹ The partial electron density reconfiguration presented among Cu, Ti, and O atoms can be the dominant reason for the peaks shift.

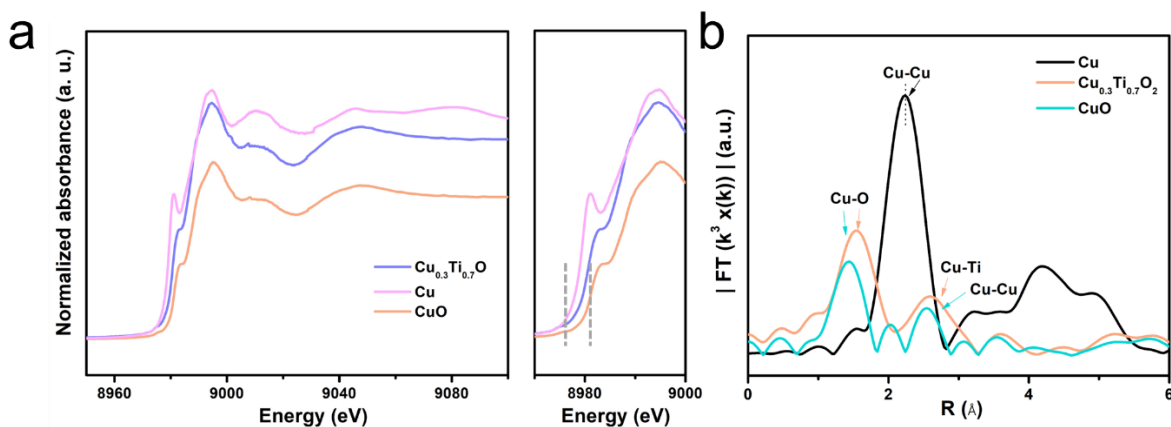


Figure 4.3 a) Cu K-edge XANES spectra and b) corresponding Fourier-transform k³-weighted EXAFS spectra for various samples.

X-ray absorption near edge structure (XANES) measurements and Extended X-ray absorption fine structure (EXAFS) spectroscopy displays the detailed information of Cu_{0.3}Ti_{0.7}O₂ catalyst on the fine structure and coordination environment. Cu K edge XANES spectra (Figure 4.3a) presents that the purple line intensity of Cu_{0.3}Ti_{0.7}O₂ is higher than Cu foil and lower than CuO, indicating that the valence of Cu in Cu_{0.3}Ti_{0.7}O₂ is between 0 and +2 and the insertion of Ti

can change the oxidation state of Cu.¹²² The Fourier transformations of k^3 -weighted EXAFS oscillations for $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ are shown in Figure 4.3b. The Fourier-transform EXAFS spectrum of Cu foil shows that the peak of Cu-Cu (2.2 Å). The Cu-O peak of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ was located at 1.55 Å in Cu k-edge EXAFS Fourier transformed spectra, which is larger than Cu-O bond shown in CuO spectra, may be due to introduction of Ti to build the ternary system. In contrast, peaks corresponding to Cu-Cu bond were not detected, suggesting the strong interaction among Cu, Ti and O.¹⁴²

To certificate the electrochemical performances of ORR for a series of ternary materials, including $\text{Cu}_{0.4}\text{Ti}_{0.6}\text{O}_2$, $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Cu}_{0.2}\text{Ti}_{0.8}\text{O}_2$, and $\text{Cu}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and Pt/C as comparison reference materials. Depicted by Figure 4.4a, the LSV curves demonstrate that $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ displays a half-wave potential of 0.80 V vs RHE, only slightly lower than the value of Pt/C (0.86V vs RHE), but higher than other reference materials. To investigate insights into ORR kinetics, the RDE experiment (Figure 4.4b) was conducted at different rotating speeds and current density linearly rising with rising rotating speeds. Koutecky–Levich (K-L) plots are shown by Figure 4.4c, the electron transfer number of each O_2 molecular for Ti atoms embedded into CuO was obtained to be around 4, confirming the catalyst undergoing the desirable four-electron transfer pathway. $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst was endowed with a superior ORR activity and surface-rich mixed-valence metal cations due to the alteration of the atomic environment.¹²⁹ The electrocatalytic performance of OER was carried out for various ternary materials. Besides, the polarization curves were obtained for OER in a 0.1M KOH solution with a sweep rate of 5 mV s^{-1} . $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst achieves a low overpotential (Figure 4.4d) of 300 mV at a current density of 20 mA cm^{-2} , lower than the value of RuO_2 (340 mV at a current density of 20 mA cm^{-2}), implying the superior OER performance. Moreover, Tafel plots derived from the polarization

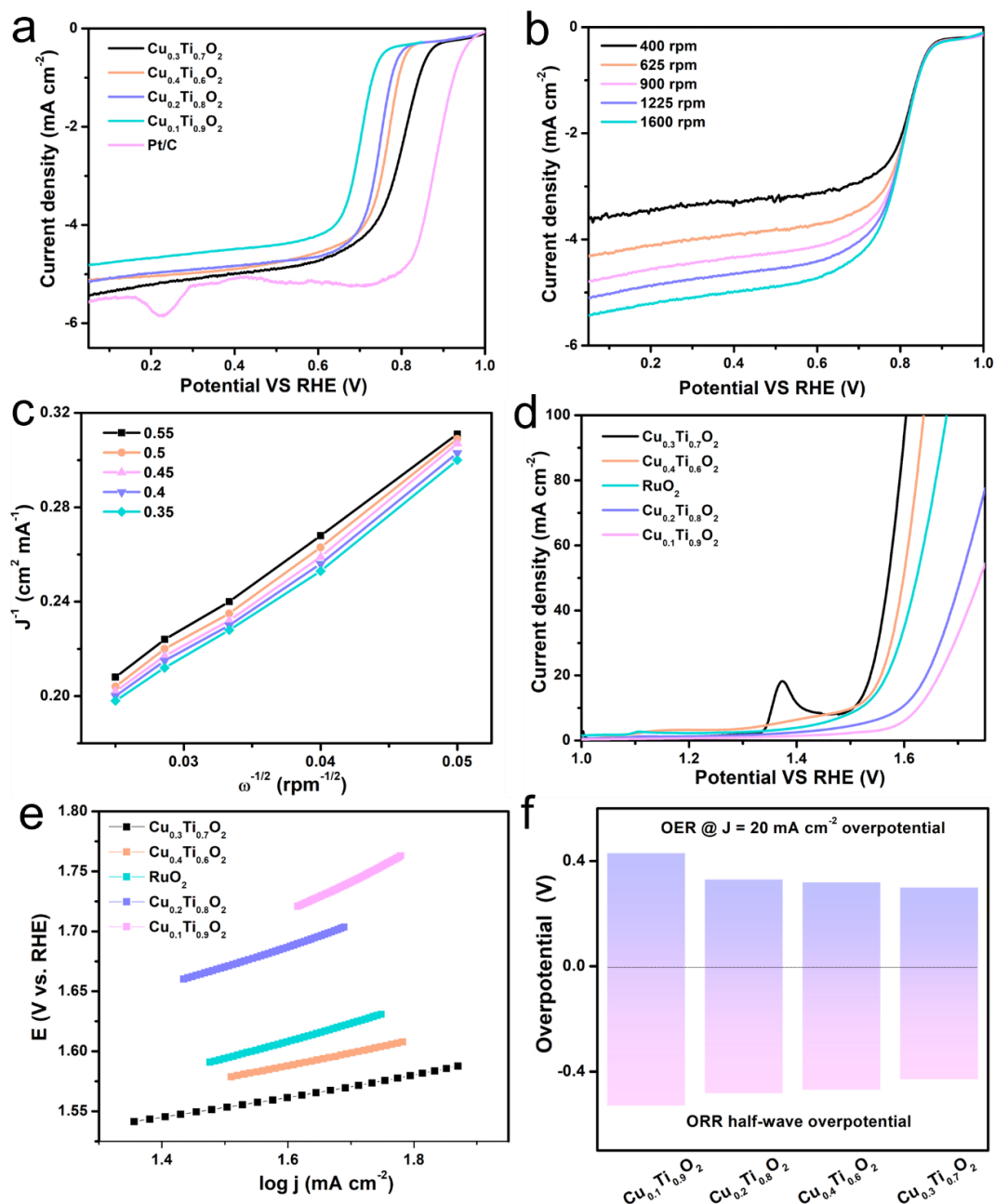


Figure 4.4 a) LSV curves of different catalysts in O_2 -saturated solution with a scan rate of 5 mV s^{-1} . b) LSV curves of the $Cu_{0.3}Ti_{0.7}O_2$ in O_2 -saturated 0.1 M solution at different rotation rates with a scan rate of 5 mV s^{-1} . c) K-L plot obtained from LSV curves of (b) at various potentials. d) LSV curves of different catalysts in N_2 -saturated solution with a scan rate of 5 mV s^{-1} . e) Tafel

plot of the $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$ and RuO_2 catalyst. f) overpotential differences between the $E_{\text{half-wave}}$ of ORR and $E_j = 20 \text{ mA cm}^{-2}$ of OER different electrocatalysts in 0.1 M KOH.

plots were analyzed to explore the intrinsic kinetic activity of the catalysts. The Tafel slope of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is lowest (89 mV dec^{-1}) at kinetic control region, suggesting the improved OER kinetic of introduction Ti for $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (Figure 4.4e). The smallest $E_{\text{half-wave}}$ of ORR (300 mV) and $E_j = 20 \text{ mA cm}^{-2}$ of OER (430 mV) indicate desirable ORR and OER kinetics of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ compared to Cu-Ti-O materials with other ratio of Cu and Ti. (Figure 4.4f)

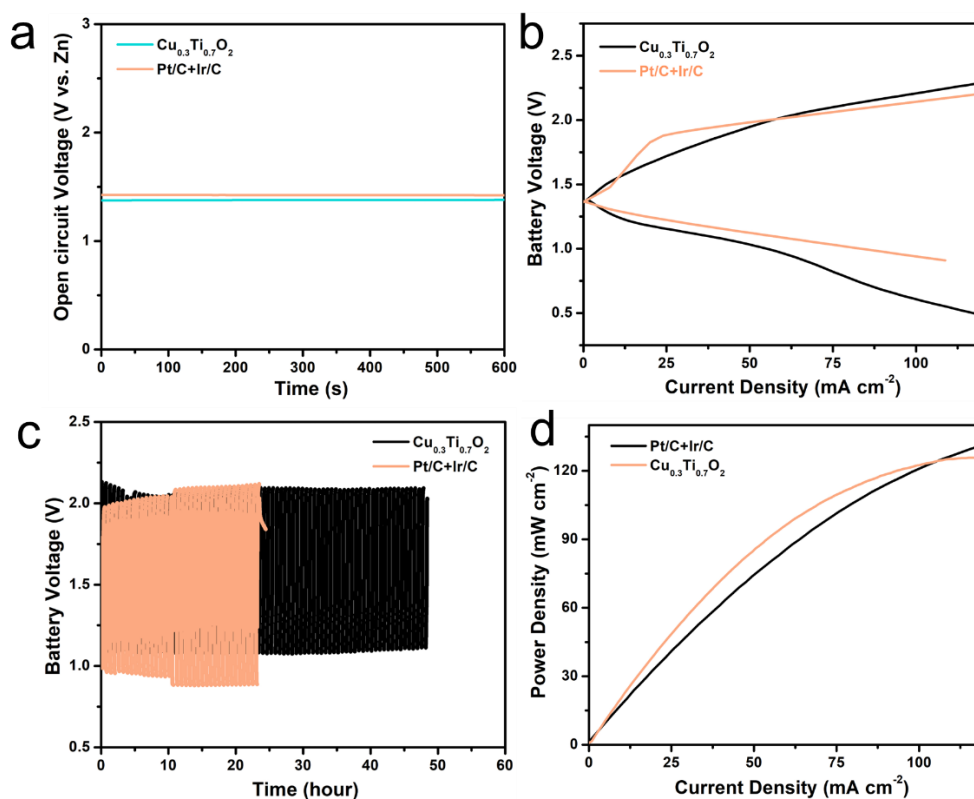


Figure 4.5 a) Open circuit plot; b) Galvanodynamic charge and discharge polarization curves of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and commercial Pt/C+Ir/C of the zinc-air batteries as air cathodes; c) Galvanostatic cycling stability of ZABs prepared with $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and commercial Pt/C+Ir/C electrode. d) Corresponding power density plots of two electrodes.

The zinc-air battery was employed to prove that Cu-Ti-O ternary catalyst can be used as bifunctional catalyst. Primary zinc-air battery assembled with $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ as air electrode was developed. The as prepared zinc-air battery displayed an open circuit voltage of up to 1.38 V (Figure 4.5a), close to that of Pt/C+Ir/C of 1.42 V. As Figure 4.5b presented, over charge process, the overall increase of potential of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is slightly higher than which of Pt/C+Ir/C. During discharge process, the distinction is small, which demonstrates that $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ has comparable catalytic activity to Pt/C+Ir/C. As shown in Figure 4.5c, galvanostatic charge and discharge battery cycling test was performed at a current density of 10 mA cm^{-2} to explore the rechargeability of the catalyst. $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ shows an excellent long battery life of 52 h, while exhibiting 0.87 V charge/discharge voltage gap, and Pt/C+Ir/C performs limited life time of 24 h during cycling. In Figure 4.5d, $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ reveals a peak power density of 125 mW cm^{-2} , slightly lower than that of Pt/C+Ir/C (131 mW cm^{-2}).

4.4 Conclusion

In summary, we have successfully fabricated a series of Cu-Ti-O ternary catalysts, displaying a simple but highly effective bifunctional material towards ORR and OER as well as zinc-air battery. With synergetic effect, the ternary system can enhance the electrical conductivity because of the different metal centers in the system. XPS and XANES results demonstrate that the strongest interaction between Ti and Cu/O of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst due to the change the oxidation state of Cu and the depletion of electron density existing in Ti. The unique structure is stable to maintain the rechargeable zinc-air battery cycling experiments for 52 hours at 10 mA cm^{-2} . The zinc-air battery assembled with $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst displays a power density of 125 mW cm^{-2} . Based on the electrochemical performance, our study opens a unique

synthetic strategy for the synthesis of functional hierarchical ternary materials which is promising for the efficient preparation of other bifunctional electrocatalysts for zinc-air batteries.

Chapter 5 Three-dimensionally ordered mesoporous Co₃O₄ decorated with Mg as bifunctional oxygen electrocatalysts for high-performance zinc-air batteries

5.1 Introduction

Zinc-air batteries (ZABs) have emerged as the next-generation sustainable energy storage and conversion system owing to their low cost, high specific energy, and environmentally benign operation.^{2, 143, 144} Nevertheless, technical limitations associated with the existing air catalysts (oxygen electrocatalysts), in particular bifunctionality and rechargeability, have yet to be addressed for ZABs large-scale application. During the charging and discharging processes, the redox reactions on air electrode are kinetically slow due to non-optimal characteristics of the electrocatalyst. On the other hand, at high current densities, the degradation in air electrode's performance can arise and curtail the operating lifetime of the battery.¹⁴⁵ Besides these challenges, developing an electrocatalyst that efficiently drives both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is a great hurdle owing to the intrinsic reaction pathways of oxygen redox reactions.¹⁴⁵⁻¹⁴⁸ For instance, the best ORR catalyst, platinum, performs poorly in OER, while ruthenium and iridium oxides deliver satisfactory OER efficiency and minimal ORR activity.^{85, 149, 150} Needless to say, the scarcity and high cost of these noble metals suppress the market penetration of ZABs.^{134, 151, 152}

Plenty of research efforts have been devoted to designing highly efficient and durable bifunctional electrocatalysts in recent years.^{37, 131, 153} In the majority of these studies, the main focus has been the impact of electrocatalyst's physicochemical and electrical properties on the performance of battery.^{37, 131, 154} Transition metal oxides with a spinel structure (denoted as A_xB₃-

$x\text{O}_4$ (A, B = Co, Zn, Ni, etc.)) have attracted great attention in ZAB systems due to their low price, facile synthesis, tunable morphologies, ability to be doped, and high electrochemical activity and stability.¹⁵⁵ Among various transition metals, cobalt, manganese, nickel, and iron have been widely explored as bifunctional catalysts.¹⁵⁶⁻¹⁵⁸ However, considering the fact that many single metal oxides are active for either ORR or OER, mixed-valence transition metal oxides have been put forward as promising bifunctional oxygen electrocatalysts.^{159, 160} Grouping transition metal oxides or doping them with another metal can improve the electrical conductivity through alteration in the distribution of electrons, presence of multiple valence states, and the synergetic effect within two metals.¹⁶¹⁻¹⁶³ Moreover, the co-presence of metallic cations (redox couples) with different ORR/OER activity within the same interconnected structure endows mixed transition metal oxides unique capability to facilitate the progress of redox reactions.^{48, 164} In this regard, incorporating Ni,^{165, 166} Zn,^{167, 168} and Mn^{169, 170} in cobalt-based spinel oxides have demonstrated to boost the ORR and OER performances.

In the present study, we have designed and fabricated a three-dimensionally ordered mesoporous $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ (3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$) with outstanding bifunctional activity for rechargeable ZABs. The oxygen catalysts were synthesized via a facile hard templating approach, in which polystyrene spheres initially served as host for Co and Mg precursors and ultimately were removed through pyrolysis. The hierarchically ordered porous structure of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ enables large surface area, homogeneous distribution of Co and Mg elements, and high electrical conductivity. Comprehensive physicochemical characterization along with density functional theory (DFT) studies of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ uncovered the genuine mechanisms behind its superior activity as cathodic material in ZAB. Firstly, substituting Co^{2+} with Mg^{2+} in the tetrahedral sites creates more Co^{3+} occupying the octahedral sites, which in turn boosts the

oxygen catalysis. Apart from the dominant active sites associated with Co-O and Mg-O, a large number of reaction sites are formed from Mg-O-Co. Secondly, the interconnected macropores and mesopores in the 3DOM structure shorten the diffusion lengths of ions and electrons, enhancing the ORR/OER reaction kinetics and charging/discharging rate, while reducing voltage polarization. Moreover, the large surface area of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ increases the interfacial area between the electrode and electrolyte and, thus, the charge/mass transfer at the interface. Finally, the synergetic effects between Mg^{2+} and Co_3O_4 substantially lower the ORR and OER overpotentials due to the more optimal free energies of redox reactions' intermediates on $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Our work offers a highly active and durable bifunctional oxygen electrocatalyst for ZABs and, more importantly, a mechanistic understanding of the ORR/OER pathways on metal-doped cobalt oxide-based catalysts.

5.2 Experimental section

5.2.1 Synthesis of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and bulk $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$

Synthesis of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. All chemicals are purchased from Sigma-Aldrich Canada and used without any further purification. Polystyrene spheres (PS) beads are employed to be the hard template for the 3DOM composites. By simple polymerization of polyvinylpyrrolidone (PVP), potassium persulfate, and styrene monomer. In order to remove O_2 , distilled de-ionized (DDI) water was boiled for several minutes. In a three-neck flask, 2.5 g polyvinylpyrrolidone was added in 200 mL DDI water. Then 0.2 g potassium persulfate was dissolved in 40 mL DDI water. The PVP solution was heated up to 70 °C at oil bath under stirring with N_2 gas to form an inert environment. After 10 min, 24 mL styrene monomer was dissolved to the PVP solution and resulting mixture was stirred for 15 min. Eventually, the potassium persulfate solution was added into PVP solution drop-wise employing separatory

funnel. The solution was then under stirring for 24h to achieve milky white PS spheres.¹⁹ The synthesis of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ is as following, preparing the solution compose of 5 mL ethanol, 1 mL hydrochloric acid (HCl) and 1mL titanium butoxide $\text{Ti}(\text{OBu})_4$ at room temperature. Then the cobalt acetate hexahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and magnesium acetate hexahydrate $[\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ were dissolved in the mixed solution. Socking the PS beads into the solution in a vial overnight following with infiltration process. Afterwards, the formed PS template was heat-treated at 300 °C under oxygen gas flowing for 3h, and washed by the mixture of ethanol and acetone. Drying the sample at 40 °C for 24h, then heat-treated again at 400°C under oxygen gas flowing for 3h. When cooling down to the room temperature, the as obtained sample is targeted 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. The synthesis of 3DOM Co_3O_4 is similar as the method of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, but without adding magnesium acetate hexahydrate $[\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ in the precursor solution. The precursor of 3DOM Co_3O_4 was composed of adding the cobalt acetate hexahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ into the mixed solution including 5 mL ethanol, 1 mL hydrochloric acid (HCl) and 1mL titanium butoxide $\text{Ti}(\text{OBu})_4$ at room temperature. Adding PS beads into the precursor in a vial overnight. The PS beads were obtained after infiltration process and then dried at 40 °C overnight in an oven. Following the calcination process at 300 °C with oxygen gas flowing for 3h, the PS template was washed by the mixture of ethanol and acetone, and dried at 40 °C for 24h in an oven. After that, the PS template was calcinated again at 400°C with oxygen gas flowing for 3h. The as synthesised product is 3DOM Co_3O_4 .

Synthesis of bulk $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. The synthesis of bulk $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ is acquired by a simple one pot hydrothermal method. Adding 1 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mM $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into 30 mL deionized water, after ultrasonication for 40 min, with 6 M KOH

solution to regulate the pH of 13. Then the mixture was moved to a 50 mL Teflon liner and a stainless-steel autoclave, with heat treatment at 180 °C for 48h. As cooling down to the room temperature, washing the solution with ethanol and drying at 80 °C overnight. The targeted bulk $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ can be obtained by heat treated at 400 °C for 3h.

5.2.2 Materials Characterization

The transmission electron microscope (TEM; JEOL, JEM-2010F, 200 kV) with energy-dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED) pattern were employed to explore the morphology and hierarchical structure as well as energy-dispersive spectrum elemental mappings. X-ray diffraction (XRD) (Rigaku Miniflex 600 X-ray Diffractometer) was adopted to analyze the cubic spinel structure of the sample. X-ray photoelectron spectroscopy (XPS) (Thermal Scientific K-Alpha XPS spectrometer) was used to identify the chemical composition of the enhanced catalysts. Brunauer–Emmett–Teller (BET) method can be utilized to assess the surface area and nitrogen adsorption and desorption isothermal plots were carried out on Folio Micromeritics ASAP 2020. X-ray absorption near-edge spectroscopy (XANES) of Co K-edge and Mg K-edge and extended X-ray absorption fine structure (EXAFS) of Co K-edge were conducted at the SXRMB, HXMA, and SGM beamline at Canadian Light Source. All the XANES and EXAFS data were analyzed by Athena program.

5.2.3 Electrochemical measurements

A three-electrode system and rotating disc electrode (Pine Instruments Co., AFMSRCE) on the electrochemical workstation (Biologic VSP 300) was employed to measure ORR and OER performances for the series of composites. Conventionally, the three-electrode system is composed of working electrode, reference electrode and counter electrode. Saturated calomel electrode (SCE) was used as reference electrode, glassy carbon electrode as working electrode, and graphite rod as counter

electrode. All the data can be calibrated to the reversible hydrogen electrode (RHE) by Nernst equation. The ink of all the composites were prepared as following, 2mg sample and 2mg Vulcan Carbon (XC-72) in the solution consisting of 1mL ethanol and Nafion solution (0.2 wt. %) along with ultrasonication for 1h. 20 μ L as-obtained ink was dropped on the glassy carbon with area of 0.196 cm^2 and the loading is 0.4 mg cm^{-2} . The electrolyte is 0.1M KOH solution and applied in both ORR and OER measurements. The ORR tests were conducted with continuous O_2 bubbling, at a scan rate of 10 mV s^{-1} from 0 to -1.0 V vs. SCE, with a series of rotating electrode speeds (400, 900, 1225, 1600 and 2500 rpm). The OER curves were executed with N_2 constant bubbling, from 0 to 1 V vs. SCE at a scan rate of 10 mV s^{-1} at 900 rpm of rotation speed. The overpotentials are calculated of the difference for $E^\circ (\text{OH}^-/\text{O}_2) = 1.23 \text{ V}$ and OER potential at 10 mA cm^{-2} .

The zinc-air battery measurements were proceeded by prototypes composed of zinc plate, gas diffusion electrode with catalyst coated (SGL Carbon 39 BC), and polypropylene separator. The electrolyte is made of mixed solution of 6 M KOH and 0.2 M zinc acetate. The Zinc plate can be treated as anode, while GDE is used as the cathode for charge and discharge process. The ink was made up of catalysts dispersing in 0.3 wt. % Nafion and isopropanol for ultrasonication about 1h and then sprayed onto the carbon paper. Galvanodynamic charge and discharge measurements were conducted on a potentiostation (Princeton Applied Research, VersaSTAT MC) with the current density ranging from 0 to 100 mA cm^{-2} . The cycling tests were carried out at the current density of 10 mA cm^{-2} and each cycle had 10min discharge and charge time.

5.2.4 DFT simulation details

All the spin-polarized computations were performed by using Vienna ab initio simulation package (VASP). The ion-electron interactions were described by the projector augmented wave method^{101, 102} and the general gradient approximation in the Perdew–Burke–Ernzerhof (PBE) form was used.^{103, 104} During the structure relaxation, the convergence criterion was set to 0.04

eV/Å and 10^{-5} eV for the residual force and energy, respectively. A supercell consists of $1 \times 2 \times 1$ Co_3O_4 (220) facet was used as the model for Co_3O_4 . On this basis, one-third of Co atoms were replaced by Mg atoms, to construct the model of Mg-doped Co_3O_4 ($\text{Mg}_1\text{Co}_2\text{O}_4$). Brillouin zones were sampled by a Monkhorst-Pack $4 \times 3 \times 1$ k-point grid. To avoid the interaction between two periodic units, a vacuum space over 15 Å was employed.

The free energy change (ΔG) of each elementary reaction was calculated based on the computational hydrogen electrode (CHE) model.

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$$

where ΔE , E_{ZPE} , T and S is the reaction energy difference, zero-point energies, temperature and entropy, respectively.

5.3 Results and discussion

The porous structured 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ with well-defined morphology was synthesized via a facile sacrificial polymer template strategy (using polystyrene (PS) spheres) (Figure 5.2) followed by a thermal decomposition process as illustrated in Figure 5.1a. The details of electrocatalysts synthesis protocols are provided in the Supplementary Information. Scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) (Figure 5.3) imaging of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ reveals a highly ordered and uniform nanostructured framework with regular porosity and average pore diameter of ~160 nm (Figure 5.1b). The well-organized 3-D networks can provide 1-D paths which enhance mass transport and reduce tortuosity throughout the electrode, suppressing concentration gradients that can degrade cell performance.¹⁷¹ The corresponding energy-dispersive X-ray spectroscopy (EDS) mappings (Figure 5.1c-f) clearly show the homogeneous distribution of Co and Mg elements in catalyst's skeleton. The transition electron microscopy (TEM) (Figure 5.1g-i) demonstrates the honeycomb

structure and high degree of crystallinity of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. It is worth mentioning that the micrometer sized crystalline particles in the 3DOM structure allow interparticle contact, which evades electronic particle isolation.^{172, 173} The high-resolution TEM (HRTEM) images of electrocatalyst (Figure 5.1h and i) show lattice fringes with d-spacings of 0.48 nm and 0.26 nm which correspond to the (111) and (311) planes of spinel Co_3O_4 and MgCo_2O_4 , respectively. As shown Figure 5.1h and j, these findings were well corroborated by the results of selected area electron diffraction (SAED) pattern.

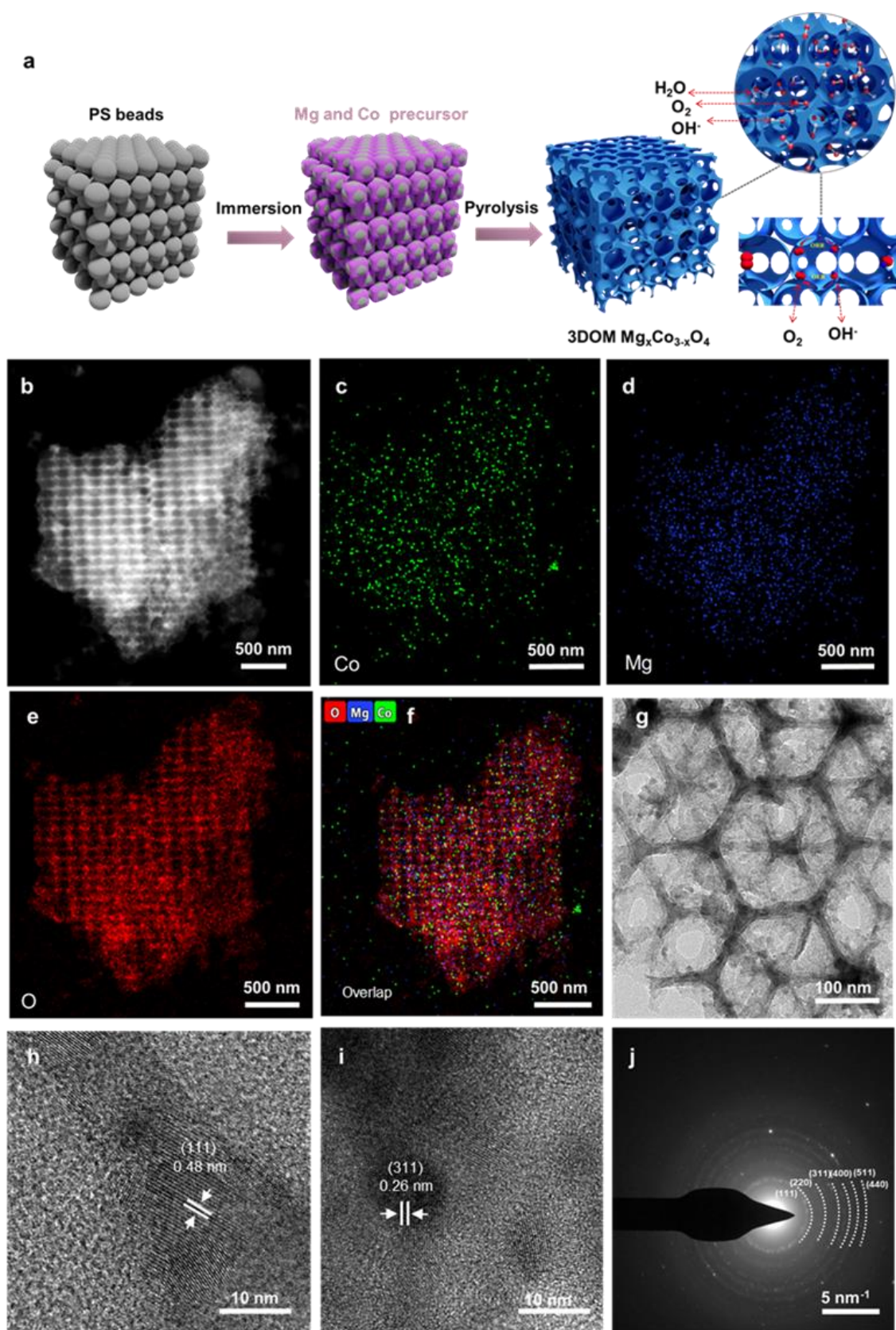


Figure 5.1 (a) Schematic illustration of the preparation procedure of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. (b) STEM image and (c-f) corresponding EDS elemental mapping, and (g-i) TEM and HRTEM image and (j) corresponding SAED pattern of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$.

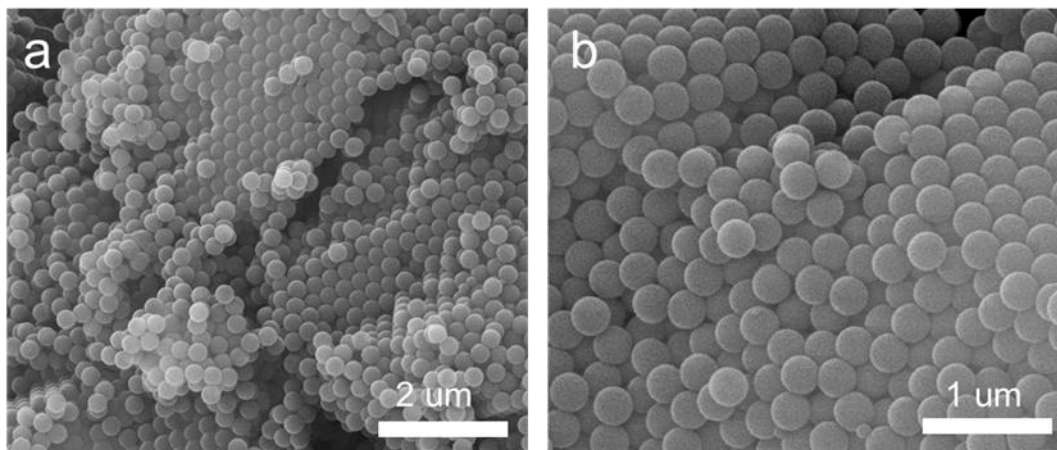


Figure 5.2 SEM images of PS beads.

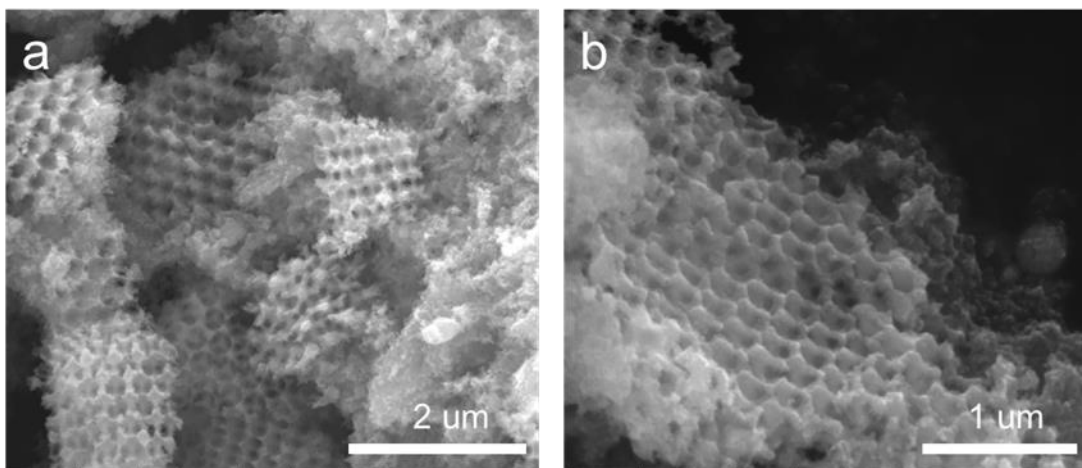


Figure 5.3 SEM images of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$.

To demonstrate the crucial role of Mg atom in the developed hybrid electrocatalyst, the control sample, 3DOM Co_3O_4 , was prepared by a similar method applied for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ except that the Mg precursor was not included. Furthermore, to show the structural merits of

3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, we also prepared the bulk $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ by mechanically mixing magnesium nitrate hexahydrate and cobalt nitrate hexahydrate and subsequent calcination process. X-ray diffraction (XRD) was employed to determine the compositions and crystallinity of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ catalysts (Figure 5.4a). The 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ possesses a $Fd\bar{3}m$ spinel structure, and the crystallite sizes are consistent with those observed in the HRTEM analysis. The XRD pattern of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ resembles that of 3DOM Co_3O_4 with some minor differences which stem from the partial Co^{2+} substitution with Mg^{2+} in the crystal structure. Additionally, the lattice constant of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ measured at room temperature is 8.1143 Å, which is between the values for MgCo_2O_4 ($a = 8.123$ Å, PDF#02-1073) and Co_3O_4 ($a = 8.084$ Å, PDF#43-1003), further indicating the incorporation of Mg ions into Co_3O_4 .^{32, 174} N_2 adsorption/desorption analysis was performed to investigate the pore texture of materials. The nitrogen adsorption isotherms and pore size distribution (PSD) of Barrett–Joyner–Halenda (BJH) profiles of catalysts are presented in Figure 5.4b and c, respectively. 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ has a specific surface area of $245.5 \text{ m}^2 \text{ g}^{-1}$, slightly larger than $209.1 \text{ m}^2 \text{ g}^{-1}$ for 3DOM Co_3O_4 and much higher than that of $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ ($92.9 \text{ m}^2 \text{ g}^{-1}$). The isotherm of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ can be characterized as type IV (according to BDDT classification) with a hysteresis loop in the high-pressure region ($0.8 < p/p_0 < 1$) which originates from the existence of abundant mesopores. The narrower PSD of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ compared to the other two samples mainly centers at ~ 29 nm, further confirming the existence of ample mesopores as well as macropores (> 50 nm). To gain more insight into the valence states and chemical composition of the catalysts, X-ray photoelectron spectroscopy (XPS) was conducted (Figure 5.4d-g). The survey XPS spectrum of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ confirms that the material consists of Co, Mg, and O elements. The high-resolution spectrum of Mg 1s (Figure 5.4e) shows

only one peak at 1304.7 eV, which is attributed to Mg^{2+} .¹⁷⁵ Regarding the Co 2p spectrum, the two pairs of spin-orbit doublets, Co 2p_{3/2} and Co 2p_{1/2}, suggest the coexistence of Co^{2+} and Co^{3+} species (Figure 5.4f).¹⁷⁴ With the appearance of two satellite peaks, the characteristic peaks verify the Co^{2+} at 797.2 and 781.7 eV and Co^{3+} at 796.1 and 780.1 eV. As illustrated by Figure 5.4g, the XPS spectrum of O 1s possesses a strong characteristic peak at 529.7 eV, which is ascribed to oxygen atoms bound to basal plane and reflects the presence of Co-O and Mg-O. Besides, the O 1s peaks at 531.3, 532.1, and 533.1 eV indicate hydroxyl groups, defects with low oxygen coordination, and adsorbed water, respectively, on the surface of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$.

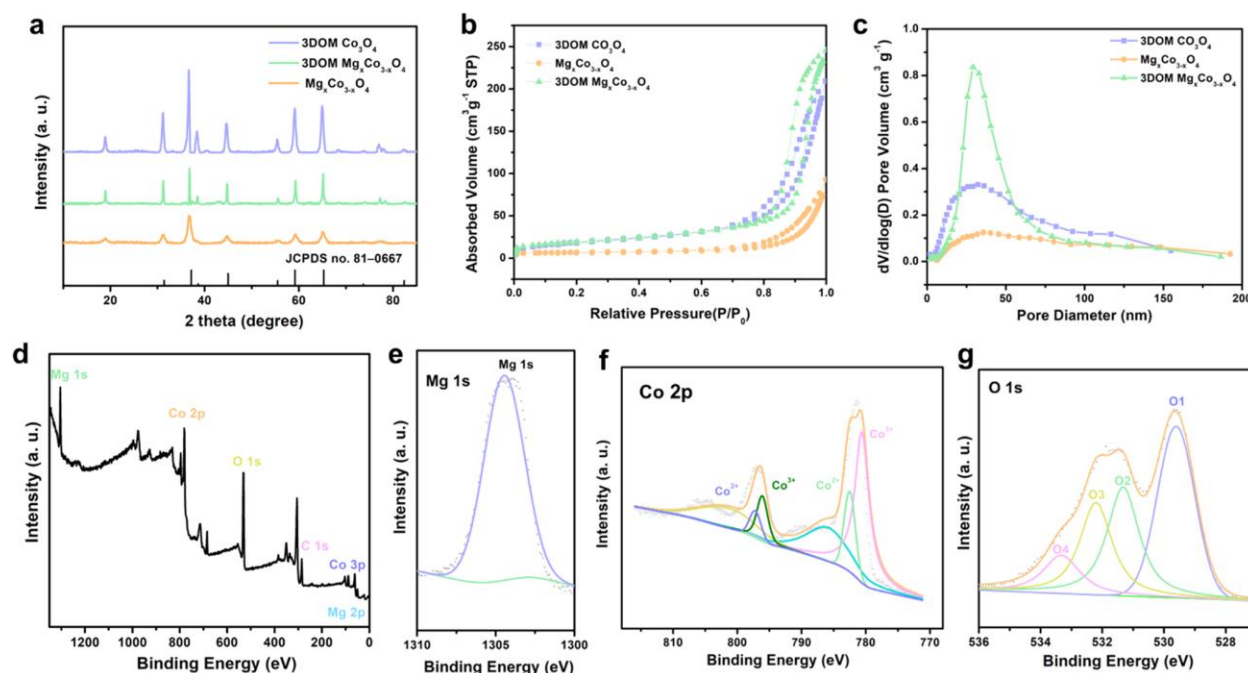


Figure 5.4 (a) X-ray diffraction pattern, (b) N_2 adsorption-desorption isotherms, and (c) pore size distribution plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ catalysts. (d) XPS spectra and high-resolution spectra of (e) Mg 1s, (f) Co 2p and (g) O 1s of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$.

In order to investigate the bifunctional electrochemical performances of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and control electrocatalysts, the rotating disk electrode technique has been employed. The

polarization curves of catalysts tested at a rotation speed of 1600 rpm are shown in Figure 5.5a. 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ exhibits the lowest onset potential (0.95 V vs reversible hydrogen electrode (RHE)) and the best half wave potential of 0.839 V vs. RHE compared to 3DOM Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, which results from its superior mass and electron transfer properties through Mg doping as well as unique hierarchically porous structure. Figure 5.5b illustrates the linear sweep voltammetry (LSV) behavior of catalysts in N_2 saturated 0.1 M KOH.

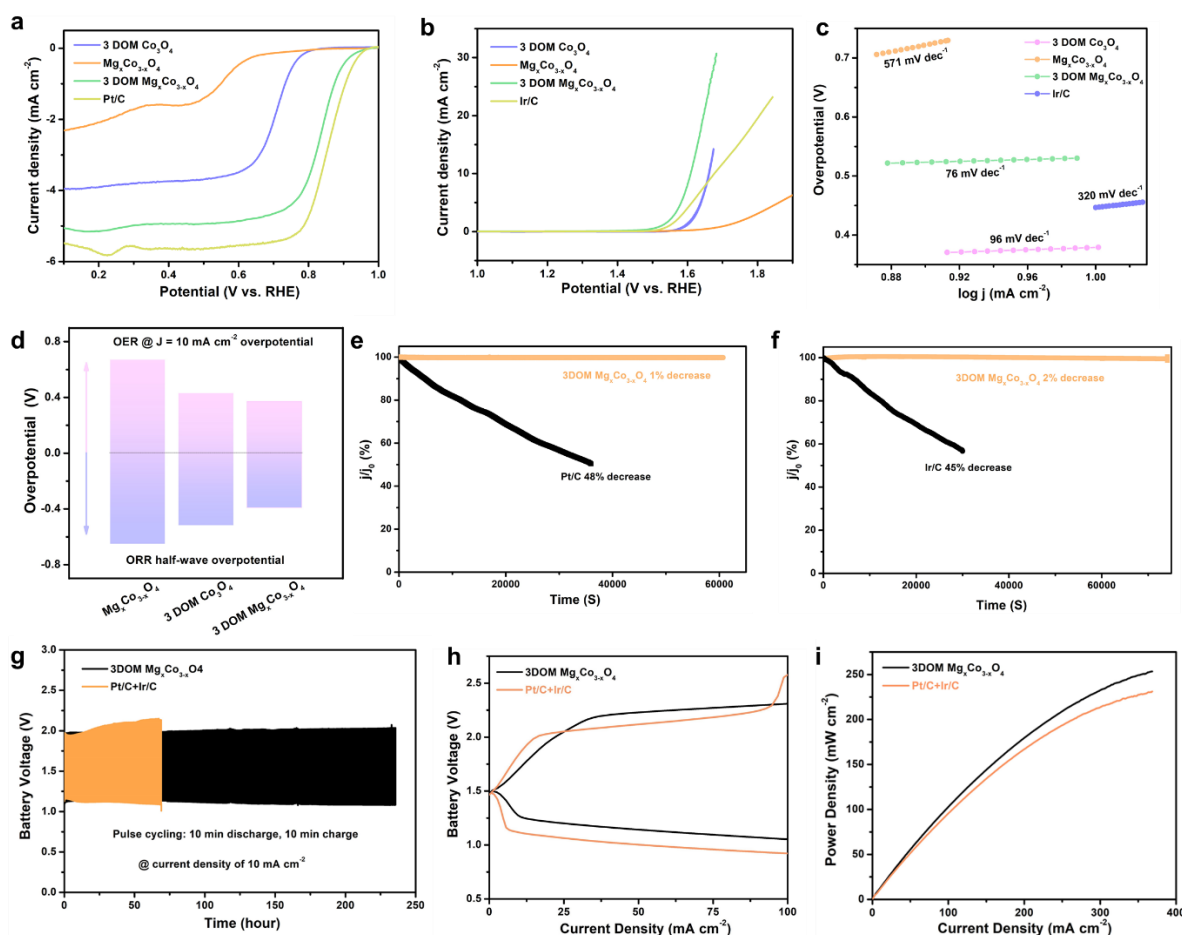


Figure 5.5 (a) ORR polarization curves, (b) OER LSV curves, and (c) OER Tafel plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 , $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrocatalysts, and commercial Ir/C. (d) overpotential differences between the $E_{\text{half-wave}}$ of ORR and $E_j = 10 \text{ mA cm}^{-2}$ of OER for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 , $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrocatalysts in 0.1M KOH. (e) ORR

chronoamperometric response at 0.6 V vs. RHE for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C. (f) OER chronoamperometric response of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Ir/C at a fixed potential of 1.6 V vs. RHE. (g) Galvanostatic discharge–charge long-term cycling test using 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and commercial “Ir/C+ Pt/C” electrodes at a constant density 10 mA cm^{-2} . (h) Charge and discharge polarization curves and (i) power density plots for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and commercial “Ir/C+ Pt/C” electrodes.

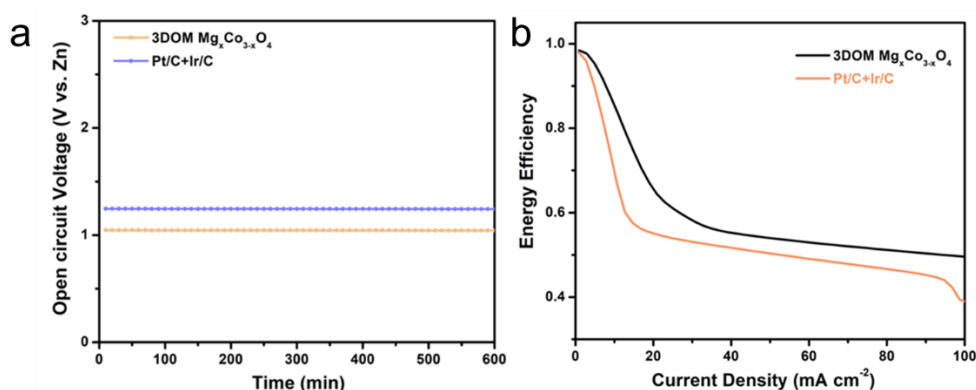


Figure 5.6 a) Open-circuit voltage curves of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C+Ir/C electrode. b) Energy efficiency plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and Pt/C+ Ir/C electrode.

Among the developed electrocatalysts, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ offers the lowest OER potential of only 1.60 V vs. RHE at the current density of 10 mA cm^{-2} , which even outperforms the Ir/C reference material (1.66 V vs. RHE at 10 mA cm^{-2}). Furthermore, the much smaller Tafel slope (76 mV dec^{-1}) of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ in regard to other catalysts signifies the improved OER kinetics (Figure 5.5c). The differences between OER potential at 10 mA cm^{-2} and ORR half wave overpotential have been calculated for 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, 3DOM Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and are depicted in Figure 5.5d. As can be noted, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ has the smallest gap value for ORR-OER, which can significantly enhance the efficiency and stability of ZABs. This was

further demonstrated by the much higher durability of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ in comparison to noble-metal benchmark catalysts measured via chronoamperometric (CA) technology (Figure 5.5e and f). 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ successfully retains 99% of its initial ORR current after 16 h, while Pt/C current declines by 48% in less than 9 h. Likewise, as shown in Fig. 3f, the commercial Ir/C catalyst experiences a much more severe performance drop during OER (45% current decay in 9 h) with respect to 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ which loses only 2% of its initial current after 16 h. The LSV testing was conducted at different rotation rates and the corresponding Koutecky-Levich (K-L) plot (Figure 5.7a and b) was created to obtain the number of transferred electrons ($n = 4.0$) for ORR. K-L plots demonstrate good linearity and fast kinetics with a four-electron-transfer reaction pathway to reduce oxygen directly to OH^- .

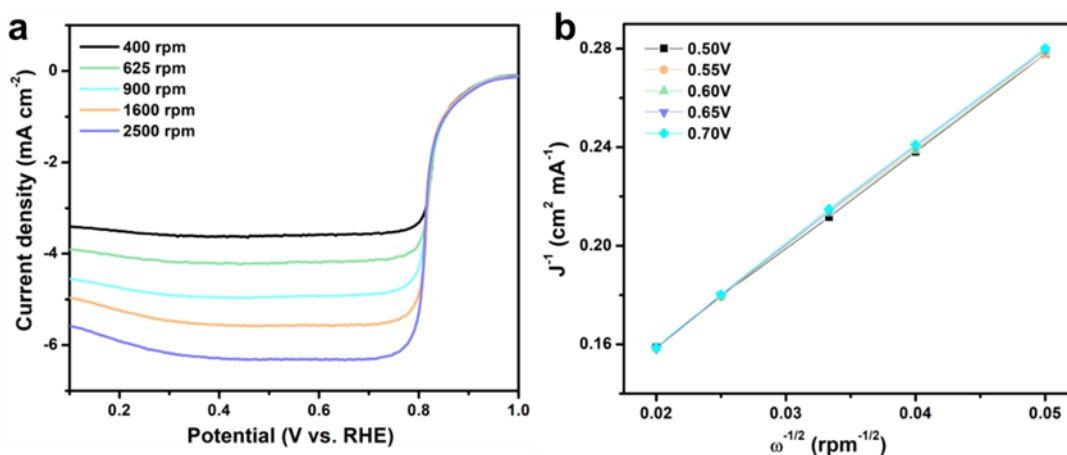


Figure 5.7 a) LSV curves of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ in 0.1 M KOH at different rotation rates and sweep rate of 10 mVs^{-1} ; b) K-L plots (J^{-1} versus $\omega^{-1/2}$) at different potentials.

To assess the practical application and potential of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, rechargeable zinc-air batteries were assembled with the developed catalyst as air electrode. The open-circuit voltage of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ is 1.40 V vs. RHE, which is modestly lower than that of commercial Pt/C+Ir/C reference (1.42 V vs. RHE, Figure 5.6a). In Figure 5.5g, the discharge–

charge cycling tests manifest that compared with commercial Pt/C+Ir/C electrode, the zinc-air battery with 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ cathode delivers much better activity, reliably working for more than 236 h. As shown in Figure 5.5h, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrode exhibits a discharge current density of 100 mA cm^{-2} at 1.05 V vs. RHE. In addition, comparing the discharge polarization curves of the two electrodes, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ displays higher voltages compared to Pt/C+Ir/C. More importantly, the 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrode outperforms the benchmark material even at high current densities, with a maximum power density of 253 mW cm^{-2} versus 231 mW cm^{-2} for the noble-metals electrode (Figure 5.5i). It is notable that 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ also achieves better energy efficiency values than Pt/C+Ir/C (Figure 5.6b). The remarkable activity and durability provided by 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ as air cathode along with its low cost compared to noble metal-based bifunctional catalysts clearly emphasize its great potential for practical applications and in commercially rechargeable ZABs. As displayed by Table 5.1, the bifunctional performance and performance of zinc-air batteries for 3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ surpassed those of the majority of bifunctional Co-based catalysts reported recently.

Table 5.1 Comparison of bifunctional performance and performance of zinc-air batteries of 3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ with recently reported Co-based electrocatalysts.

Catalyst	ORR:	OER:	Cyclability (h)	Power density (mW/ cm^2)	Ref.
	$E_{\text{half-wave}}$ (V)	$E_{j=10 \text{ mA/cm}^2}$ (V)			
3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$	0.839	1.60	236	253	This work
NiFe-LDH/Co	0.79	1.54	80	25	¹⁷⁶
Co- Co_3O_4 @NAC	0.795	1.61	35	164	¹¹⁴

FeCo@MNC	0.86	1.48	24	115	70
CoMn ₂ O ₄ /NCNTs@Ni	0.80	N. A.	238	95.77	177
N-Co/CNF-300-10	0.853	N. A.	25	229	178
Fe ₁ Co ₁ -CNF	0.87	1.73	200	201.7	179
Co-NiO NFs	0.79	1.53	110	93	34
0.1-Co-NHCs	0.81	1.65	50	239.8	180
PB@Met-700	0.853	1.62	90	148	181

The critical role of Mg atom in 3DOM Mg_xCo_{3-x}O₄ for enhanced performance is further revealed by first-principles calculations based on DFT. All the spin-polarized computations were performed by using Vienna ab initio simulation package (VASP). During the structure relaxation, the convergence criterion was set to 0.04 eV/Å and 10⁻⁵ eV for the residual force and energy, respectively. To investigate the function of coordinating process for Mg, two models have been constructed: (i) one supercell consists of 1 × 2 × 1 Co₃O₄ (220) facet was used as the model for Co₃O₄ and (ii) one-third of Co atoms in the model (i) was replaced by Mg atoms to build the model of Mg-doped Co₃O₄ (Mg₁Co₂O₄). As shown in Figure 5.8a, the proposed ORR mechanism includes four steps: hydrogenation of O₂ into *OOH, break of O-O bond transforming *OOH into *O, protonation of *O to *OH, and the desorption of surface-bound *OH to create OH⁻. An ideal electrocatalyst should be able to drive the ORR with no overpotential, meaning that the required potential equals the difference between the Gibbs free energies of *OOH and *OH, 2.46 eV. As depicted in Figure 5.8b, 3DOM Mg_xCo_{3-x}O₄ possesses a lower energy barrier than 3DOM Co₃O₄ for *OH to *OOH reaction. In this regard, the free energy plots unveil that the Mg doping in fact alters the potential determining step (PDS) during

the ORR process (Figure 5.8c): the first elementary reaction, $O_2 \rightarrow *OOH$, for 3DOM $Mg_xCo_{3-x}O_4$ and the second reaction, $*OOH \rightarrow *O$, for 3DOM Co_3O_4 . Overall, it could be deduced that the more challenging $*OOH$ transformation into $*O$ step on Co_3O_4 rendered 3DOM Co_3O_4 less ORR-active compared to 3DOM $Mg_xCo_{3-x}O_4$. From another perspective, ORR overpotentials ($\eta_{ORR}^{\dagger}$) were also calculated for both electrocatalysts by the thermodynamic equilibrium potentials at $U = 1.23$ V (the standard reversible potential). Clearly, 3DOM $Mg_xCo_{3-x}O_4$ exhibits a lower overpotential (0.57 V) than 3DOM Co_3O_4 (0.88 V), which could be mainly attributed to the partial Co substitution with Mg, which created a second adsorption/desorption site and enhanced the ORR performance.

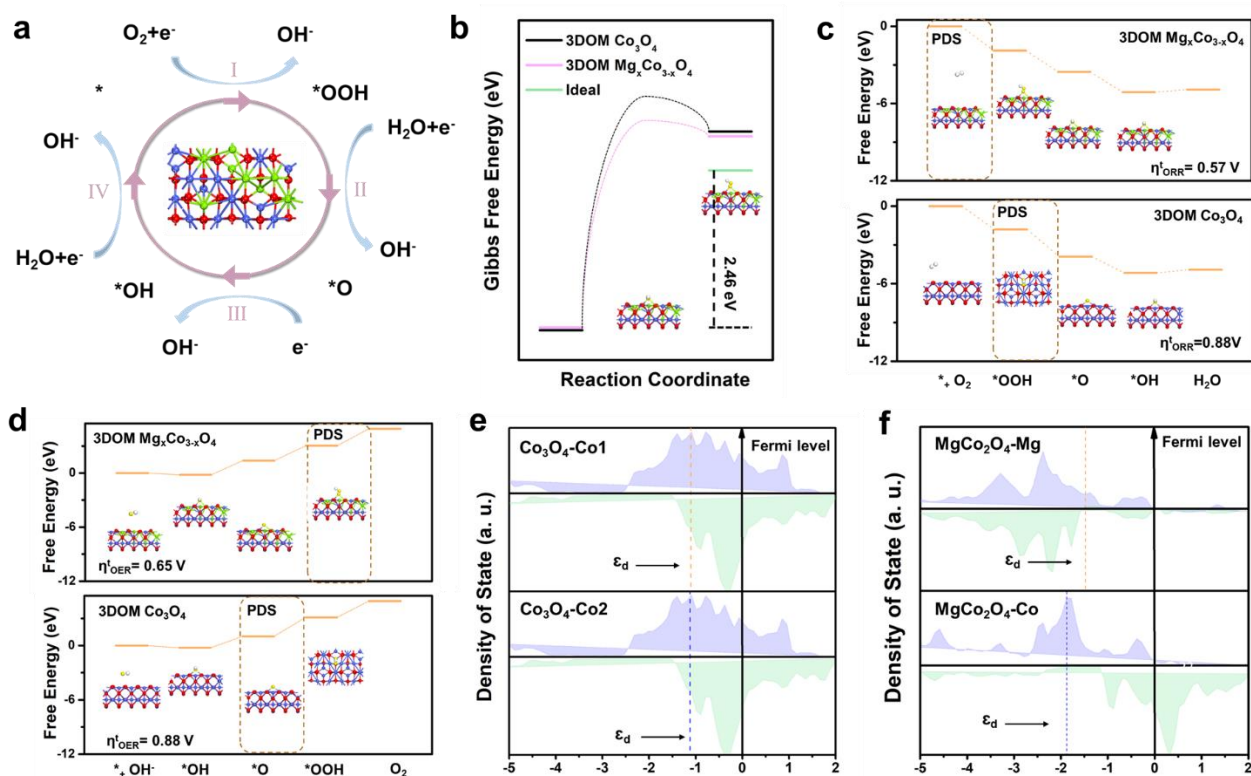


Figure 5.8 a) The proposed ORR mechanism on 3DOM $Mg_xCo_{3-x}O_4$. (b) Calculated energy barriers of $*OH$ transformation to $*OOH$ at active sites of 3DOM Co_3O_4 and 3DOM $Mg_xCo_{3-x}O_4$.

Calculated free energy for (c) ORR and (d) OER on 3DOM Co_3O_4 and 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Calculated density of states (DOS) of d orbitals of surface active sites in (e) 3DOM Co_3O_4 (two Co sites) and (f) 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ (one Mg site and one Co site). The blue dashed line represents the corresponding energy level of d band center; the Fermi level is set to 0 eV.

Analogous to ORR, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and 3DOM Co_3O_4 also have different PDSs for OER due to their Gibbs free energies for the key reaction coordinates, as shown in Figure 5.8d. For 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, formation of O_2 from *OOH with an energy barrier of 1.88 eV is the PDS, while for 3DOM Co_3O_4 , the formation of *OOH from *O with an energy barrier of 2.11 eV is the PDS. Besides, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ benefits from a smaller OER overpotential compared to 3DOM Co_3O_4 , which is due to the modulation of chemical environment and electronic structure of active sites and the decreased energy level of d band center (ϵ_d) with Mg doping. For 3DOM Co_3O_4 , the Co sites possess relatively strong binding strength with the intermediates, with the calculated ϵ_d being -1.11 and -1.12 eV for two Co sites (Figure 5.8e). According to the Bader charge analysis, the Co atoms will donate extra electron (0.05 e per Co atom) to the neighbouring O atoms with the substitution of Mg, leading to lower ϵ_d values for active sites. As shown in Figure 5.8f, the calculated ϵ_d of the surface Co and Mg sites are -1.88 and -1.47 eV, respectively. Therefore, the binding strength of reaction intermediates (such as *O and *OH) on 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ are weakened as compared to that on Co_3O_4 , leading to the enhancement in OER and ORR activity.^{144, 182}

X-ray absorption near edge structure (XANES) measurements and extended X-ray absorption fine structure (EXAFS) spectroscopy were conducted to explore the electronic structure and local coordination environment of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and other reference catalysts. As illustrated in Figure 5.9a, the chemical state of Co in 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ with higher energy

is larger than that of CoO and other samples, indicating the existence of Co^{III} due to the electron donation of Co atom.^{183, 184} Moreover, Fourier transformed (FT) $k^3 \chi(k)$ functions of EXAFS (Figure 5.9b) in R space of Co K-edge reveal that the Co coordination environment in 3DOM Mg_xCo_{3-x}O₄ corresponds to Co-Co bond at 2.4 Å and Co-O bond at 1.42 Å.^{131, 185} The valence state of Co in 3DOM Mg_xCo_{3-x}O₄ could also be verified by XAS with soft X-ray excitation with the absorption edge at Co L-edge shift (Figure 5.9c), in which the low and high energy peaks corresponding to the two arrows respectively represent Co²⁺ and Co³⁺.

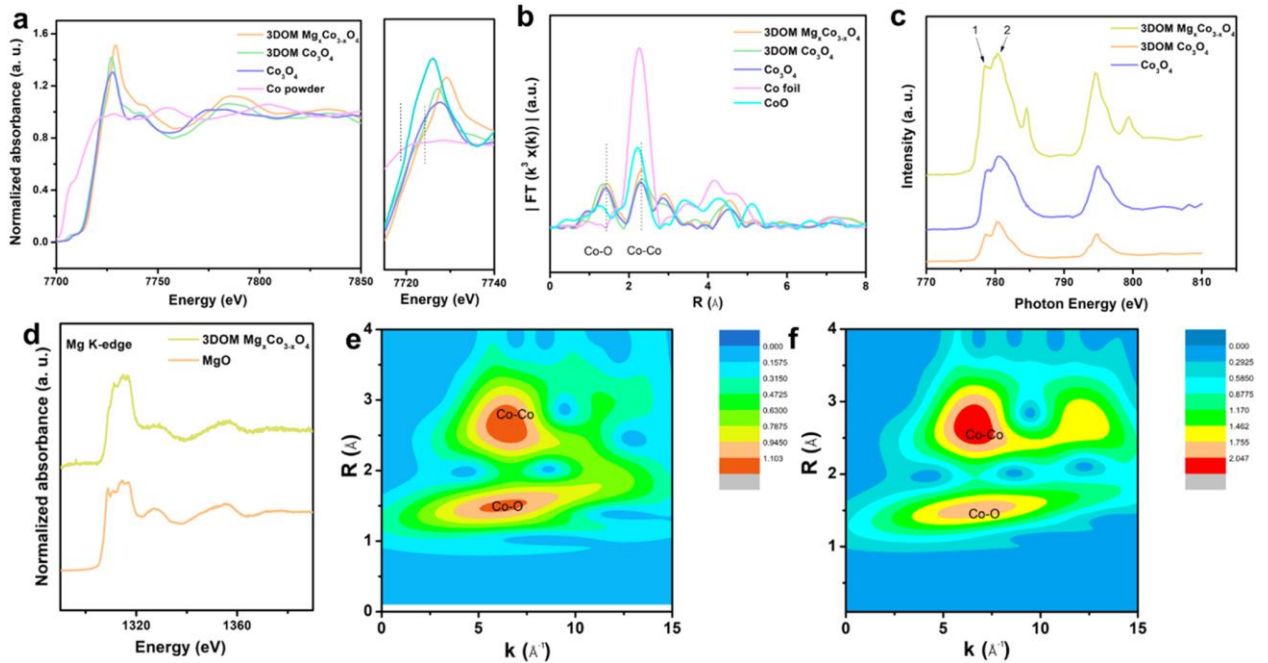


Figure 5.9 a) Co K-edge XANES spectra and (b) corresponding Fourier-transform k^3 -weighted EXAFS spectra for various samples. (c) Co L-edge XANES and (d) Mg K-edge XANES spectra of 3DOM Mg_xCo_{3-x}O₄ and some reference samples. (e) Wavelet transforms for the k^3 -weighted Co K-edge EXAFS signals of 3DOM Mg_xCo_{3-x}O₄ and (f) Co₃O₄.

In the XANES spectra of Mg K-edge for 3DOM Mg_xCo_{3-x}O₄ and MgO (Figure 5.9d), it is evident that the shift of 3DOM Mg_xCo_{3-x}O₄ is consistent with that of MgO, manifesting that

the Mg valence state of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ is +2.^{186, 187} The EXAFS wavelet transforms contour plots of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and pristine Co_3O_4 (Figure 5.9e and f) further demonstrate the chemical coordination of Co-Co and Co-O bonds, suggesting that the inclusion of Mg in Co_3O_4 manipulates the electronic structure of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, and effectively boosts the intrinsic catalytic performances during charge and discharge processes.¹⁸⁸

5.4 Conclusion

In summary, a hard-templating strategy has been employed to synthesize a highly efficient and stable hybrid bifunctional oxygen catalyst, 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, with hierarchically ordered porous structure for rechargeable zinc-air battery applications. In 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$, Co^{2+} substitution with Mg^{2+} in tetrahedral sites created more Co^{3+} occupying the octahedral sites, which enabled modulation of the chemical environment and electronic structure of Co sites and considerable decrease in the energy level of *d* band center (ϵ_d). The more optimal interactions (in terms of free energy) between the redox reaction intermediates and catalytic sites along with the reduced energy barrier for ORR and OER processes endow 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ with a much superior bifunctional performance compared to pristine Co_3O_4 . Furthermore, the large surface area and macro-mesoporous structure of 3DOM increase the interfacial area for the air electrode and electrolyte as well as accessibility of Co and Mg catalytic sites, remarkably improving the mass/charge transfer rate and ORR/OER reaction kinetics. 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ electrode could deliver outstanding bifunctional performances, surpassing those reached by noble-metal based electrodes (Pt/C and Ir/C). 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ exhibited an enhanced half-wave potential of 0.839 V for ORR and a low OER potential of 1.60 V at 10 mA cm^{-2} . Moreover, the OER Tafel slope of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ (76 mV dec^{-1}) was much lower than that of undoped 3DOM Co_3O_4 and even the benchmark Ir/C catalyst (320 mV dec^{-1}), originating from the faster reactions over

3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$. Notably, the zinc-air battery with 3DOM- $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ as air cathode achieved a high power density of 253 mW cm^{-2} and excellent charge-discharge stability for over 236 h. On the basis of comprehensive electrochemical assessments and theoretical studies, we demonstrated that Mg doping of Co_3O_4 together with rational design of 3DOM architecture could be promising strategies to develop low-cost, durable, and highly active bifunctional oxygen electrocatalysts which can expedite the large-scale applications of rechargeable zinc-air batteries.

Chapter 6 Conclusions and Recommendations

The goal of the present thesis is to engineer and develop porous non-precious metal-based materials for rechargeable zinc-air batteries. Thus, a series of 3DOM materials under different engineering processes were fabricated to be applied in zinc-air batteries. These materials are beneficial to overcome the intrinsic sluggish ORR and OER kinetics owning increased active sites and advanced electrocatalytic activities. This thesis also inspires the exploration of the as-synthesized advanced electrocatalysts on mechanism study.

In first work, we design 3DOM Fe_2N_x with nitrogen vacancies embedded on TiO_y as an effective electrocatalyst ($\text{Fe}_2\text{N}_x@\text{TiO}_y$). The engineered nitrogen vacancies effectively modulate the electronic configuration of Fe active site with enhanced affinity to oxygen species, reducing the energy barrier of potential determining step (PDS) of ORR for promoted oxygen electrocatalytic capability. Moreover, the ordered mesoporous structure enables the exposure of a high density of active sites, while a stable interconnected skeleton facilitates transport of oxygen species and electrons, accelerating the kinetics of ORR. The theoretical calculations and X-ray absorption studies unveil the enhanced oxygen electrocatalytic reactivity and durability driven by a combination of electronic and geometric effects. Therefore, the designed $\text{Fe}_2\text{N}_x@\text{TiO}_y$ catalyst exhibits excellent ORR performance in alkaline media, including high half-wave potential (0.88 V vs. RHE) and improved durability as compared to the noble-metal benchmark. The assembled zinc-air battery achieves a high capacity of 809 mAh g^{-1} . This study not only presents a high-performance ORR electrocatalyst, but also provides a new strategic direction for designing defective and ordered porous catalyst materials for efficient energy conversion.

In the following study, a series of Cu-Ti-O materials with advanced synergetic effect have been developed as great electrocatalysts. In the ternary system, the different metal centers

can effectively enhance the electrical conductivity. XANES technology demonstrates that partial electron density has been altered among Cu, Ti and O to bring about more active sites due to the adding of Ti atoms. Moreover, the hierarchical 3DOM structure of $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ provides a large specific surface area, facilitating the ion (OH^-) infiltration and the continuous electron transfer from during charge and discharge process. Compared with Pt/C, the as-prepared electrocatalyst exhibits comparable half wave potential for ORR. An overpotential of 300 mV and a Tafel slope of 89 mV dec^{-1} were obtained, which is superior to the OER performance of commercial RuO_2 . The primary zinc-air battery based on $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ can work stably for 52 hours at 10 mA cm^{-2} in cycling experiments. The zinc-air battery assembled with $\text{Cu}_{0.3}\text{Ti}_{0.7}\text{O}_2$ catalyst displays a power density of 138 mW cm^{-2} . The chemical environment modulation of the metal active centers by adding of Ti can increase exposure of active sites, redistribution of charge, and coordination of Cu-Ti-O for the good OER and ORR activity.

In final research, we employ a hard-template method to engineer Mg doping into Co_3O_4 with hierarchically three-dimensionally ordered mesoporous (3DOM) structure as an effective bifunctional oxygen electrocatalyst. The substitution of Mg modulates the electronic structure and bonding configuration of Co atom, triggering prominent electron density reconfiguration which greatly enhances the interaction between Co sites and oxygen species. Moreover, the interconnected ordered mesopores and macropores in the 3DOM architecture facilitate diffusion of oxygen species and electrons, thus enhancing the kinetics of ORR and OER. The theoretical calculations and X-ray absorption studies unveil the enhanced reactivity and durability driven by a combination of geometric and electronic effects. Therefore, the resulting 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ exhibits comparable oxygen electrocatalytic activity and much longer cycling stability than noble-metals in alkaline conditions. The zinc-air battery using 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ catalyst

delivers a high power density of 253 mW cm^{-2} and long-term cyclability over 236 h. This study not only presents a high-performance bifunctional oxygen electrocatalyst, but also provides a new strategic direction for designing catalysts for efficient energy conversion.

The abovementioned discussion indicated the interconnected porous functional transition metal-based electrocatalysts for zinc-air batteries. There are some recommendations have been proposed for future work to address the issues still existing.

i) *Single atom dispersion catalysts.* For the purpose of better utilizing the largest atom, the size of nanoparticles can be reduced to clusters or single-atom level. As the size changed, the energy level structure and electronic structure will also alter, thus, it makes the electrocatalysts achieve excellent activity and stability. Among the projects in this thesis, the size of 3DOM $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Fe}_2\text{N}_x@\text{TiO}_x$ can be adjusted to smaller values. Then the chemical environment and the adsorption energy will be tuned, leading to the synergistic effect of uniformly dispersed single atoms and adjacent metallic centers. Therefore, more active sites will be created causing the optimized adsorption/desorption characteristics and reduced the reaction barriers.

ii) *In situ techniques to investigate ORR and OER mechanisms.* Due to the different reaction kinetics and complex mechanisms of zinc-air battery, it is hard to estimate the specific charge and discharge process. Recently, in situ X-ray absorption spectroscopy (XAS), and in situ X-ray diffraction (XRD) have been found to be useful technologies for exploring the intermediates and alteration of coordination environment. By employing these advanced technologies, electrical reactions could be deeply explored and the change of active centers could be clearly observed. For instance, in situ XRD and in situ Raman spectroscopy can be used to detect the structure and chemical transformation during charge and discharge processes for Cu-

Ti-O ternary system. Then, the intrinsic activity and mechanism of the catalysts would be systematically analyzed.

iii) *Synthesis and development of metal carbides and nitrides (MXenes)*. For a typical MXene, it is composed of layered ternary carbides and nitrides with a composition of $M_{n+1}AX_n$, where M is an early transition metal, A is mostly group 13 and 14 elements, X is carbon and/or nitrogen, and $n = 1-4$. Generally, MAX phases were etched by HF to selectively remove the A layer in the MAX phases, and the family of 2D metal carbides and nitrides derived from MAX phase materials was termed MXenes. MXene heterostructures exhibit outstanding performance when used as an electrocatalyst for the OER in alkaline aqueous solutions. For example, Ti_3C_2 interacts with graphitic carbon nitrides (g- C_3N_4) to form a porous matrix. This results in strong coupling between the nitrogen-rich network and transition metal centers, in which the $Ti-N_x$ motifs provide electroactive sites to enhance the oxygen electrochemistry activity and stability.

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Three-dimensionally ordered mesoporous Co₃O₄ decorated with Mg as bifunctional oxygen electrocatalysts for high-performance zinc-air batteries

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Ordered mesoporous Fe₂N x electrocatalysts with regulated nitrogen vacancy for oxygen reduction reaction and Zn-air battery

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