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Transition metal-based composites for oxygen evolution electrocatalysis and lithium ion storage

Wei Huang

Ph.D. Thesis October 2020

Transition metal-based composites for oxygen evolution electrocatalysis and lithium ion storage

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Preface and Acknowledgments

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October 2020, Kgs. Lyngby

Wei Huang

Abstract

Green energy technologies are urgently needed due to an increasing global energy demand as well as critical environmental and climate concerns associated with the burning of fossil fuels. Electrochemical energy devices allowing direct conversion between chemical energy and electrical energy in an environmentally friendly way are of great interest. Efficient oxygen evolution reaction (OER) electrocatalysts and high-performance anode materials are crucial for rechargeable metal-air batteries and lithium ion batteries (LIBs), respectively. This Ph.D. project aims at using cheap and environment friendly iron compounds for OER electrocatalysts and anode materials of LIBs. The critical role of the crystalline structure, morphology and functional properties of final active iron-based materials is systematically investigated, as summarized below:

1. Ultrafine Fe₃O₄ nanoparticles (diameter: 6 ± 2 nm) are homogeneously immobilized on 2D Ni based metal-organic frameworks (MOFs) for OER. Electronic structure modulation and morphology changes for optimized catalytic activity are studied via varying the amount of Fe₃O₄ in the composite (Fe₃O₄/Ni-BDC). The optimized Fe₃O₄/Ni-BDC achieves the best OER performance at an overpotential of 295 mV at 10 mA cm⁻², a Tafel slope of 47.8 mV dec⁻¹ and considerable catalytic durability (40 h). The effect of valance state of the transition metal upon OER performance in the composites is carefully discussed. In conclusion, the optimized Fe₃O₄/Ni-BDC shows a promising OER catalytic performance.

2. A flower-like composite consisting of internal Fe₂O₃ nanocrystals and outer hierarchal iron doped K-birnessite type MnO_x layers (Fe₂O₃@Fe doped K-birnessite) is synthesized by a facile one-pot microwave-assisted heating synthesis (MAHS). The crystallinity and morphology evolution of Fe₂O₃@Fe doped K-birnessite composite are studied by characterizing the products at various reaction times. Key factors affecting the morphology such as reaction temperature and stoichiometric ratio of precursors are systematically investigated. When tested for LIBs, the optimized hybrid Fe₂O₃@Fe doped K-birnessite composite exhibits a high reversible capacity of 758 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles, outperforming the pure K-birnessite (203 mA h g⁻¹). Compared with other related report, the composite (Fe₂O₃@Fe doped K-birnessite) exhibits a comparable performance for lithium ion storage.

Abstract in Danish

Grønne energiteknologier er presserende nødvendige på grund af stigende globalt energibehov samt kritiske miljø- og klimaproblemer forbundet med brugen af fossile brændstoffer. Elektrokemiske energianordninger, der muliggør direkte konvertering mellem kemisk energi og elektrisk energi på en miljøvenlig måde, er af stor interesse. Effektive elektrokatalysatorer til iltudviklingsreaktion (OER) og højtydende anodematerialer er afgørende for henholdsvis genopladelige metal-luft-batterier og litiumionbatterier. Dette ph.d.-projekt sigter mod at bruge billige og miljøvenlige jernbaserede komponenter til OER-elektrokatalysatorer og anodematerialer fra litiumionbatterier. Den kritiske rolle af jernkomponenternes krystallinske struktur, morfologi og funktionelle egenskaber for de endelige aktive materialer undersøges systematisk som opsummeret nedenfor:

1. Ultrafine Fe₃O₄-nanopartikler (diameter: 6 ± 2 nm) immobiliseres ensartet på 2D Nibaserede MOF'er (Fe₃O₄/Ni-BDC) til OER. Elektronisk strukturmodulering og morfologiændringer for optimeret katalytisk aktivitet undersøges ved at variere mængden af Fe₃O₄ i kompositmaterialet. Den optimerede Fe₃O₄/Ni-BDC opnår den bedste OER-ydeevne med et overpotentiale på 295 mV ved 10 mA cm⁻², en Tafel-hældning på 47,8 mV dec⁻¹ og betydelig katalytisk holdbarhed (40 timer). Effekten af oxidationstrin af overgangsmetallet på OER-ydeevne i kompositterne diskuteres i detaljer. Afslutningsvis viser den optimerede Fe₃O₄ / Ni-BDC en lovende OER-katalytisk ydelse.

2. En blomsterlignende komposit bestående af interne Fe₂O₃-nanokrystaller og ydre hierarkisk jerndopet K-birnessite-type MnO_x-lag (Fe₂O₃@Fe-dopet K-birnessite) syntetiseres ved hjælp af en let mikrobølgestøttet opvarmningssyntese (MAHS). Den krystallinske og morfologiske udvikling af Fe₂O₃@Fe-dopet K-birnessit-kompositten undersøges ved at karakterisere produkterne ved forskellige reaktionstider. Nøglefaktorer, der påvirker morfologien, såsom reaktionstemperatur og støkiometrisk forhold mellem reaktanter undersøges systematisk. I LIB-tests, udviser den optimerede hybrid Fe₂O₃@Fe-dopet K-birnessit-komposit en høj reversibel kapacitet på 758 mA h g⁻¹ ved 500 mA g⁻¹ efter 200 cyklusser, der overgår den rene K-birnessite (203 mA h g⁻¹). Sammenlignet med andre relaterede rapporter udviser kompositten (Fe₂O₃ @ Fe doteret K-birnessit) en sammenlignelig ydelse til lithiumionlagring.

Synopsis

Depletion of fossil fuels along with a rapid increase in energy demand drives the development of sustainable energy conversion technologies. Electrochemical techniques are furthermore considered to directly convert chemical energy of renewable fuels into electrical energy in an environmentally friendly way. Efficient OER electrocatalysts for rechargeable metal-air batteries or high-performance anode materials for LIBs are promising systems for the storage and conversion of renewable electricity. The project aims at finding simple, low-cost and high-efficiency strategies for scalable production via low-toxic and earth-abundant transition metal-based raw materials for next-generation OER electrocatalysts and LIBs. The purpose of this project is to incorporate the cheap iron components into related transition metal-based materials used as OER electrocatalysts and anode materials of LIBs with simple synthetic methods.

The Ph.D. thesis is composed of five chapters, including an introduction to the research background, methodologies, experimental details, results, discussion, conclusions and perspectives.

Chapter 1 is a general introduction to transition metal-based materials for OER and LIBs with concepts, theory and typical applications reviewed. The recent progress is initially summarized in the preparation and characterization of 2D transition metal-based MOFs (e.g. Ni, Co), as well as their composites and derivatives, for OER electrocatalysis. Challenges and perspectives of applying 2D MOFs and their derivatives for OER electrocatalysis are also discussed. Meanwhile, the two main transition metal composites including metal oxides and metal chalcogenides used for anode materials of LIBs are also summarized. Half of the chapter has been accepted by the journal *ChemElectroChem* as a mini-review entitled "Recent progress of 2D metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis".

Chapter 2 summarizes the methodology used for characterization of the synthesized materials and performance evaluation of OER and LIBs. It describes the principles of the methods employed.

Chapter 3 describes the fabrication of ultrafine Fe_3O_4 nanoparticles (diameter: 6 ± 2 nm) that are homogeneously immobilized on 2D Ni based MOFs (Fe_3O_4/Ni -BDC) to tackle the aggregation issue for OER. The composite is prepared through in situ growth of Ni-BDC (thickness: 5 ± 1 nm) in the presence of water-dispersible Fe_3O_4 nanoparticles with abundant surface hydroxide groups. Different from a physically mixed composite showing poor OER performance, the in situ prepared Fe_3O_4/Ni -BDC with strong interaction efficiently modify the electronic structure of the transition metals. Different ratios of Fe_3O_4/Ni -BDC composites are tested for OER electrochemical catalytic performances, and

the resulting electrochemical behaviour and mechanisms are discussed in detail. The results presented in this chapter are included in the manuscript "Ultrafine Fe_3O_4 nanoparticles immobilized on two-dimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction" (submitted).

Chapter 4 describes the fabrication of a flower-like composite consisting of internal Fe₂O₃ nanocrystals and outer hierarchal iron doped K-birnessite type MnO_x layers (Fe₂O₃@Fe doped K-birnessite), which is synthesized by a facile one-pot microwave-assisted heating synthesis (MAHS). The crystallinity and morphology evolution of Fe₂O₃@Fe doped K-birnessite composite are studied by characterizing the products at various reaction times, using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) as well as scanning and transmission electron microscopy (SEM & TEM). Key factors affecting the morphology, such as reaction temperature and stoichiometric ratio of precursors are systematically investigated. When tested for LIBs, the performances of assembled LIBs as anode materials for lithium ion storage are recorded and compared with related literature. The results presented in this chapter are also in the included article "Microwave assisted crystalline and morphology evolution of flower-like Fe₂O₃@ iron doped K-birnessite composite and its application for lithium ion storage" published in *Applied Surface Science*, 2020.

Chapter 5 summarizes conclusions of the entire Ph.D. thesis and offers perspectives of the construction of transition metal-based composites for energy storage and conversion applications.

Acronyms and instructional notes

0D: zero dimensional 1D: one dimensional 2D: two dimensional **3D**: three dimensional AC: alternative current AFM: atomic force microscopy Ag/AgCl: saturated silver/silver chloride BDCA: benzene 1,4-dicarboxylic acid BE: binding energy BET: Brunauer, Emmett and Teller **BEV**: battery electric vehicles BJH: Barrett-Joyner-Halenda **BPDC**: 4,4'-biphenyldicarboxylate CC: carbon cloth Cdl: electrochemical double-layer capacitance CE: counter electrode **CNFs**: carbon nanoflowers CNT: carbon nanotube CP: carbon paper **CP**: chronopotentiometry CUMSs: coordinatively unsaturated metal sites CV: cyclic voltammetry DABCO: 1,4-diazabicyclo[2.2.2]octane **DFT**: density functional theory DHAA: dehydroascorbic acid DMF: N, N-dimethylformamide DTU: Technical University of Denmark

E_B: binding energy ECSA: electrochemical surface area **EDS**: energy dispersive spectroscopy EIS: electrochemical impedance spectroscopy EK: kinetic energy E_n: peak potential EPR: electron paramagnetic resonance ETD: Everhart-Thornley Detector ETEM: environmental transmission electron microscope Fc: carboxyferrocene FE: faradaic efficiency FeCo-MB: iron-cobalt bulk MOF-74 FeCo-MNS: iron-cobalt MOF-74 nanosheets FeCo-ONS: iron-cobalt oxide nanosheets FTIR: Fourier transform infrared spectroscopy FTO: fluorine-doped tin oxide GCE: glassy carbon electrode GDC: galvanostatic discharge/charge GDY: graphdiyne GNSs: graphene nanosheets H₂NTA: 2-aminoterpthalate HOMO: highest occupied molecular orbitals **HPA**: hypoxanthine HPNA: hierarchical porous nanosheets arrays ICP-OES: inductively coupled plasma

optical emission spectrometry

Ir: iridium	RHE : reversible hydrogen electrode		
KB: Ketjen Black	RHE : reversible hydrogen electrode		
LDHs: layered double hydroxides	RRDEs : rotating ring disk electrodes		
LIBs: lithium ion batteries	$\mathbf{R}_{\mathbf{s}}$: ohmic solution resistance		
LSV: linear sweep voltammetry	Ru : ruthenium		
LUMO: lowest unoccupied molecular	SAED : selected-area electron diffraction		
orbitals	SCE: saturated calomel electrode		
MAHS: microwave-assisted heating synthesis	${f SEI}$: solid-electrolyte interphase		
MOFs: metal-organic frameworks	SEM: scanning electron microscopy		
MPN: metal polyphenolic networks	SHE: standard hydrogen electrode		
NFs: nickel foams	SNC : sulfur/nitrogen carbon		
NMP: N-methyl-2-pyrrolidone	SPDP : 4,40-(sulfonylbis(4,1 phenylene))dipyridine		
NPG: nanoporous gold	TAA: thioacetamide		
NPs: nanoparticles	TEA: triethylamine		
OCP: open circuit potential	TEM: transmission electron microscopy		
OER : oxygen evolution reaction	TEM: transmission electron microscopy		
PDS: potential-determining step	TMOs: transition metal oxides		
PPF-3 : porphyrin paddlewheel framework-3	UNSs: ultrathin nanosheets		
PVDF : polyvinylidene fluoride	Vo: oxygen vacancies		
PXRD: powder X-ray diffraction	WE: working electrode		
\mathbf{R}_{ct} : charge-transfer resistance	XAFS : X-ray absorption fine structure		
RDE: rotating disk electrode	XAS: X-ray absorption spectroscopy		
RE : reference electrode	XPS : X-ray photoelectron spectroscopy		
RGO: reduced graphene oxide	XPS: X-ray photoelectron spectroscopy		

ZIF-L: zeolitic imidazolate framework-L

 η : overpotential

Instructional notes

Figures and equations are abbreviated to "Fig." and "Eq." respectively in the text. Acronyms of terms ending in -microscopy, -chemistry, -voltammetry or -spectroscopy, refer to -microscope, -chemical, -voltammogram and -spectrum/spectra, as well. Abbreviations are used in plural form by adding "s". VIII

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Chapter 1. Overview of transition metal-based composites for oxygen evolution electrocatalysis and lithium ion batteries

This chapter offers a general introduction to transition metal-based materials for oxygen evolution reaction (OER) and lithium ion batteries (LIBs). It introduces concepts and theory necessary for the discussion in the following chapters. Half of the chapter has been accepted by the journal *ChemElectroChem* as a review entitled "Recent progress of 2D metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis", co-authored by Wei Huang, Jing Tang, Fangyuan Diao, Christian Engelbrekt, Jens Ulstrup, Xinxin Xiao and Kristian Mølhave.

To meet the decreasing availability of fossil fuels and environmental issues, electrochemical energy storage and conversion devices (electrochemical capacitors, batteries and fuel cells) with economic and environmental-friendly features have become the critical technologies to produce electrical energy for human being's daily life. The typical Ragone plot (Fig.1.1) shows the relationship between specific energy and power in different electrochemical devices. Batteries have been widely used with a biggest market share among the three main energy storage and conversion systems, demonstrating intermediate energy and power characteristics. Compared with the conventional combustion engines and gas turbines, the current electrochemical performance of batteries is hard to reach the increasing demand in many practical applications. Thus enhancing the output abilities in energy and power densities and reducing the cost of batteries are critical. Metal-air batteries or LIBs as typical systems in batteries. Exploring earth-abundant and relatively low-price transition metal-based composites as good OER electrocatalysts used for rechargeable next-generation metal-air batteries or as excellent anode materials used for high-performance LIBs, are attracting more and more attention for investigation. In this chapter, recent advance of transition metalbased composites for oxygen evolution electrocatalysis to be used in metal-air batteries and LIBs are summarized.



Fig. 1.1 Ragone plot of the current electrochemical energy storage systems with conventional capacitors and internal combustion engines and turbines. Reprinted with permission from Ref.^[1] Copyright (2019) Springer Nature.

1.1 Recent progress of 2D transition metal-based metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis

1.1.1 Introduction

Green energy technologies are urgently needed due to forthcoming insecurity of fossil fuel supply, increasing global energy demand as well as critical environmental and climate concerns.^[2-8] Rechargeable metal-air batteries and electrochemical water splitting (Fig. 1.2a)^[9], are promising systems for the storage and conversion of renewable electricity, such as from solar and wind energy, and have attracted much attention due to their environmental friendliness, high efficiency and safety.^[10-13] The OER is a crucial element for such devices, highlighting the importance of high-performance OER electrocatalysts.

The OER is the process in which H₂O or OH⁻ is oxidized to dioxygen gas at the anode of an electrolyzer cell. Ideally the process proceeds around the thermodynamic limit of 1.23 V versus the reversible hydrogen electrode (RHE) but typically requires large overpotentials of several hundreds of millivolts. The OER mechanisms vary depending on pH of the electrolyte and catalyst surface.^[14, 15] The well-accepted OER includes four separated steps with overall four-electron transfer in acidic (eq. 1.1) and alkaline (eq. 1.2) conditions, respectively. X^{*} indicates one active site on the surface of electrocatalyst, while X^{*}OH, X^{*}O and X^{*}OOH refer to different OER intermediates absorbed on the active site during OER (Fig. 1.2b).^[14, 16]

 $2H_2O \rightarrow O_2 + 4 H^+ + 4e^-$ (acidic condition) (1.1)

$\mathrm{H_2O} + \mathrm{X^*} \rightarrow \mathrm{X^*OH} + \mathrm{H^+} + \mathrm{e^-}$	(1.1.1)	
$X^*OH \rightarrow X^*O + H^+ + e^-$	(1.1.2)	
$\mathrm{H_2O} + \mathrm{X*O} \rightarrow \mathrm{X*OOH} + \mathrm{H^+} + \mathrm{e^{-}}$	(1.1.3)	
$X^*OOH \rightarrow X^* + O_2 + H^+ + e^-$	(1.1.4)	
$4OH^{\cdot} \rightarrow 2H_2O + O_2 + 4e^{\cdot}$ (alkaline c	ondition)	(1.2)
$OH^{\cdot} + X^{*} \rightarrow X^{*}OH + e^{\cdot}$	(1.2.1)	
$X^*OH + OH^{\cdot} \rightarrow X^*O + H_2O + e^{\cdot}$	(1.2.2)	
$X^*O + OH^{\cdot} \rightarrow X^*OOH + e^{\cdot}$	(1.2.3)	

The benchmark OER electrocatalysts are noble metal–based catalysts e.g. of ruthenium (Ru) or iridium (Ir).^[17, 18] Nevertheless, the low crustal reserve, high cost and poor stability of these metals are obstacles for their large-scale implementation. As an alternative, earth-abundant and cost-effective transition metal–based electrocatalysts are promising candidates for OER.^[19-22] Rossmeisl *et al.*^[16] constructed a volcano-type plot (Fig. 1.2c and d) showing the relationship between adsorption energy descriptors (Δ Go^{*} and Δ GHO^{*}) and OER overpotential (η), which can be used as a guide in searching for excellent OER catalysts. According to their description, η is determined by the critical step forming the *O (eq. 1.1.2 and 1.2.2) or *OOH (eq. 1.1.3 and 1.2.3) adduct. The difference in adsorption free energy for *OH and *OOH (Fig. 1.2c) is a constant (about 3.2 eV). ^[16, 23] Disregarding solvent dynamic effects (reorganization free energies)^[24], the theoretical η at standard conditions can be obtained by^[16]

$$\eta = \{\max \left[(\Delta G_{0^*} - \Delta G_{H0^*}), 3.2 \text{ eV} - (\Delta G_{0^*} - \Delta G_{H0^*}) \right] / e \} - 1.23 \text{ V}$$
(1.3).

RuO₂ is located close to the top of the volcano (Fig. 1.2d), but some non-noble transition metal oxides, e. g. NiO and Co₃O₄, are very close to RuO₂. Transition metal-based catalysts could be optimized by adjusting (Δ Go* - Δ GHO*).^[25, 26] For example, Ho and coworkers reported that the (012) facet of α -Fe₂O₃ (Fig. 1.2e) has an optimal adsorption/desorption position for favorable OER.^[25] Overall, OER performance is determined by the maximum adsorption free energy value among the four steps. The critical step is named as the potential-determining step (PDS). Besides, the generation process of dioxygen during OER also is accompanied by some side reactions, such as the formation of hydroxyl radical, or H₂O₂ evolution. In depth understanding of OER process and catalytic mechanism is significant for the development of OER electrocatalysts.



Fig. 1.2 a) Schematic illustration of rechargeable metal-air batteries and electrochemical water splitting. The magenta dashed box highlights the key process, *i.e.* OER in both devices. b) The OER mechanism under acidic (blue round) and alkaline (orange round) conditions. Not drawn to real scale. c) The universal scaling relation plot between adsorption energies of HOO* and HO* on perovskites, rutiles, anatase, Mn_xO_y , Co_3O_4 , and NiO oxides. The red star indicates the ideal electrocatalyst. Reprinted with permission from Ref.^[16]. Copyright (2011) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Volcano plot of the computed OER overpotential against the descriptor 4

value of Δ Go*- Δ G_{HO*} for selected transition-metal oxides. Reprinted with permission from Ref.^[16]. Copyright (2011) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. e) Impact of facets on the OER activity descriptor. Inset, eg occupancy of six- and seven- coordinated configurations. Reprinted with permission from Ref.^[25] Copyright (2018) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As an emerging group of transition metal-based materials, metal-organic frameworks (MOFs) are a class of highly porous crystalline materials composed of transition-metal units and strongly coordinating organic ligands.^[27] MOFs are being studied extensively with wide-ranging application prospects, *e.g.* gas storage and separation, batteries, catalysts *etc.*, benefiting from their high specific surface area, tunable porosity and abundance of active metal sites.^[28, 29]. To date, a large library of MOFs has been fabricated with a wide spectrum of metal nodes and organic linkers.^[9, 30] Besides the variety of components and structures, different morphologies of MOFs have been designed and prepared, including zero dimensional (0D, *e.g.* nanoparticles or quantum dots), one dimensional (1D, *e.g.* nanowires or nanorods), two dimensional (2D, *e.g.* nanosheets or plates) and three dimensional (3D, *e.g.* networks) structures.^[31-35] These different morphologies and microstructures open new research opportunities for OER if using them as precursors or templates for OER catalysts, as OER is an interfacial reaction that is strongly dependent on the surface physicochemical features of the catalysts.

Since the discovery of graphene,^[36] 2D materials (*e.g.* MoS₂, MXene and black phosphorus) have been widely studied in past decades due to their unique physicochemical features.^[37-42] 2D MOFs offer some additional advantages, particularly facile electron transfer between the active site and the electrode substrate as well as the vast number of coordinatively unsaturated metal atoms exposed at the surface. Further, surface atom and bonding organization in 2D MOFs or their derivatives can be tailored for superior OER electrocatalysis. However, so far MOFs have been considered to have low electrical conductivity and often poor OER performance. Recently, π -conjugated 2D MOFs with benzene- or phthalocyanine-based organic groups have been synthesized, and directly used for OER with high intrinsic electrical conductivity.^[43, 44] 2D MOFs have further been combined with conductive agents (carbon components or conductive substrates) or pyrolyzing 2D MOFs have been adopted to improve the conductivity and enhance OER electrocatalysis. It is therefore not surprising that 2D MOF-based materials are emerging as efficient OER electrocatalysts.

In this part, I critically summarize recent progress in the preparation and characterization of 2D transition metal-based MOFs (*e.g.* of Ni, Co), as well as their derivatives including the corresponding metal/alloys, metal oxide/chalcogenides and metal phosphides/hydroxides for OER electrocatalysis. Design principles and preparation routes are presented. The performance of electrocatalysts is directly compared in terms

of η (thermodynamics) and electrocatalytic current density (kinetics), as well as operational stability (economics). Challenges and perspectives are also discussed.

1.1.2 Preparation and characterization of 2D MOFs

2D MOFs can be synthesized *via* either top-down or bottom-up approaches.^[9, 30, 45] The top-down methods include physical [46, 47] and chemical exfoliation [48, 49], which rests on breaking the weak van der Waals interactions between layers in bulk layered materials. For example, Moorthy and co-workers^[46] synthesized 2D Cd-DP MOF nanosheets by ultrasonicating layered Cd-DP MOFs in ethanol. Scanning electron microscopy (SEM) images (Fig. 1.3a) showed the presence of stacked 2D sheets from the solvothermal formation of the bulk MOF. Transmission electron microscopy (TEM) images of the 2D Cd-DP MOF obtained after ultrasonication displayed a sheet-like morphology with wrinkles (Fig. 1.3b). The 2D Cd-DP nanosheet thickness, determined by atomic force microscopy (AFM, Fig. 1.3c and d) was about 3 nm. Zhang et al.^[49] fabricated 2D Coe-O(dhbdc)₂(OH)₂(H₂O)₁₀ (dhbdc: 2,3-dihydroxy-1,4-benzenedicarboxylic) nanosheets (2D-Co-NS, thickness: 2 nm) through electrochemical exfoliation by removing the pillar ligands (H₄dhbdc) in the 3D MOF. The prepared 2D-Co-NS showed a catalytic OER performance on nickel foams (NFs) with a low overpotential of 211 mV. 2D MOFs synthesized by top-down methods often exhibit inhomogeneous morphologies and thicknesses, attributed to numerous surface defects originating from the breakup of interlayer interactions in the 3D MOF precursors. Moreover, the abundant surface defects on the 2D MOFs are considered helpful for catalytic applications.^[49, 50]



Fig. 1.3 Examples of top-down (left) and bottom-up (right) approaches to 2D MOF synthesis. a) SEM image of pristine Cd-DP crystals show the presence of stacked 2D

sheets. b) TEM and c) AFM images and d) height profile of 2D Cd-DP nanosheets. Reprinted with permission from Ref.^[46]. Copyright (2018) Elsevier. e) Digital photograph, and f) Scheme that shows the spatial distribution of different liquid regions during the synthesis of CuBDC MOF nanosheets. Regions labelled i, ii and iii correspond to benzene 1,4-dicarboxylic acid (BDCA) solution, intermediate solution region containing the generated CuBDC MOF, and the aqueous solution of Cu^{2+} ions, respectively. g) AFM image of CuBDC MOF nanosheets. h) Height profiles measured along the blue and red lines in (g). Reprinted with permission from Ref.^[51]. Copyright (2014) Nature Publishing Group.

In contrast to the top-down method, the morphology and thickness of synthetic 2D MOFs by bottom-up approaches can be controlled well, leading to high-quality and high-yield production. Common bottom-up strategies include two-phase interfacial/intermediate layer growth ^[51, 52], surfactant/template-assisted approaches^[53, 54]. For example, Gascon and co-workers^[51] prepared dispersible 2D copper 1,4-benzenedicarboxylate MOF (CuBDC) nanosheets through the two-phase method (Fig. 1.3e). Cu²⁺ ions and BDC linkers slowly diffused to the interface of two solutions, generating highly diluted 2D CuBDC nanosheets. AFM images (Fig. 1.3f-h) demonstrated lateral dimensions above one micrometer and thicknesses in the range 5–25 nm. Zhang *et al.* ^[54] synthesized 2D zeolitic imidazolate framework-L (ZIF-L) nanosheets by template-assisted deposition. Horizontally aligned 1D halloysite nanotubes were used as templates, acting as nucleation sites and guiding the vertical growth of the 2D MOF. Although the weak structural stability and surface additives of 2D MOFs fabricated by bottom-up approaches prevent the direct application in surface-related applications, it is easy to control the formation of various metal-doped 2D MOFs.^[50, 55]

Hybrid 2D MOFs resulting from the introduction of hetero-components (atoms, molecules *etc.*) into the structure could efficiently inherit the controllable morphology and modify the integral electronic structure to facilitate the catalytic activity for OER. The most universal and facile approach to synthesizing hybrid 2D MOFs is adding extra metal ions or metal-organic compounds during the formation of 2D MOFs, whose metal nodes are thus partially replaced or modified by the foreign metal ions or metal-organic compounds. In addition, the template-assistant approach is another emerging method to fabricate hybrid 2D MOFs featuring superior interfacial connection for good electrical conductivity, robust structural stability and thus good catalytic performance. For example, Dong's group^[56] used the template-assisted approach to prepare ultrathin Co_9Ni_1 -MOF nanosheet arrays on Co_9Ni_1 foam substrates. The surface layer of the metallic Co_9Ni_1 self-dissociated in the presence of benzenedicarboxylic acid (BDC) solution during a hydrothermal process, forming 2D Co_9Ni_1 -MOF nanosheet arrays on the substrate. This 2D MOF exhibited good OER catalytic activity with a η of 215 mV at 10 mA cm⁻².

The morphology and structure of 2D MOFs can be characterized by a variety of techniques. SEM and TEM can be used for the observation of the spontaneous curling at 2D MOF edges after drying, while the thickness can be precisely measured by AFM. Further, the atomic arrangement in 2D MOFs can be identified *via* scanning TEM (STEM) with near-atomic resolution and high Z-contrast.^[57] The crystallinity of 2D MOFs can be examined by bulk powder X-ray diffraction (PXRD) or selected-area electron diffraction (SAED) of individual nanosheets. The elemental composition can be obtained by energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), which also allows for chemical analysis of the elemental components in the 2D MOF. In addition, EDS mapping using STEM can image the distribution of metal nodes in bimetallic or trimetallic 2D MOFs with high resolution.^[43] X-ray absorption spectroscopy (XAS) with synchrotron radiation can analyze oxidation states, local atomic structure and unoccupied metal electronic states in 2D MOFs associating with intrinsic OER catalytic activity.^[58]

Different electrode substrates and electrode preparation routes are employed, when using 2D MOF-based materials for OER electrocatalysis. Drop-casting of the as-fabricated 2D MOF inks onto a glassy carbon electrode (GCE), fluorine-doped tin oxide (FTO) on glass, or carbon cloth (CC) is a widely used approach.^[44, 59-61] It allows efficient control of the mass loading of the catalyst on the substrate for quantitative investigation of the intrinsic catalytic OER activity. However, the interface between the substrate and the catalysts may suffer considerable impedance as insulating binders are typically used in the ink, leading to reduced OER performance. In-situ strategies to grow 2D MOFs directly on conductive substrates, such as NFs, is another approach.^[62, 63] The resulting 2D MOF electrodes could not only maintain good electronic connection between substrate and catalyst improving the electrical conductivity, but also inherit the hierarchical frameworks of the substrates for improved O_2 mass transport away from the catalyst surface and good OER performance. However, determination of the precise mass loading of catalysts in these systems is difficult. Besides, the capillary effect on the hierarchical substrates may offer extra active sites for OER electrocatalysis that are not calculated when geometric area used.^[64] Furthermore, it is recommended to report the catalyst loading and effective surface area so that appropriate comparison of OER performance across studies can be made.

1.1.3 2D MOFs for OER

1.1.3.1 2D Ni-based MOFs hybrids

2D transition metal-based MOFs (*e.g.* of Ni, Co) have attracted extensive attention. Among them, 2D Ni-based MOFs have demonstrated excellent catalytic performance for OER, as summarized in Table 1. 2D Ni-based MOFs consisting of Ni units with different organic linkers have been investigated in the past few years.^[44, 61, 65] Du *et al.*^[44] utilized a phthalocyanine (Pc) unit as a key organic fragment to construct a π -conjugated 2D NiPc-8 MOF via a bottom-up method, exhibiting a layered morphology (thickness: 100–200 nm) as confirmed by AFM. The NiPc-MOF registered an OER n of 350 mV at 10 mA cm⁻² on a fluorine-doped tin oxide (FTO) substrate. It could be concluded that lack of heteroatom doping in the 2D NiPc-MOF and low loading may limit the OER performance (Table 1). Similarly, a 2D pure Ni-based MOF, which was prepared with physical exfoliation by ultra-sonicating 3D pillared-layer MOFs ($[M_2(bdc)(dabco)]$ -guest (M = Ni, H₂bdc = 1,4benzenedicarboxylic acid, dabco = 1.4-diazabicyclo-[2.2.2]octane)) in water, showing an OER η of 581 mV at 10 mA cm⁻² on CC.^[61] However, there is still a large room for improvement in OER performance (Table 1). Recently, some researchers have introduced metal heteroatoms to 2D Ni MOFs as hybrid electrocatalysts, enabling improved OER performance.^[43, 66, 67] Tang and co-workers^[43] fabricated NiCo-based ultrathin 2D MOF (NiCo-UMOFNs) consisting of Ni²⁺/Co²⁺ and organic linkers of BDC nanosheets with a uniform thickness of 3.1 nm via sonication. The NiCo-UMOFNs exhibited a superior OER catalytic activity with a lower n (250 mV at 10 mA cm⁻²) than that of the single-metal 2D Ni-UMOFN (321 mV). In-situ X-ray absorption spectroscopy (XAS) indicated that the Ni K-edge peaks of NiCo-UMOFNs shifted to higher binding energy after applying a potential in the range of 1.43 to 1.53 V vs. RHE, confirming the Ni sites in NiCo-UMOFNs were more easily oxidized to high valence states for enhanced catalytic sites than that of bulk NiCo-MOFs.^[43, 68] Density functional theory (DFT) simulation results further revealed that unsaturated metal atoms were the main active sites and the coupling effect between Ni and Co metals was crucial for the enhanced electrocatalytic activity. In addition, the nanometer-thick 2D structure increased the amount of exposed surface and thus unsaturated active metal sites.^[43] Following this report, a number of bimetallic 2D Ni-based MOFs hybrids (NiFe-UMNs^[66] and Ni_{0.75}Fe_{0.25} BDC^[67]) have been explored. For instance, Wang's group^[66] synthesized NiFe 2D ultrathin MOF nanosheets with a thickness of ~10 nm, showing a η of 260 mV at 10 mA cm⁻². Meanwhile, Li *et al.*^[67] tuned the Fe doping in a 2D Ni MOF, with the optimized Ni_{0.75}Fe_{0.25} BDC registering a η of 310 mV at 10 mA cm^{\cdot 2}. These reports indicate that the doping of metal heteroatoms in the 2D Ni MOFs could efficiently allow for 2D morphology while optimizing the integral electronic structure for excellent OER performance.

Catalyst	Overpotential	Tafel slope	Catalytic stability (h)	Loading	Substrate	Ref.
	@ 10 mA cm ⁻² (mV)	(mV dec ⁻¹)		(mg cm-2)		
NiPc-MOF	350	N/A	50	0.076	FTO	[44]
2D-Ni-single-layer	581	182	N/A	0.2	$\mathbf{C}\mathbf{C}$	[61]
$\rm NH_2TA-MOF$	356	105	3.3	N/A	GCE	[65]
Ni-UMOFNs	321	65	N/A	0.2	GCE	[43]
Ni BDC	420	92.5	N/A	0.2	GCE	[67]
Ni-MNS/NF	$425@~50~{ m mA~cm^{-2}}$	100	N/A	N/A	NF	[62]
Ni-MOF	370	139	N/A	0.2	GCE	[69]
NiCo-UMOFNs	250	42	120	0.2	GCE	[43]
NiFe-UMNs	260	30	2.8	0.4	GCE	[66]
$Ni_{0.75}Fe_{0.25}$ BDC	310	43.7	11.1	0.2	GCE	[67]
Ni-MOF@Fe-MOF	265	82	N/A	0.2	GCE	[69]
Ni-BDC/Ni(OH) ₂	320	41	20	0.19	GCE	[70]
NiFe MOF/OM-NFH	270	123	11.1	0.4	GCE	[71]
NiFeZn-MNS/NF	$350@~50~{ m mA~cm^{-2}}$	49	120	N/A	NF	[62]
Ni-ZIF/Ni-B@NF-4	234	57	36	N/A	NF	[72]

Table 1.1 OER activity of reported 2D Ni-based MOFs electrocatalysts in 1 M KOH. The widely different Tafel slopes are notable and indicative of quite different rate determining OER steps on the different MOF surfaces.

N/A: not available

In addition, incorporating heterogeneous components into 2D Ni-based MOFs can also enhance the catalytic ability for water oxidation.^[69-72] Rational design of the composition and structure could efficiently mitigate the aggregation of 2D Ni MOF. For example, Sun et al.^[69] synthesized hybrid 2D dual MOFs (Ni-MOF@Fe-MOF) by in-situ generation of Fe-MOFs nanocrystals on the surface of 2D Ni MOFs resulting in a 100 mV lowering of the overpotential (to 265 mV at 10 mA cm⁻²). Qiao and coworkers^[70] developed a 2D Ni-BDC/Ni(OH)₂ heterostructure for OER electrocatalysis, exhibiting a n of 320 mV at 10 mA cm⁻² and a good catalytic durability of 20 h. Besides, Zhu et al.^[71] designed a unique 2D NiFe MOF nanosheets inlayed on a 3D ordered macroporous NiFe hydroxide template (NiFe MOF/OM-NFH), with partial NiFe hydroxide of the template *in-situ* transformed into 2D NiFe MOF nanosheets. The combination of the highly exposed active centers in the ultrathin NiFe MOF nanosheet inlay and efficient electron/mass transfer in the 3D hierarchical structure ensured excellent OER catalytic activity with a n of 270 mV at 10 mA cm⁻². In addition, generating hybrid 2D Ni MOFs on porous NF skeletons with large accessible surface areas and active site concentration, could accelerate mass/charge transfer. Wei and co-workers^[62] grew NiFeZn-based MOF nanosheets containing Fe₂O₃ nanoparticles (size < 5 nm) on NF substrates (NiFeZn-MNS/NF), registering better OER performance (350 mV@ 50 mA cm⁻²) than the pure Ni- MNS/NF (425 mV@ 50 mA cm⁻²). It is noteworthy that constructing crystalline-amorphous interfaces on the crystalline surface of Ni-based MOFs could optimize adsorption energy of OER intermediates for enhanced OER performance. Wu et al.^[72] synthesized ultrathin Ni-ZIF/Ni-B nanosheets with abundant crystalline-amorphous phase boundaries via a room temperature boronization of as-prepared Ni-ZIF nanorods on NF (Fig. 1.4a). High-resolution TEM images (Fig. clearly showed the crystalline-to-amorphous (HRTEM) 1.4b-d) transformation process from Ni-ZIF to Ni-B with boronization time. The optimal samples (Fig. 1.4c) with 4 h boronization (Ni-ZIF/Ni-B@NF-4) contained a large number of crystalline-amorphous phase boundaries. The corresponding STEM imaging and EDS mapping (Fig. 1.4e) revealed the co-existence and uniform dispersion of C, N, Ni and B in the sheet-like structure. Among various controls, Ni-ZIF/Ni-B@NF-4 exhibited the best catalytic activity for OER (Fig. 1.4f and g) with the lowest η of 234 mV at 10 mA cm⁻², and high catalytic stability with negligible decay after 36 h at 10 mA cm⁻² by maintaining the initial 2D nanosheet morphology (inset of Fig. 1.4g). DFT calculations indicated that the potential-determining step (PDS) of Ni-ZIF was the adsorption of *OH (2.36 eV at U =1.23), while it was the formation of *OOH (1.23 eV at U =1.23) for amorphous Ni-B. The combination of 2D Ni-ZIF and amorphous Ni-B reduced the energy barrier of adsorption of *OH and formation of *OOH, thus leading to enhanced intrinsical OER catalytic activity.



Fig. 1.4 a) Schematic illustration of the synthesis process of Ni-ZIF/Ni-B@NF. HRTEM images of b) Ni-ZIF, c) Ni-ZIF/Ni-B-4, and d) Ni-B@NF-24, respectively. e) STEM and the corresponding EDS elemental mapping of Ni-ZIF/Ni-B-4. f) OER performance of Ni-ZIF@NF, Ni-ZIF/Ni-B@NF-2, Ni-ZIF/Ni-B@NF-4, Ni-ZIF/Ni-B@NF-9, and Ni-B@NF-24 characterized by LSV with a scan rate of 1 mV s⁻¹ in 1.0 M KOH. g) The operational stability of Ni-ZIF/Ni-B@NF-4 at 1.464 V vs. RHE. Inset in (g) is an SEM image of the cycled Ni-ZIF/Ni-B@NF-4 catalyst after long-term test. Reprinted with permission from Ref.^[72]. Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In summary, 2D Ni-based MOFs hybrids used for OER have been studied over several years recently. Most pristine 2D Ni MOFs demonstrate relatively weak OER catalytic capacity due to the poor catalytic activity of active sites and strong tendency to agglomerate during OER, leading to limited catalytic stability. Heterogeneous metal atoms or compounds are therefore introduced in the 2D Ni MOFs to modulate the electronic structure for enhanced intrinsic catalytic activity and avoid the agglomeration for improved catalytic stability. Some improvement has been achieved (Table 1.1), while the detailed understanding of OER catalytic mechanism is still ahead of us.

1.1.3.2 2D Co-based MOFs hybrids

2D Co-based MOFs also exhibit high catalytic OER performance, as summarized in Table 2. 2D Co-based MOFs with a range of organic linkers have been recently studied.^[49, 63, 73-12]

^{75]} For example, Fischer's group^[73] utilized 2D cobalt ion (Co²⁺) and benzimidazole (bIm) to prepare zeolite-imidazole framework (Co-ZIF-9(III)) nanosheets (thickness: 2-4 nm) *via* mechanochemical grinding and subsequent ultrasonication assisted liquid-phase exfoliation. The Co-ZIF-9(III) nanosheets exhibited a η of 380 mV at 10 mA cm⁻², better than that of bulk Co-ZIF-9 counterparts (η : 420 mV), which can be explained by more accessible active sites and faster mass diffusion than bulky MOF crystals. Similarly, the introduction of a second organic linker to 2D Co-based MOFs ^[74, 75] by top-down approaches can also enhance OER catalysis outperforming bulky Co MOFs. Besides, Bu and co-workers^[63] provided a bottom-up method to *in-situ* grow quasi-2D Co MOF nanoarrays consisting of Co²⁺ and organic linkers of thiophenedicarboxylic acid (H₂TDC) on NF substrates (Co MOF/NF), with a slight reduction in η relative to drop-casting the same MOF powders on NF (270 vs 297 mV at 10 mA cm⁻²). The enhanced catalytic performance was mainly attributed to the well attachment of the catalyst on the hierarchical and porous NF skeleton for fast electron/ion transfer.

Catalyst	Overpotential	Tafel	Catalytic stability	Loading	Substrate	Ref.
	@ 10 mA cm ⁻²	slope	(h)	(mg cm ⁻		
	(mV)	(mV dec ⁻¹)		²)		
Exfoliated Co-ZIF-	380	55	10	0.21	GCE	[73]
9(III)						
2D-Co-NS@Ni	211	46	96	N/A	NF	[49]
Ultrathin Co-MOF	263	74	3.3	0.25	GCE	[74]
Co-MONs	309	75.7	30	N/A	CP^{a}	[75]
Co MOF/NF	270	75	30	N/A	NF	[63]
Co-UMOFNs	371	103	N/A	0.2	GCE	[43]
Co-MOF	341	111	N/A	N/A	GCE	[76]
Co@HPA-MOF	386	61	N/A	0.21	GCE	[77]
CoNi(1:1)-MOF	265	56	20	N/A	Cu foil	[76]
Co-Ni@HPA-MOF	320	58	N/A	0.21	GCE	[77]
Co3Fe-MOF	280	38	10	0.42	GCE	[78]
FeCo-MNS-1.0	298	21.6	13.9	0.36	GCE	[79]
CoNi-MOFNA	$\frac{1}{215}$	51.6	300	2.0	Co ₉ Ni ₁	[56]
					foam	
CoFe-MOF	277	31	N/A	0.34	GCE	[80]
Ti ₃ C ₂ T _x -CoBDC	410	65	N/A	0.21	GCE	[81]
Co-BPDC/Co-BDC-3	335	72.1	80	0.28	GCE	[82]
CoBDC-Fc-NF	178	51	80	1.80	NF	[83]

 Table 1.2 OER activity of reported 2D Co-based MOFs electrocatalysts in 1 M KOH.

^a CP: carbon paper.

In contrast to pure 2D Co MOFs, 2D hybrid Co-based MOFs with metal heteroatoms (e.g. Fe, Ni), inheriting the controllable morphology and allowing for tailoring of the integral electronic structure, have demonstrated improved OER catalytic activity.^[56, 76-80] For example, Lee *et al.*^[76] grew 2D CoNi-MOFs with different atom ratios of Co and Ni on Cu foil substrates using a hydrothermal procedure. The optimal material, CoNi(1:1)-MOF (thickness: 5.3 nm), showed a η of 265 mV at 10 mA cm⁻², lower than that of pure Co MOF (341 mV). *In-situ* conducting AFM and two-point conductivity measurements indicated that the good catalytic activity was related to the dominant (220) facets with enhanced conductivity along the Z-axis, facilitating the electron transfer from substrate to active centers. Similarly prepared 2D bimetallic Co-based MOFs including Co-Ni@HPA-MOF (HPA: hypoxanthine)^[77] and Co₃Fe-MOF^[78] also showed enhanced OER performance compared to the corresponding single-metal Co MOFs.

In addition, Zhu and co-workers^[79] designed a unique template-assisted approach for ironcobalt MOF-74 nanosheets (FeCo-MNS) by solvothermal reactions (Fig. 1.5a), where the as-prepared iron-cobalt oxide nanosheets (FeCo-ONS) were used as sacrificial templates for the reaction with different amounts of 2,5-dihydroxyterephthalic acid (H₄dobdc). TEM and AFM images (Fig. 1.5b-c) indicated that FeCo-ONS transformed to the optimal FeCo-MNS-1.0 nanosheets (thickness: 2.6 nm). FeCo-MNS-1.0 (Fig. 1.5d) showed superior OER performance with a lower η (298 mV at 10 mA cm⁻²) and an unusually Tafel slope (21.6 mV dec⁻¹) compared with those of FeCo-ONS, cobalt MOF-74 nanosheets (Co-MNS) and iron-cobalt bulk MOF-74 (FeCo-MB). X-ray absorption fine structure (XAFS) characterization demonstrated an increased amount of coordinatively unsaturated metal sites (CUMSs) on FeCo-MNS-1.0, which contributed to the superior OER activity. Besides, Jia et al.^[80] prepared hierarchically structured 2D CoFe-MOFs using ultrasound-assisted synthesis and subsequent solvothermal treatment. This route could remove unstable domains and generate continuous mesopores on the 2D MOFs in-situ, resulting in 2D CoFe-MOFs with hierarchical porosity using holey ultrathin crystalline nanosheets (thickness: 1.3 nm). The designed 2D porous structure significantly improved the OER catalytic performance with a η of 277 mV at 10 mA cm⁻².



Fig. 1.5 a) Schematic illustration of the sacrificial 2D metal oxide approach to achieving the conversion of M-ONS to M-MNS in the presence of H₄dobdc ligand. b) TEM image of FeCo-ONS. c) TEM image of FeCo-MNS-1.0. d) OER polarization curves of FeCo-ONS, FeCo-MNS-1.0, iron-cobalt bulk MOF-74 (FeCoMB) and Co-MNS in 0.1 M KOH. Reprinted with permission from Ref.^[79]. Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

There are also reports focusing on the combination of heterogeneous components and 2D Co-based MOFs to optimize the integral electronic structure.^[81-83] Such a hybridization can also prevent MOF nanosheet agglomeration. For instance, Huang's group^[81] incorporated 2D cobalt 1,4-benzenedicarboxylate (CoBDC) with $Ti_3C_2T_x$ nanosheets via an inter-diffusion reaction-assisted process. An OER η of 410 mV at 10 mA cm⁻² was optained with the hybrid Ti₃C₂T_x-CoBDC, which was an improvement over the pure CoBDC. Metal-like $Ti_3C_2T_x$ nanosheets promoted the charge transfer kinetics of the hybrid material and prevented the porous CoBDC MOF layers from aggregating. Besides, Ni et al.^[80] reported a 2D Co-BPDC (BPDC: 4,4'-biphenyldicarboxylate)/Co-BDC heterojunction nanostructure for OER electrocatalysis. Co-BPDC was grown on presynthesized Co-BDC nanosheets under stirring at 80 °C for different durations. The optimal electrocatalyst, Co-BPDC/Co-BDC-3, showed better OER performance (n of 335 mV at 10 mA cm⁻²) than that of Co-based MOFs. In addition, Li and co-workers^[83] incorporated non-bridging linkers such as carboxyferrocene (Fc) into Co₂(OH)₂(C₈H₄O₄) MOF nanosheets (CoBDC-Fc). DFT simulation predicted that the modification of the electronic structure for CoBDC-Fc could change the band gap and charge distribution, thus optimizing adsorption strengths of OER intermediates (Fig. 1.6a). After introducing Fc as a modulator in the CoBDC, SEM and TEM images (Fig. 1.6b-d) of CoBDC-Fc showed

nanosheet-like morphologies and EDS mappings (Fig. 1.6e) clearly indicated that Fc was homogeneously incorporated. CoBDC-Fc (Fig. 1.6f-i) delivered a low η of 178 mV at 10 mA cm⁻², a Tafel slope of 51 mV dec⁻¹ and long-term stability (80 h) at a high current density of 100 mA cm⁻². DFT calculations revealed that the PDS for CoBDC was the formation of *OH with a large energy barrier (3.74 eV). This was reduced significantly on Fc incorporation, which shifted the PDS to the generation of *O with a much lower energy barrier (1.85 eV).

Concludingly, 2D Co-based MOFs hybrids have been widely investigated for OER. Heterogeneous metal atoms or compounds are introduced in the 2D Co-based MOFs to tune the electronic structure and surface physicochemical features for enhanced OER catalytic activity. Compared with 2D Ni-based MOF hybrids, a wider range of 2D Cobased MOF hybrids are obtained (Table 2), demonstrating better OER catalytic performance and deeper understanding of the catalytic mechanisms.



Fig. 1.6 a) Modulating the electronic structure of CoBDC MOF *via* introduction of missing linkers for improved OER. b-c) SEM and d) TEM images of CoBDC-Fc-NF. e) STEM image and STEM-EDS mappings of CoBDC-Fc-NF. f) LSV curves, g) overpotentials at different current densities and h) Tafel plots of different catalysts toward OER in 1 M KOH. i) Operational stability of CoBDC-Fc-NF for 80 h at 100 mA cm⁻² in 1 M KOH. Reprinted with permission from Ref.^[83]. Copyright (2019) Nature Publishing Group.

1.1.3.3 2D Cu-based MOFs hybrids

In addition to the widely investigated 2D Ni- or Co-based MOF hybrids for OER electrocatalysis, some researchers have explored the potentials of other 2D MOFs, especially Cu-based ones.^[84-86] For example, Fu and co-workers^[84] prepared CoNi-Cu(BDC) electrocatalysts by utilizing Cu(BDC) as a template with a facile one-step impregnation

approach, delivering a lower n of 327 mV at 10 mA cm⁻² than the pure Cu(BDC). The enhanced OER activity may be attributed to the transformed 2D lamellar morphology and synergistic effects of the metal species. Thus, doping transition metal heteroatoms (Ni, Co) into the 2D Cu-based MOFs to modify the electronic structure could be a promising route for improved OER catalysis. Further, combining the hybrid 2D Cu-based MOFs with conductive materials (i.e., graphene) can improve the electrical conductivity for fast electron transfer, leading to enhanced OER catalytic activity. As an example, a 2D bimetallic porphyrinic MOF (Co-CuTCPP) combined with reduced graphene oxide (Co-CuTCPP/rGO) exhibited a OER catalytic performance, with a η of 396 mV at 10 mA cm⁻² and Tafel slope of 58 mV dec^{-1,[85]} In addition, Fang's group^[86] combined CoCu-based zeolitic imidazolate framework nanosheets (CoCu-ZIF NSs) and graphdiyne (GDY), showing good OER catalytic activity with a low n of 250 mV at 10 mA cm⁻² and Tafel slope of 57 mV dec⁻¹. This material is believed to be benefiting from the fast electron transport ability and high number of exposed active sites. Considering that the price of Cu is lower than those of Ni and Co, approaches to preparing excellent 2D Cu-based MOFs as OER electrocatalysts is very appealing.

1.1.4 2D MOFs derivatives for the OER

Although 2D MOF electrocatalysts are intensively studied in the past few years, the unsatisfied stability and conductivity of 2D MOFs limit their further OER application. For example, Biradha et al.^[65] synthesized a Ni MOF (NH₂TA-MOF) composed of a flexible tripodal tris-pyridyl ligand and 2-aminoterpthalate (H₂NTA), displaying a η of 356 mV at 10 mA cm⁻² and a poor stability of 3.3 h. Alternatively, 2D MOF derivatives, either with or without metal component, obtained via straightforward pyrolysis in certain atmosphere and other post-treatment routes can potentially overcome these challenges.^{[50,} ^{87]} Among these, MOF-derived metal-free carbon materials exhibit relatively poor OER catalytic performance,[88, 89] which is likely due to water oxidation occurring at overpotentials, where oxidation of the carbon components can occur compromising the structure. It thus highlights the importance of metal components, which can be oxidized into a high-valence state and recycled between valences during OER catalysis, as the OER active site. 2D MOF-derived metal-based components (e. g. metal/alloys, metal oxides/chalcogenides or metal phosphides/hydroxides etc.) containing carbon materials demonstrate enhanced OER activity and stability.^[50, 90] 2D MOF derivatives can not only efficiently inherit the morphology and structure of the 2D MOF precursors, but display porous or hierarchical nanostructures of carbon with exposed metal sites on the surface for improved mass transfer. Moreover, the formed carbonaceous components originating from the organic linkers can improve the integral electrical conductivity for fast electron transfer and impart structural stability during OER. In this section, we summarize recent advances (Table 3) in 2D transition metal-based MOF derivatives for OER electrocatalysis.

Catalyst	Overpotential	Tafel slope	Catalytic	Loading	Substrate	Ref.
-	@ 10 mÅ cm ⁻² (mV)	(mV dec ⁻¹)	stability (h)	$(mg \ cm^{-2})$		
Ni@NC	280	45	10	0.31	GCE	[91]
HXP@NC800	307	48	8	0.4	GCE	[92]
Co-NCS@CNT	360	92.9	N/A	0.17	GCE	[93]
Co@N-carbon	400	61	N/A	0.21	GCE	[94]
FeNi@CNF	356	62.6	24	0.34	GCE	[95]
Ni-MOF-250	$250@50~{ m mA~cm^{-2}}$	88.6	20	N/A	NF	[96]
Co_3O_4/C_{BDC} nanosheet	208	50.1	36	N/A	Ni foil	[97]
arrays						
CoTFBDC/EG_250	365	39.8	10	0.25	GCE	[98]
Co ₃ O ₄ flakes array	205	65.3	24	N/A	NF	[99]
$M-Co_3O_4$	370	74.0	25	N/A	NF	[100]
Co–MOF/H ₂	312	89.7	40	N/A	NF	[101]
$CC@NiCo_2O_4$	340	72	20	0.60	$\mathbf{C}\mathbf{C}$	[102]
Fe1Co3/Vo-800	260	53	15	N/A	$\mathbf{C}\mathbf{C}$	[103]
NiCo/Fe ₃ O ₄ /MOF-74	238	29	36	0.76	GCE	[104]
$FeNi_3$ - Fe_3O_4	234	37	20	0.28	GCE	[105]
NPs/MOF-CNT						
Ni-BDC@NiS (12h)	$330@20 \text{ mA cm}^{-2}$	62	12	0.20	Ni foil	[106]
$Ni-Ni_3S_2$ @Carbon	284.7	56	8	0.20	GCE	[107]
Nanoplates						
Co_9S_8 @TDC-900	330	86	7	N/A	GCE	[108]
Ni-Co-S HPNA	270	74	24	N/A	$\mathbf{C}\mathbf{C}$	[109]
Co-P@/NC-800	370	79	12	0.28	GCE	[110]
CoP-NS/C	292	64	24	0.14	GCE	[111]

Table 1.3 OER activity of reported 2D MOF-derived electrocatalysts in 1 M KOH.

HP-CoP NA/NF	258	91.7	12	N/A	NF	[112]
$Co_{0.7}Fe_{0.3}P/C$	270	27	N/A	0.40	GCE	[113]
CoNi	324	33	2.8	0.20	GCE	[114]
hydroxide UNSs						
FeCo _{0.5} Ni _{0.5} -LDH	248	38	50	N/A	Cu foil	[115]

1.1.4.1 Metals/alloys

Metal/alloy nanostructures can be synthesized from 2D MOF precursors pyrolyzed at high temperature (> 600 °C) and inert atmosphere. The metal/alloy nanostructure and carbonaceous components generated, originating from the metal units and organic ligands in the 2D MOFs, respectively, ensure high conductivity and active site concentration for OER.^[91-95] Metal/alloy nanostructures are formed by the reduction of the metal units of the 2D MOFs with the organic linker as the reducing agents at high temperature. Metal nanoparticles (e. g Ni or Co) embedded in carbon components with different compositions and morphologies derived from 2D MOFs are of special interest. Xu's group^[91] constructed Ni nanoparticles (Ni NPs) locked in few-layered nitrogen-doped graphene (Ni@NC) obtained by high-temperature annealing of Ni MOFs in nitrogen atmosphere (Fig. 1.7a). SEM and TEM demonstrated a hierarchical structure of the Ni MOFs comprising aggregated 2D nanosheets with a lateral size of 500–800 nm (Fig. 1.7b and c). The carbonized product Ni@NC displayed a spheroidal nanostructure (diameters: 20-30 nm, Fig. 1.7d and e). TEM and HRTEM further revealed that the spheres were composed of Ni nanoparticle cores and 3-5 layers graphene shells (Fig. 1.7f and g). Ni@NC exhibited a low η of 280 mV at 10 mA cm⁻² and excellent catalytic stability (duration of 10 h at 1.52 V vs. RHE) for OER (Fig. 1.7h and i). In addition, Liu and co-workers^[92] designed a novel approach to prepare distorted hexagonal (3,4)-connected Ni₂(BDC)₂(DABCO) (BDC = 1,4-benzenedicarboxylic acid, DABCO = 1,4-diazabicyclo[2.2.2]octane) framework nanoplates, which were transformed to Ni@N-doped carbon nanoplates by pyrolysis, exhibiting a n of 307 mV at 10 mA cm⁻² for OER. Meanwhile, Dong et al.^[93] reported 2D carbon framework-encapsulated highly-dispersed Co nanoparticles on N-doped carbon nanotubes (Co-NCS@CNTs) by carbonizing 2D ZIF (ZIF-L) nanosheets in an atmosphere of H₂ and Ar. Co-NCS@CNTs exhibited OER catalytic activity with a η of 360 mV at 10 mA cm⁻². Similar Co@N-carbon nanosheets^[94] were also synthesized showing a η of 400 mV at 10 mA cm⁻². 2D MOF-derived alloy nanoparticles embedded in carbon components have been also explored for OER electrocatalysis. Alloys can provide additional synergetic effects between metal components and tenability of the electronic structure for enhanced OER performance.^[116, 117] Gao et al.^[95] prepared FeNi alloy nanoparticles incorporated in carbon nanoflowers (FeNi@CNFs) using 2D bimetallic nanosheet-assembled nanoflowerlike MOFs as precursors. The optimized FeNi@CNFs showed a n of 356 mV at 10 mA cm⁻ ², benefiting from the aligned nanosheets and complex nanoflower morphology for rich active sites and fast electron transfer. Derived metals/alloys nanostructures can thus be formed by reduction of the metal units of the 2D MOFs with the organic linker as the reducing agents at high temperature. Most current related catalysts exhibit relatively weak catalytic stability (Table 3). New strategies are needed to explore for robust OER electrocatalysts.



Fig. 1.7 a) Schematic illustration of the preparation of Ni@NC materials from Ni-based MOF precursors. b) SEM and c) TEM images of the Ni-based MOFs. d and e) SEM, f) TEM, and g) HRTEM images of Ni@NC-800. The inset of (g) is a schematic illustration of the Ni@NC structure. h) The OER polarization curves of various Ni@NC samples and commercial IrO₂ catalyst in 1.0 M KOH solution. i) Polarization curves of before and after 1000 potential cycles of Ni@NC-800. The inset of (i) is the chronoamperometric curve at 1.52 V vs. RHE for 10 h. Reprinted with permission from Ref.^[91]. Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.1.4.2 Metal oxides/chalcogenides

2D MOF-derived metal oxides can be prepared with maintained morphologies and structures from the 2D MOF precursors, because relatively low annealing temperatures (200-600 $^{\circ}$ C) are needed. The derived carbon components can serve as conductive and 22

protective frameworks by enclosing the metal oxides from the metal sites of the 2D MOFs.^[50, 90] 2D MOF-derived metal oxides, such as NiO^[96, 97], Co₃O₄^[97-100] and hybrid metal oxides encapsulated in carbon nanostructures^[101-105], are attracting growing attention. For instance, He *et al.*^[96] fabricated ultrafine NiO nanoparticles (NPs) within ultrathin 2D Ni MOFs by partial heating decomposition. Benefiting from the ultrathin 2D nanosheet-like structure and highly active sites from the defect-rich NiO NPs, the optimized Ni-MOF-250 demonstrated excellent OER catalytic performance with a η of 250 mV at 50 mA cm⁻², achieving an industrially relevant current density of 1000 mA cm⁻² at a small η of 410 mV. Besides, Li and co-workers^[97] prepared 2D Co₃O₄/C_{BDC} composites on Ni foil by annealing, exhibiting a η of 208 mV at 10 mA cm⁻². This was attributed to the improved conductivity and more exposed active sites offered by the 2D structure with rich hierarchical pores of the derived carbon.

Meanwhile, 2D MOF-derived bimetallic or trimetallic oxides are believed to have unique hetero-structures and modified electronic structure, thus leading to better OER catalytic performance than single metal oxide-based electrocatalysts. Zhou et al.^[103] performed plasma-enabled Fe doping in 2D Co MOF nanosheets with considerable oxygen vacancies (Vo), which were carbonized into triangular-shaped "cheese-like" Fe/Co-carbon nanosheets. The optimized Fe1Co3/Vo-800 exhibited a good OER performance with a n of 260 mV at 10 mA cm⁻². The authors claimed that filling the oxygen vacancies with Fe heteroatoms helped to achieve the unique heterostructure for fast electron transfer. Besides, Li's group^[104] reported a controlled partial pyrolysis of trimetallic NiCoFe-MOF-74 in nitrogen atmosphere at 400 °C for 60 min to construct robust NiCo/Fe₃O₄ heteroparticles within 2D MOF-74 (Fig. 1.8a). STEM imaging of NiCoFe-MOF-74 (Fig. 1.8b) showed a nanosheet-like structure. Numerous uniform nanoparticles were formed in the 2D MOFs structure after carbonization (Fig. 1.8c). High-resolution STEM images and corresponding STEM-EELS elemental mapping of NiCo/Fe₃O₄ nanoparticles (Fig. 1.8d-h) indicated the presence of metallic NiCo alloy cores with thin Fe₃O₄ shells. The as-prepared NiCo/Fe₃O₄/MOF-74 delivered remarkable OER performance (Fig. 1.8i-j) with a n as low as 238 mV at 10 mA cm⁻² and catalytic stability of 36 h. DFT calculations revealed the PDS of pure Fe_3O_4 was the escape of the O_2 product with an energy barrier of 1.56 eV, while the PDS was the formation of *O on the NiCo/Fe₃O₄ surface representing a slightly smaller energy barrier (1.48 eV). These results confirm that the underlying NiCo alloy promoted the OER activity of Fe_3O_4 through exchanging stabilized active oxygen species. Compared with other 2D MOFs derivatives, 2D MOFs derived metal oxides could easily maintain stable crystalline structure in ambient conditions with high catalytic activity. Meanwhile, the facile synthetic process can promote scalable production with low cost.


Fig. 1.8 a) Scheme of the fabrication of trimetal NiCoFe-MOF-74 and the partial pyrolysis of NiCoFe-MOF-74 to NiCo/Fe₃O₄/MOF-74. STEM images of b) NiCoFe-MOF-74 and c) the derived NiCo/Fe₃O₄/MOF-74 after controlled partial pyrolysis at 400 °C for 1 h. d) High-resolution STEM image of NiCo/Fe₃O₄ nanoparticle and (e) corresponding STEM-EELS elemental mappings of NiCo/Fe₃O₄ showing the hierarchical elemental distributions of Ni, Co, and Fe. f–h) Enlarged high-resolution STEM images taken from the areas highlighted in d), with simulated atomic models overlapped on the images. i) 24

OER polarization curves of NiCoFe-MOF-74 and the derived partial pyrolyzed and completely pyrolyzed samples at 1600 rpm in O₂ saturated 1.0 KOH. j) Relative chronoamperometric test under a constant potential of 1.47 V. Reprinted with permission from Ref.^[104]. Copyright (2018) American Chemical Society.

Similar to the features of 2D MOF-derived metal oxides for OER, 2D MOF-derived metal chalcogenides (Ni-, Co- or NiCo-based) are also explored as oxygen evolution electrocatalysts.^[106-109] The MOF-derived transition metal chalcogenides have a tunable metal-sulfur coordination environment and good electrical conductivity for OER.^[118] For example, Li et al.^[106] developed a liquid-state partial sulfurization to prepare Ni-BDC@NiS OER catalysts. The 2D [Ni₃(OH)₂(1,4-BDC)₂-(H₂O)₄] 2H₂O (Ni-BDC: 1,4-BDC) = 1,4-benzenedicarboxylate) MOF was *in-situ* grown on the surface of Ni foil, which was then immersed in a thioacetamide (TAA) solution for sulfurization of different durations. The optimal Ni-BDC@NiS (12 h sulfurization treatment), with ordered Ni-BDC nanosheets for more accessible active sites and efficient mass transfer, demonstrated a n of 330 mV at 10 mA cm⁻². In comparison to liquid-state partial sulfurization, solid-state sulfurization is more controllable and the generated carbon species could further enhance the electrical conductivity and improve the structural stability during OER process. Liu and co-workers^[107] reported 2D free-standing nitrogen-doped Ni-Ni₃S₂@carbon nanoplates by annealing NiSO₄ based MOF nanoplates as the precursor through a "selfsulfidation" procedure in an inert atmosphere. The resulting nanoplates were constructed by a carbon matrix with homogenously embedded Ni-Ni₃S₂ nanoparticles, exhibiting a n of 284.7 mV at 10 mA cm⁻² for OER. Similar self-sulfidation methods have been adopted to synthesize N, O and S-tridoped carbon matrix encapsulated with Co₉S₈ nanocomposites (Co₉S₈@TDC) via direct carbonization of a 2D Co MOF [Co(BDC)₂(SPDP)₂(DMF)(H₂O)] 1,4-benzenedicarboxylic (H₂BDC: acid. SPDP: 4,40-(sulfonylbis(4,1phenylene))dipyridine, DMF: N,N-dimethylformamide). The Co₉Ss@TDC showed reasonable OER performance with a n of 330 mV at 10 mA cm⁻². Besides, Zhou and coworkers^[109] synthesized hierarchical porous metal sulfide (Ni-Co-S) nanosheets arrays (HPNA) directly on conductive CC substrates using 2D CoNi MOF nanosheet arrays as precursors, which underwent an initial annealing and a subsequent sulfurization. The hierarchical porous nanostructures, affording high specific surface area, abundant active sites and short diffusion paths, ensured a better OER performance of the Ni-Co-S HPNA with a η of 270 mV at 10 mA cm⁻² than that of Co-S HPNA. Compared with 2D MOFderived metal oxides (Table 3), most 2D MOF-derived metal chalcogenides electrocatalysts suffer from insufficient stability, which is likely due to that metal chalcogenides transformed to metal oxides to be active for OER,^[118, 119] thus suffering irreversible component and structure change with long-term operation. Exploring novel hybrids to find more robust 2D MOF-derived metal chalcogenides could be a possible solution. In summary, 2D MOFs derived metal oxides/chalcogenides have been widely investigated as OER electrocatalysts, and much progress on the OER catalytic capability and understanding of the catalytic mechanisms have been obtained over the past several years.

1.1.4.3 Metal phosphides/hydroxides

Metal phosphides are emerging as a class of OER catalysts that display good electrical conductivity and metalloid characteristics.^[120, 121] The 2D MOF-derived carbon layer is expected to enhance the electron transfer and limit the agglomeration of metal phosphide nanoparticles. Thus, 2D MOF-derived metal phosphide-carbon composites show appealing OER electrocatalytic properties.^[110-113] For example, Du et al.^[110] reported the synthesis of cobalt phosphide nanoparticles embedded in N-doped carbon materials (Co-P@NC) using 2D Co-based porphyrin paddlewheel framework-3 (PPF-3) nanosheets as the sacrificial template. The template was initially carbonized followed by low temperature phosphorization using NaH₂PO₂ as the phosphor source. The Co-P@NC demonstrated a η of 370 mV at 10 mA cm⁻² for OER. Using a similar phosphorization approach, Zhu and co-workers^[111] prepared a cobalt phosphide nanosheet and amorphous carbon composite (CoP-NS/C) using as-prepared 2D Co-ZIF nanosheets as the template. The MOF-derived porous crystalline CoP nanosheets provided highly-exposed active sites. and the existence of carbon afforded fast electron transfer, ensuring the good OER performance with a η of 292 mV at 10 mA cm⁻². Further, constructing metal phosphidebased composites on the NF substrate shows enhanced OER performance, due to highly exposed active sites, shortened ion diffusion path and promoted gas release during OER. Gong and co-workers^[112] designed hierarchical porous CoP nanoarrays on NF (HP-CoP NA/NF), exhibited good OER electrocatalytic activity with a low η of 258 mV at 10 mA cm⁻². A three-step procedure was followed: i) Interconnected 2D cobalt-based MOFs were grown on NF via an aqueous solution reaction at room temperature; ii) The MOFs were uniformly converted into porous CoP arrays through a Co²⁺-etching process and iii) subsequent phosphorization. Meanwhile, additional metal doping to the 2D MOF-derived metal phosphides is believed to modulate electronic structures to lower energy barriers, resulting in bimetallic phosphides typically outperforming monometallic counterparts for OER. Wang et al.[113] fabricated Co1-xFexP/C nanosheets using 2D CoFe MOFs as precursors, retaining the well-defined 2D morphology of the MOFs. The optimized Co_{0.7}Fe_{0.3}P/C showed good OER catalytic performance with an as low as 270 mV at 10 mA cm^{-2} . The enhanced OER performance was attributed to the 2D morphology of the carbon matrix and the ultrafine character of Co1-xFexP nanoparticles. Moreover, moderate iron doping preserved the catalytically active sites and improved the oxidation ability of the surfaces of Co1-xFexP nanoparticles. Overall, 2D MOF-derived metal phosphides demonstrate relatively good OER catalytic performance, but in-depth understanding of OER catalytic mechanism is still lacking. More *in-situ* technologies and DFT simulations to study the OER active sites of 2D MOF-derived metal phosphides are critically required.



Fig. 1.9 a) Schematic illustration of *in-situ* synthesis of LDHs from oxalate MOFs. SEM images of (b) FeCo_{0.5}Ni_{0.5}-MOF and (c) FeCo_{0.5}Ni_{0.5}-LDH. d) HRTEM images of FeCo_{0.5}Ni_{0.5}-LDH. e) STEM images of FeCo_{0.5}Ni_{0.5}-LDH and corresponding EDS mapping of C, O and Fe, Co and Ni. f) iR-corrected LSV curves and g) Tafel plots of various catalysts in 1 M KOH. h) Operational stability of FeCo_{0.5}Ni_{0.5}-LDH. Reprinted with permission from Ref.^[115]. Copyright (2019) Elsevier.

2D MOF-derived metal hydroxides especially layered double hydroxides (LDHs) with better ionic conductivity than the conventional bulk LDHs, are attracting intensive attention for OER.^[114, 115] For instance, Ding *et al.*^[114] prepared 2D CoNi hydroxide ultrathin nanosheets (UNSs) *via* liquid exfoliation of a CoNi MOF precursor in 0.1 M KOH. The obtained CoNi hydroxide UNSs demonstrated a η of 324 mV at 10 mA cm⁻² for OER. In addition, Gu and co-workers^[115] have initially prepared a series of oxalate MOFs (Fe_xNi_{1-x}-MOF) grown on Cu foils, which were *in-situ* transformed into LDHs in 1 M KOH for 30 min (Fig. 1.9a). FeCo_{0.5}Ni_{0.5}-MOF (Fig. 1.9b) showed an octahedron morphology with a clearly layered structure, the derived FeCo_{0.5}Ni_{0.5}-LDH showed a rougher structure (Fig. 1.9c and d) composed of ultrathin hierarchical nanosheets (thickness: 1 nm). The STEM images of FeCo_{0.5}Ni_{0.5}-LDH and the corresponding EDS mapping images (Fig. 1.9e) showed a uniform distribution of elemental C, O, Fe, Co and Ni. The optimized FeCo_{0.5}Ni_{0.5}-LDH delivered superior OER catalytic activity (Fig. 1.9f-h) with a low η of 248 mV at 10 mA cm⁻², a Tafel slope of 38 mV dec⁻¹ and long-term catalytic stability over 50 h. The dynamic OER process at the electrocatalyst surface was characterized by *in-situ* Raman spectroscopy. The Raman spectra of FeCo_{0.5}Ni_{0.5}-LDH exhibited a signal at ~ 530 cm⁻¹ at 1.1 V vs. RHE (no OER), ascribed to the Ni-O stretching mode.^[122] When the potential was raised to 1.6 V vs. RHE (OER on-going), the Raman spectra showed new peaks at ~470 and 550 cm⁻¹ arising from the NiOOH,^[123] indicating that the OER active sites were Ni atoms. Besides, the electron paramagnetic resonance (EPR) spectroscopy of FeCo_{0.5}Ni_{0.5}-LDH indicated the modulating effect of Co cation on the electronic structure of FeNi-LDH. In summary, 2D MOF-derived metal hydroxides have recently attracted increasing interest for OER electrocatalysis. Heterocomponents (atoms, molecules etc.) can straightforwardly be incorporated in the layered host matric for tunable electronic structure and enhanced OER catalytic activity, but further comprehensive studies of the OER focused on the metal hydroxides are needed as noted.



Fig. 1.10 a) The number of related publications during the past years (2016-2019). Data also presented in Table 1, 2 and 3. b) Chronological trend in overpotential of OER catalysts including 2D Ni-based MOFs, 2D Co-based MOFs and 2D MOFs derivatives in alkaline electrolytes. The grey dashed line shows the overpotential of RuO₂ in alkaline electrolytes. Red line shows the corresponding trend of overpotential. c) The experimental data summary between overpotential and catalytic stability of 2D Ni-based MOFs, 2D Co-based MOFs and 2D MOFs derivatives in alkaline electrolytes.

1.1.5 Perspectives

I have summarized the motivation for efforts in the areas of preparation, characterization, and use of 2D transition metal MOFs and their derivatives, including metals/alloys, metal oxide/chalcogenides and metal phosphides/hydroxides, as OER electrocatalysts reported over the past five years with increasing publications (Fig.1.10a), and the evolution and performance summarized in Fig.1.10b-c. As shown in Fig.1.10b, many of these materials exhibit superior catalytic activity ($\eta < 300 \text{ mV}$ at 10 mA cm⁻²) compared to the noblemetalbased catalysts such as RuO_2 , and considerable stability with only negligible decay after tens of operating hours as shown in Fig.1.10b and Table 1.1-1.3. Comparing to the evolution of other OER catalysts^[124] where the overpotential dropped from around 400 mV to 200 mV over 7 years, the evolution of performance has been similar for 2D MOFs, with no clear trend of any specific type seeming likely as best leading to future improvements. The advantages and disadvantages of the materials were discussed. Although exciting scientific achievements have been reported, challenges to be overcome and new perspectives to be explored still remain in this field: First, the limited stability and strong tendency of pristine 2D MOFs to agglomerate during OER are limitations to their long-term applications. Despite approaches such as introduction of metal ion/metalorganic components into the 2D MOFs and *in-situ* 2D MOF generation on NF have been adopted to improve the structural stability of 2D MOFs and prevent agglomeration, more efficient and facile strategies should be developed. Damage to surface morphology and pore structure of 2D MOF derivatives during operation is also a critical issue, which could be addressed, for example by suitable partial annealing methods reported by Li et al.^[104] Secondly, the presently reported 2D MOFs rely on expensive organic ligands and their derivatives, and the OER electrocatalysts obtained are mostly evaluated under alkaline solution conditions. Exploring cheap raw materials and scale-up strategies for reproducible 2D MOF-based electrocatalysts with superior OER catalytic activity and high stability over a wide range of pH values are urgently needed, especially those can operate in neutral electrolytes. Thirdly, bifunctional electrocatalysts capable of simultaneously catalyzing hydrogen evolution reaction and OER, or dioxygen reduction reaction and OER, hold great prospects for simplifying setups for water splitting and secondary metal air batteries.

So far, the FeP/Ni₂P^[125] catalyst exhibits a lowest overpotential (154 mV@10 mA cm⁻²) for OER, and the currently best OER electrocatalyst (CoBDC–Fc–NF) in 2D MOFs and their derivatives delivers an ultra-low overpotential (178 mV@10 mA cm⁻²)^[83]. However, most OER catalysts cannot provide a large OER current density (> 200 mA cm⁻²)^[125] with relatively small overpotential required by the industry. Besides, although the FeCoW oxyhydroxides shows a superior OER catalystic stability with more than 500 h,^[126] the life time of most current OER catalysts is not enough for the industrial application (negligible decay after at least hundreds of operating hours). The current research of OER

electrocatalysts mainly focuses on the understanding of the fundamental and properties. It can be suggested that upscaling to test OER performance with industrial level (higher current density and life time) system would be interesting. Thus, the developed OER electrocatalysts can be used for practical application in secondary metal air batteries and water splitting in the near future.

1.2 Recent advance of transition metal-based materials for lithium ion batteries

1.2.1 Introduction

Renewable energy conversion and storage technologies are attracting growing attention due to the fossil energy exhaustion and global environmental issues. Rechargeable lithium ion batteries (LIBs) as an efficient and promising candidate, have been widely investigated and applied in the past 30 years, since the company Sony developed the first commercialized LIBs in 1991.^[127] Recently, John Goodenough, M. Stanley Whittingham and Akira Yoshino jointly received the 2019 Nobel Prize in Chemistry, due to their significant contribution to the development of LIBs. The energy density of LIBs is over 250 Wh kg⁻¹ at cell level (18650-type cell). Besides, the overall cost (Fig. 1.11) has gone down substantially from initially about 1000 to now less than 200 \in kWh⁻¹.^[128, 129] Nextgeneration LIBs (Fig. 1.11) featuring larger capacity, faster discharge/charge, better safety and lower cost^[130] are critical.



Fig. 1.11 Cost of Li-ion battery packs based on a battery electric vehicle (BEV) scenario of cumulative sales of 60 million BEV by 2030. Reprinted with permission from Ref.^[130]. Copyright (2019) Elsevier.

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A LIB (Fig. 1.12A) is composed of three major components (cathode, electrolyte and anode). The cell voltage depends on the electrochemical potential of each electrode (μ_{anode} and $\mu_{cathode}$), but limited by the related positions to the HOMO (highest occupied molecular orbitals)-LUMO (lowest unoccupied molecular orbitals) of the electrolyte. Thus, the electron transfer can lead to the electrolyte reduction in anode materials and the electrolyte oxidation in cathode materials during cycling. The maximum cell-voltage (Fig. 1.12B) can be reached in a LIB with the maximum electrochemical potential difference of anode and cathode if the electrolyte is stable.^[131] This Ph.D. project focuses on the anode materials of LIBs. Graphite is greatly used as the anode material for LIBs, however, the limited theoretical capacity (372 mA h g⁻¹) cannot meet the increasing demand of next-generation LIBs. Thus, high-performance and low-cost new anode materials (Fig. 1.12C) are required.



Fig. 1.12 (A) The discharge-charge process of LIBs, not drawn to scale. (B) Relative energy diagram of electrode potentials and electrolyte energy gap in LIBs. Reprinted with

permission from Ref. ^[131]. Copyright (2018) Royal Society of Chemistry. (C) Schematic illustration of active anode materials for the next generation of lithium batteries. Reprinted with permission from Ref. ^[132]. Copyright (2014) Elsevier.

Tarascon et al^[133] initially reported nano-sized transition metal oxides as the anode materials of LIBs in 2000, revealing new lithium ion reaction mechanisms during the discharge/charge process with a conversion-type reaction:

 $M_xA_y + y \cdot n Li^+ + y \cdot n e^- \leftrightarrows xM^0 + yLi_nA$ (1.4)

where M is the transition metal, A is the related anions (O, S etc.). The reaction involves several electrons transferred per formula unit of transition metal compounds, with a number much higher than that of graphite (maximum one electron transfer), leading to a much higher theoretical specific capacity over graphite.^[112, 132, 134] However, transition metal based compounds suffer from low intrinsic electrical conductivity and serious volume expansion during cycling, accompanied with drastic capacity damping. Besides, the rate of lithium ion intercalation/de-intercalation strongly depends on its diffusivity properties. The lithium ion diffusion in a host material is associated with the lithium diffusion coefficient and diffusion length in the material and represented by the time constant, τ :^[135]

 $\tau = L_{ion}^2 / D_{Li} \quad (1.5)$

where L_{ion} is the diffusion length and D_{Li} is the diffusion coefficient. D_{Li} depends on the intrinsic state of the material. L_{ion} is related to the size of the material.

In order to meet the demand of high energy density and rate stability, many approaches are developed to synthesize transition metal-based composites with different morphology and components for LIBs. Recent advances within the two main promising transition metal composites including metal oxides and metal chalcogenides for LIBs are summarized in following sections.

1.2.2 Transition metal-based materials for LIBs

1.2.2.1 Metal oxides

Transition metal (Mn or Fe) oxides are promising alternatives for graphite as the anode material for LIBs, due to the high theoretical lithium storage capacities. Besides, metal oxides could react with lithium ions reversibly, avoiding lithium-metal alloy formation and capacity loss.

Manganese oxides (MnO_x) are promising anode materials, including Mn₃O₄ (936 mA h g⁻¹), MnO₂ (1230 mA h g⁻¹) and MnO (755 mA h g⁻¹). To address the aforementioned issues, incorporating carbonaceous components with pristine MnO_x is an effective approach.^[111, 136-138] The additive carbon could not only enhance the electrical conductivity of electrode

materials, but also help to maintain structural stability during cycling. For example, Cui and co-workers^[136] used two-step solution-phase reactions (Fig. 1.13A) to fabricate hybrid materials of Mn_3O_4 nanoparticles on reduced graphene oxide (RGO) sheets as a high-capacity anode for LIBs. Transmission electron microscopy (TEM) images (Fig. 1.13B and C) revealed that the size of the Mn_3O_4 nanoparticles was ~10–20 nm. The high-resolution TEM image demonstrated the crystal lattice fringes throughout a Mn_3O_4 nanoparticle immobilized on RGO. The Mn_3O_4/RGO (Fig. 1.13D) exhibited a good specific capacity of ~900 mA h g⁻¹ at the current density of 40 mA g⁻¹. The rate capability indicated a specific capacity of ~390 mA h g⁻¹) at a high current density of 1600 mA g⁻¹, higher than the theoretical capacity of graphite (~372 mA h g⁻¹).



Fig. 1.13 (A) Schematic two-step synthesis of Mn₃O₄/RGO. (B) TEM image of Mn₃O₄/RGO; inset shows the electron diffraction pattern of the Mn₃O₄ nanoparticles on RGO. (C) High-resolution TEM image of an individual Mn₃O₄ nanoparticle on RGO. (D) Capacity retention of Mn₃O₄/RGO at various current densities. Reprinted with permission from Ref.^[136]. Copyright (2010) American Chemical Society.

Iron oxides (Fe₃O₄, α -Fe₂O₃) have been also used as promising candidates for anode materials of LIBs due to the earth-abundant and environment-friendly features. Tarascon's group^[139] initially reported Fe₃O₄ used for the anode materials of LIBs in 2006, where they developed a two-step route consisting of electrochemically assisted template growth of copper nanorods onto a current collector and subsequent electrochemical plating of Fe₃O₄. Such electrodes exhibited a six-fold enhancement in power density with a higher rate capability than bulk electrodes. Since, Fe₃O₄ based electrode materials have been widely investigated as anode materials of LIBs.^[140-142] Cheng and co-workers^[140] developed a flexible composite of graphene nanosheets (GNSs) decorated with Fe₃O₄ particles through *in situ* reduction of iron hydroxide between GNSs. The GNS/Fe₃O₄ composite showed an improved cycling stability and excellent rate capability with 580 mA h g⁻¹ after 100 cycles at 700 mA g⁻¹. Especially α -Fe₂O₃ as the most thermodynamically stable iron oxide with high theoretical capacity (1007 mA h g^{-1}) has attracted much attention.^[143-145] For instance, Wang et al.^[144] have initially designed unique yolk-shell octahedral MIL-53(Fe) particles with assistance of microwave irradiation and following annealing in air. The transformed unique mesoporous yolk-shell octahedron-inoctahedron Fe₂O₃ nanostructure was used as the anode materials of LIBs, demonstrating a reversible capacity of 1176 mA h g^{-1} after 200 cycles at 100 mA g^{-1} . The reversible capacity is larger than the theoretical value, which could be ascribed to the large active surface area and more active sites in porous yolk-shell structure for lithium storage. Meanwhile, the reversible decomposition of a polymeric solid-electrolyte interphase (SEI) film by the kinetically activated electrolyte degradation and interfacial charging at the metal/Li₂O interface are possible reasons for the extra amount of Li-ion storage capacities. Besides, Ruoff and co-workers^[145] have synthesized a nanostructured RGO/Fe₂O₃ composite for high-performance anode materials. The total specific capacity of RGO/Fe₂O₃ is higher than the sum of pure RGO and Fe₂O₃ nanoparticles, indicating a positive synergistic effect of RGO and Fe_2O_3 on the improvement of the electrochemical performance.



Fig. 1.14 (A) Schematic representation of the low-temperature assembly of ultrathin amorphous MnO₂ nanosheets over Fe₂O₃ nanospindles for enhanced lithium storage. (B) In situ ETEM observation of the morphological evolution of the Fe₂O₃@MnO₂-95 electrode during lithiation/delithiation process. (C) Specific capacity of different electrodes in

varying C rates, with 1C being defined as 1000 mA g⁻¹. Reprinted with permission from Ref.^[146]. Copyright (2018) American Chemical Society.

Carbon coating is a useful method to improve the lithium storage of metal oxide. There are some drawbacks due to the compromised capacity from presence of low capacity carbon and harsh conditions in high-temperature hydrolysis of organic component at inert atmosphere. Some researchers investigated a composite of several metal oxides, e.g. Co_3O_4 , SnO_2 or MnO_2 with α -Fe₂O₃ as hetero-nanostructures, which were found to be an excellent candidate in LIBs due to the synergistic effect between α -Fe₂O₃ and other metal oxides.^[146-148] Cheng and co-workers^[148] fabricated a highly ordered Co₃O₄@MnO₂ hierarchical porous nanoneedle array on nickel foam. The Co₃O₄@MnO₂ composite was tested as the anode material for LIBs, with an improved performance with high reversible capacity of 1060 mA h g⁻¹ at a current density of 120 mA g⁻¹. Meanwhile, Xiao et al.^[146] have developed a direct assembly of ultrathin amorphous MnO_2 nanosheets (thickness < 3 nm) coated Fe₂O₃ nanospindle at 95 °C (Fig. 1.14A). An all-solid nanobattery was studied using Li metal and Li₂O layer as the counter electrode and solid electrolyte, respectively. The lithiation/delithiation processes of the Fe₂O₃@MnO₂-95 nanospindle (Fig. 1.14B) were characterized via in-situ environmental TEM (ETEM). The Fe_2O_3 matrix showed a volume expansion of 94% after lithiation. During the delithiation process, the lithiated Fe₂O₃ matrix shrank, with the volume shrinking from 194% (lithiated state) to 130% (delithiated state), an evidence that the in situ generated Fe-Mn mixed oxide layer is Li⁺ permeable. Such in situ generated Fe-Mn mixed oxide layers have better electrical conductivity, uncompromised Li⁺ penetration, and enhanced structural integration, resulting in enhanced lithium storage (Fig. 1.14C) of the Fe₂O₃@MnO₂-95 nanospindles over the pristine Fe₂O₃.

1.2.2.2 Metal chalcogenides

Metal chalcogenides are widely investigated as the anode materials of LIBs in the past years.^[112] Cobalt sulfides (CoS_x) and iron sulfides (FeS_x) are the typical conversion-type metal chalcogenides, which are introduced in the following section.

Different stoichiometric CoS_x , such as Co_9S_8 , CoS and Co_3S_4 , have been used for the anode materials of LIBs because of their good electrical conductivity, higher theoretical specific capacities than the graphite and good thermal stability.^[6, 149-151] Abundant investigation on the utilization of Co_9S_8 for LIBs anode materials have been reported. For example, Yang and co-workers^[149] have successfully fabricated mesoporous hollow Co_9S_8 nanospheres, showing a reversible capacity of ~1414 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹. The significant capacity restoration was attributed to the hollow structure, which buffered the volume expansion during cycling. The formation of a carbon shell on the hollow nanospheres further promoted the reversible capacities at high rates, for example, ~896 mA h g⁻¹ after 800 cycles at 2 A g⁻¹. In order to improve the electrical conductivity, accommodate the volume expansion and electrochemical activity of Co₉S₈ during discharge/charge process, carbon materials are used to prepare a wide range of Co₉S₈ composites. Si et al.^[6] constructed 3D hollow nitrogen-doped carbon shells decorated with well-defined cobalt sulfide nanoparticles (Co₉Ss/HNCS) for superior lithium storage. Two steps were involved in the preparation procedure (Fig. 1.15A). First, hollow intermediates with preserved cobalt components were controllably fabricated by polydopamine (PDA) wrapping. The intermediates inherited the polyhedral structure of the zeoliticimidazolate-frameworks-67 (ZIF-67) crystals. In the second step, the final Co₉S₈/HNCS composite was obtained via a combined carbonization and sulfurization treatment of the intermediates, allowing the formation (Fig. 1.15B and C) of hollow polyhedrons of nitrogen-doped carbon shells (900 ± 100 nm) derived from PDA and the encapsulation of highly uniform cobalt sulfide nanoparticles $(11 \pm 2 \text{ nm})$. This configuration was believed to not only shorten the lithium or sodium ion diffusion distance and accommodate volume change during lithium or sodium ion insertion/extraction, but also to enhance the overall electrical conductivity and the number of active sites. The Co₉S₈/HNCS composite (Fig. 1.15D and E) exhibited an impressive reversible capacity of 768 mA h g⁻¹ at 100 mA g⁻¹ and good rate capabilities.



Fig. 1.15 (A) Schematic illustration of the preparation of the $Co_9S_8/HNCS$ composite. Not drawn to real scale. (B) TEM image of the $Co_9S_8/HNCS$ composite; inset is the corresponding particle size distribution of Co_9S_8 particles. (C) TEM image of the shell of the $Co_9S_8/HNCS$ composite. (D) Cycling performance of the $Co_9S_8/HNCS$ and Co_9S_8/NC composites at a current density of 100 mA g⁻¹. (E) Rate capabilities at different current densities. Reprinted with permission from Ref. ^[6]. Copyright (2019) Elsevier.

Compared with the CoS_x , iron sulfides (FeS_x) have extra advantages such as low cost, earth abundance and low toxicity.^[152-154] FeS_x describes a variety of compounds, like FeS₂, FeS and Fe₇S₈ and so on. For example, Tu et al.^[152] prepared carbon coated FeS₂ (FeS₂/C) composites via a simple solid state reaction using glucose as carbon source. The porous FeS₂ particles were uniformly surrounded by the amorphous carbon coating. The FeS₂/C composite exhibited higher reversible capacity of 495 mA h g⁻¹ after 50 cycles than pristine FeS₂ (345 mA h g⁻¹). Incorporation of FeS_x to carbon could effectively buffer the volume expansion and enhance the electrical conductivity during cycling for an improved lithium ion storage performance. Tang and co-worker^[153] developed an interconnected porous FeS/C composite consisting of carbon nanosheets anchored with well-dispersed FeS nanoparticles (designated as FeS@CNS) via in situ facile freeze-drying/carbonization approach using sodium chloride (NaCl) crystals as a template. The FeS@CNS displayed significantly improved electrochemical performances with a capacity ~703 mA h g⁻¹ over 150 cycles at 1 A g⁻¹ and ~532 mA h g⁻¹ even at 5 A g⁻¹. Besides, Si et al.^[154] used iron-based metal-organic framework (MIL-88-Fe) as both a sacrificed template and a precursor to prepare carbon-encapsulated iron sulfide through solid-state chemical sulfurizing. Prepared carbon-film-coated iron sulfide nanorods as an advanced conversion-type lithium-ion storage material, exhibited a good electrochemical performance for LIBs.

1.2.3 Perspectives

In summary, a series of nanostructured transition metal oxides/ chalcogenides composites have been investigated to address the issues of the poor capacity retention. Carbon-based material-coated transition metal oxides/sulfides could efficiently improve the electrical conductivity and accommodate the agglomeration of metal oxides/sulfides. Some significant progress has been achieved for the next-generation of LIBs. First, facile methods for large-scale production of battery materials are desired. Second, the goal for next-generation energy storage systems is to develop devices with high energy and power density. The energy density of full cells is in close correlation to the operating voltage depending on the anode and cathode materials. Compared with graphite, the potential platform of transition metal sulfides is usually above 1.0 V. To assemble full cells with wide voltage window, high-voltage cathode materials are needed. Third, it is significantly important to understand reaction mechanisms related to the electron transport process at the electrode/electrolyte interface during cycling.

1.3 Conclusions

In this chapter, transition metal-based MOFs as precursors to tailor the surface properties for superior OER electrocatalysts have been summarized. Compared with rare and highly costly noble-metal based materials, earth-abundant and relatively low-price transition metal-based materials have been developed and investigated for advanced OER electrocatalysts with high conductivity, excellent ion diffusion ability and sufficient active catalytic sites in the past several years. Meanwhile, recent progress of transition metal-based electrode materials (metal oxides/chalcogenides) for high-performance LIBs is presented. Finding simple and high-efficiency strategies for scalable production of transition metal based raw materials for next-generation LIBs is significantly important. This Ph.D. project aims to use the cheap iron incorporated transition metal-based materials with simple synthetic methods for OER electrocatalysts and anode materials of LIBs.

Chapter 2. Methodology

This chapter summarizes techniques used for characterization of synthesized materials and performance evaluation of OER and LIBs in the following chapters. Such techniques are divided into four segments: spectroscopic, microscopic, specific surface area and electrochemical techniques.

2.1 Spectroscopic techniques

2.1.1 X-ray diffraction

X-ray diffraction (XRD) is a common technique for characterizing materials to determine the atomic and molecular structure of a crystalline material. It is also possible to calculate the relative amount of the phases and crystallite size.^[155] In XRD, when a sample is irradiated with X-ray waves at an angle, depending on the arrangement of the atoms and their distances relative to one another, the diffracted waves may interfere in a constructive, destructive or partially destructive manner. Diffraction happens when the waves interact with sample atoms, with scattered X-ray in a specific direction. The Bragg's law is the critical equation for the XRD technique:

$$n\lambda = 2 d \sin(\theta) \qquad (2.1)$$

where n is an integer that represents the 'harmonic order' of the diffraction; λ is the wavelength of the X-rays used; d is the spacing between a particular set of planes and θ is the angle of incidence at which a diffraction peak is measured on the sample. A brief illustration of Bragg's law applied on two crystalline planes can be shown in Fig. 2.1. In this Ph.D. project, XRD (D8 Advance X-Ray diffractometer (Huber), Miniflex 600, Cu-Ka radiation, $\lambda = 1.5418$ Å) was employed to characterize the crystal structure of synthesized transition metal-based materials.



Fig. 2.1 X-ray diffraction on a two-plane system, with periodically placed atoms.

2.1.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) as a quantitative, surface-sensitive spectroscopic technique can be used to measure elemental compositions, chemical state and electronic states of the elements within a material. The sample is submitted to X-ray irradiation from a high-energy source with incident beam energy (hv, h is Planck's constant and v is the photon's frequency.) in vacuum (normally better than 10–7 Pa), where the photoelectrons produced from only 1-10 nm under the surface are measured. The main reason is attributed to that electrons generated deeper in the solid may not be detected due to the loss of energy in elastic and nonelastic collisions with atoms. The kinetic energy (EK) of the ejected photoelectron is related to hv:^[156]

 $h_{\rm V} = E_{\rm K} + E_{\rm B} + \phi \tag{2.2}$

where the work function (ϕ) is from the spectrometer and the electron binding energy (E_B) of sample could be obtained from the equation 2.2. The XPS detector counts the number of electrons with the same E_B that is proportional to the number of corresponding atoms in the sample. XPS can be used to analyze the surface chemical bonding states of solid-state or nonvolatile liquid state samples. In this Ph.D. project, XPS (Thermo-Scientific K-Alpha system (Al-Ka radiation, 1484.6 eV)) was performed to characterize elemental composition and electronic state of transition metal–based materials.

2.1.3 Inductively coupled plasma optical emission spectrometry

Inductively coupled plasma optical emission spectrometry (ICP-OES), is a type of emission spectroscopy that utilizes inductively coupled plasma to excite atoms and ions which then emit electromagnetic radiation at characteristic wavelengths of a particular element. The intensity of the radiation is dependent on the concentration of the element.^[157] A sample is delivered into an analytical nebulizer by a peristaltic pump. The sample is then turned into mist and introduced directly inside the plasma flame. The sample collides with the plasma electrons and charged ions, after which breaking down into charged ions giving off radiation at characteristic wavelengths of the sample elements. The radiation is finally measured by the optical spectroscopy. In this Ph.D. project, elemental analysis of metal based samples were performed by ICP-OES (Brand, Model).

2.1.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique in which infrared (IR) radiation is passed through a solid, liquid or gas sample and an absorption or emission IR spectrum is recorded.^[158] The emitted radiation from an IR source passes through an interferometer composed of a beam splitter, a fixed mirror, and a moving mirror. The interferometer measures the wavelength of emitted light via interference patterns that 40

help to increase accuracy. IR spectra are obtained by applying IR radiation to a sample and measuring the intensity of the passing radiation at a specific wavenumber (Fig. 2.2). The signals of different wavelengths at a broad spectral range are recorded. The process is repeated multiple times. Finally, a computer calculates all the accumulated data of the light absorption for each mirror position for a specific wavelength. The raw data is called an "interferogram", while the obtained spectrum is presented as transmittance vs. wavenumber with Fourier transform. In the Attenuated Total Reflection (ATR) technique, the beam interacts with the sample through "evanescent waves" that are generated at the diamond/sample interface. The machine features a monolithic diamond crystal that withstands hard or corrosive materials. It can be used for chemical analysis of raw materials. In this Ph.D. project, FTIR measurements were performed on an Alpha-P FTIR spectrometer (Bruker) in the range of $4,000 - 400 \text{ cm}^{-1}$ with a resolution of 2 cm⁻¹.



Fig. 2.2 Scheme of FTIR spectrometer measurement principle. Reprinted with permission from Ref. ^[158]. Copyright (2016) Springer Nature.

2.1.5 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique for the elemental analysis and chemical characterization of a sample.^[159] The main principle of EDS is that each element has a unique atomic structure therefore allowing a unique set of peaks in its electromagnetic emission spectrum. After bombarding a sample with high-energy electrons within an electron microscope, the generated X-rays from the sample can be detected with an energy-dispersive spectrometer that distinguishes element-specific Xray energies. Because characteristic X-rays have specific energy corresponding to each element, the element can be identified from the peak position and the content of the element in the compound can be analyzed from the integrated intensity of the peak. In general, the emission probability of characteristic X-rays increases with the increase in atomic number. Thus, EDS is very useful for heavy elements, especially when the content of the element is small. In this Ph.D. project, EDS-mapping technique was used together with scanning and transmission electron microscopy (SEM and TEM) imaging in order to identify the elemental distribution of the transition metal-based materials.

2.2 Microscopic techniques

2.2.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is used for material characterization offering information about the surface or near surface morphology and composition via EDS in bulk materials. Fig. 2.3 shows the schematic working principle of a SEM.^[160] An electron source (gun) located at the top of the column emits electrons. The scanning coils in the column raster scans the electron beam over the surface of the sample present in the chamber at the end of the column. The gun, the column, and the specimen chamber are kept under vacuum to allow electron beam generation and advancement. Three basic types of signals, including back scatter electrons, secondary electrons, and X-rays, are generated when the electron beam hits the surface of the specimen. While, the electron beam raster scans over the surface of specimen, the electron signals are collected and converted into brightness of the corresponding points of the image by the detector. The corresponding electron image is recorded and displayed on a computer monitor. In this Ph.D. project, Quanta FEG 200 ESEM (15 kV) with the Everhart-Thornley Detector (ETD) EDS detector from FEI was used for morphology and elemental characterization of samples.



Fig. 2.3 Schematic formation of the SEM. Reprinted with permission from Ref. ^[160]. Copyright (2018) Springer Nature. 42

2.2.2 Transmission electron microscopy

Ruska and Knoll developed the idea of electron lenses into a practical reality and firstly demonstrated electron images taken by transmission electron microscopy (TEM) in 1932 (Fig. 2.4a), resulting in Ruska receiving the Nobel Prize in physics (1986).^[161] The basic components (Fig. 2.4b) of the TEM are an electron source (W, LaB₆ or field-emission gun), vacuum system, a series of electromagnetic lenses, a specimen stage and digital cameras used to image transmitted electrons. A common electron source is a W spike-shaped filament. The electron gun is connected to a high voltage source (~100 to 300 kV). Then, electrons are emitted to the vacuum by thermionic or field electron emission. The interaction of electrons are magnified and focused by the electromagnetic and electrostatic lenses. The electrons are then imaged with a digital camera obtaining atomic resolution. In this Ph.D. project, Tecnai G2 T20 (200 kV) with an EDS detector was used for morphology and nanostructure characterization of samples.



Fig. 2.4 (A) The electron microscope built by Ruska (in the lab coat) and Knoll. Reprinted with permission from Ref. ^[161]. Copyright (2009) Springer Nature. (B) Schematic formation of the TEM. Reprinted with permission from Ref. ^[160]. Copyright (2018) Springer Nature.

2.2.3 Atomic force microscopy

Atomic-force microscopy (AFM) is a high-resolution type of scanning probe microscopy. The AFM working principle (Fig. 2.5) is based on a cantilever/tip assembly (the probe) that interacts with the sample surface through a raster scanning motion.^[162] The up/down and side to side motion of the AFM cantilever scanning over the sample surface is monitored through a laser beam reflected by the cantilever. A position sensitive photodiode detector tracks the reflected laser beam. The morphology of the sample surface can therefore be imaged by recording the signal from the photodetector. AFM can be conducted in either tapping or contact mode. Tapping mode measures surface topography by utilizing repulsive (and attractive) forces between the tip and the sample surface. Tapping mode uses piezoelectric modulator to obtain the information regarding the surface topography. In this Ph.D. project, AFM (Agilent Technology SPM 5500) in tapping mode was used to characterize the surface morphology and thickness of samples on mica sheets.



Fig. 2.5 Scheme of the experiment setup of an AFM. Reprinted with permission from Ref. ^[162]. Copyright (2017) Elsevier.

2.3 Specific surface area analysis

2.3.1 Nitrogen adsorption-desorption isotherm analysis

Physical adsorption is a type of adsorption that occurs for most particles in contact with a solid or liquid surface. The use of nitrogen adsorption for pore size analysis dates from the late 1940s. In a nitrogen adsorption-desorption test, a nitrogen adsorption-desorption isotherm can be obtained, showing the relationship between the amount of nitrogen adsorption/desorption and the relative pressure. Brunauer-Emmett-Teller (BET) theory is often used for processing data obtained in a nitrogen adsorption-desorption test.^[163] As an extension of Langmuir theory that is applicable for molecular monolayer adsorption, BET theory is applicable for multiplayer molecular adsorption based on the following hypotheses: (1) gas molecules physically adsorb on a solid in an infinite number of layers; (2) gas molecules only interact with adjacent layers; and (3) Langmuir theory can be applied to each layer. If the pores in the sample mainly belong to mesopores, the pore size distribution, total pore volume and average pore diameter can be calculated by the Barrett-Joyner-Halenda (BJH) method, which is based on Kelvin model of pore filling. 44

Besides, pore size range includes micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm). In this Ph.D. project, the specific surface areas of samples were estimated by a Surface Area & Pore Size Analyzer (ASAP 2020, Micromeritics).

2.4 Electrochemical techniques

In order to investigate the electrochemical behavior including OER and lithium ion storage, different electroanalytical techniques presented below were utilized. Autolab (PGSTAT12 or PGSTAT30), CHI 760& 660E and PalmSens 4 electrochemical workstations were used to conduct the electrochemical experiments.

2.4.1 Linear sweep voltammetry

The linear potential (Fig. 2.6a) is swept from E_i to a certain potential at a defined scan rate. The corresponded current response on the electrode is plotted as a function of the applied potential. Fig. 2.6b shows the linear sweep voltammetry (LSV). To obtain a steady state I vs E curve, the scan rate is set with a very low value such as 1.0 or 5.0 mV s⁻¹.^[164] In the Ph.D. project, LSV was recorded to characterize the OER performance of synthetic samples for calculating the overpotential and Tafel slope.



Fig. 2.6 (a) Linear potential sweep beginning at E_i . (b) Resulting i-E plot of anthracene system. $E^{0'}$ is the value of reduction beginning. Reprinted with permission from Ref. ^[164]. Copyright (2001) John Wiley and Sons.

Overpotential is the potential difference between a theoretical or thermodynamically determined potential in a half reaction and the actual potential under experimental condition. Tafel slope is used to analyze the relationship between the overpotential and current density, which is originated from the Butler-Volmer equation^[164]:

$$\eta = \frac{\mathrm{RT}}{\mathrm{\alpha}\mathrm{F}} \cdot \ln j_0 - \frac{\mathrm{RT}}{\mathrm{\alpha}\mathrm{F}} \cdot \ln j \qquad (2.3).$$

Then, when a = $(2.303\text{RT/anF}) \cdot \log j_0$, b = -2.303RT/anF, where *j* is current density of samples from the LSV test, j_0 is the exchange current density at zero overpotential, a is the charge transfer coefficient, n is the number of transferred electrons during the redox

reaction, F is the Faraday constant (96485 C mol⁻¹), R the gas constant (8.314 J mol⁻¹ K^{-1}), T the temperature (K). Thus, the equation can be transformed to

 $\eta = a + b \cdot \log j \tag{2.4}.$

The b is the Tafel slope value. When the Tafel slope value is smaller, the reactive rate in the electrochemical reaction will be faster.

2.4.2 Cyclic voltammetry

Cyclic voltammetry (CV) is the potential-scan equivalent of two-direction potential step chronoamperometry (Fig. 2.7a). CV is a widely applied electrochemical technique to study the electrochemical properties and complicated electrode reactions in electrolyte solution.^[164] The CV plot (Fig. 2.7b) is the current response at the electrode versus the applied potential. A three-electrode system is most commonly employed, including a working electrode (WE) as the studied electrode, a counter electrode (CE) and a reference electrode (RE) in the electrochemical cell. In this Ph.D. project, CVs were recorded to characterize electrochemical behaviors of synthesized samples.



Fig. 2.7 (a) Cyclic potential sweep. (b) Represented cyclic voltammogram of an anthracene system. Reprinted with permission from Ref. ^[164]. Copyright (2001) John Wiley and Sons.

2.4.3 Chronopotentiometry

Chronopotentiometry (CP) is another useful electrochemical technique. In the process, the current of WE can be set with a constant value to initiate an electrode reaction for a defined period of time (Fig. 2.8a). Then, the potential response (Fig. 2.8b) is recorded as a function of time. In the Ph.D. project, CP was employed to investigate the stability of synthesized sample for OER by applying a benchmark constant current density of 10 mA cm⁻² to the prepared WE. The electrodes potential was recorded over a period of time, reflecting the stability of the electrode materials.



Fig. 2.8 (a) A profile of current versus time for CP. (b) Potential-time profile at a constant current. Reprinted with permission from Ref. ^[164]. Copyright (2001) John Wiley and Sons.

2.4.4 Galvanostatic discharge/charge

In galvanostatic discharge/charge (GDC), the current is continuously reversed at each transition (Fig. 2.9a), resulting in cyclic CP (Fig. 2.9b).^[164] The potential will move according to the current in a positive or negative direction, and a reverse transition time can be measured. GDC is widely used for the battery measurement. During GDC cycling of batteries, the charge and discharge capacity is expressed in mA h g⁻¹, which is calculated by recording the current, reverse transition time and mass of measured electrode materials. In this Ph.D. project, GDC tests in a voltage window of 0.01-3.0 V were recorded with a Neware-CT-3008 test system (Shenzhen, China).



Fig. 2.9 Cyclic chronopotentiometry: (a) positive/negative constant current versus time. (b) potential-time curve is related to the corresponded current (a). Reprinted with permission from Ref. ^[164]. Copyright (2001) John Wiley and Sons.

2.4.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measures impedance on a WE by applying alternating current (AC) in a range of potential frequencies. In this Ph.D. project, EIS characterization in a frequency range of 0.01 to 100 kHz was performed to characterize the interfacial charge transfer resistance of related electrode materials for OER and LIBs

by the Autolab instrument (Metrohm). In a typical configuration for lithium ion battery electrodes, porous electrodes (Fig. 2.10a) include particles of energy-storing material and conductive additive, coated together by polymeric binder. The battery consists of electrodes, the electrolyte and a separator, preventing electric contact (short circuiting) between opposite electrodes. Instead of focusing on particular chemical compositions, general battery kinetics can be obtained by analyzing the impedance of the above common components.^[165] Fig. 2.10b shows the kinetic steps for most of batteries,^[166] consisting of electronic conduction through the particles and ionic conduction through the electrolyte in cavities between particles. The main process includes charge transfer, diffusion and change of crystalline structure, respectively.



Fig. 2.10 (a) Kinetic steps common in most batteries; (b) typical impedance spectra of intercalation material. Reprinted with permission from Ref. ^[165]. Copyright (2005) John Wiley and Sons.

Chapter 3. Ultrafine Fe₃O₄ nanoparticles immobilized on twodimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction

This chapter focuses on the synthesis of two-dimensional Ni based metal-organic framework (Ni-BDC) immobilized ultrasmall Fe_3O_4 nanoparticles, investigating the crystalline and morphology evolution of different concentrations of Fe_3O_4 nanoparticles enclosed on the 2D Ni-BDC layers. The different ratios of Fe_3O_4/Ni -BDC composites are tested for OER electrochemical catalytic performances, related electrochemical behavior and mechanism are discussed in detail. The chapter has been involved and submitted with a manuscript entitled "Ultrafine Fe_3O_4 nanoparticles immobilized on two-dimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction", co-authored by Wei Huang, Chao Peng, Jing Tang, Fangyuan Diao, Hongyu Sun, Christian Engelbrekt, Jingdong Zhang, Xinxin Xiao and Kristian Mølhave. Besides, the partial experimental data in this chapter are included in appendix I.

3.1 Introduction

With increasing concerns of fossil fuel related environmental crisis and global warming, there is an imperative demand for developing alternative green and sustainable energy conversion and storage technologies, such as batteries, fuel cells and water splitting for hydrogen energy.^[2, 8, 142, 167-170] As a crucial reaction for secondary metal-air batteries and electrochemical water splitting, oxygen evolution reaction (OER) plays an important role to increase the efficiency and operational stability of such systems.^[171, 172] High-performance electrochemical catalysts are thus urgently required to promote sluggish reaction kinetics of the four-electron transfer during OER, to provide low overpotential

(n) and excellent catalytic stability. Considering the rarity and high cost of noble metal OER catalysts (e.g. Ir or Ru based materials),^[173, 174] earth-abundant and cost-effective transition metal-based electrocatalysts are clearly desired.

Metal-organic frameworks (MOFs) are a class of porous materials composed of organic linkers and metal nodes with covalent coordination.^[27] MOFs and derived materials have been used in a wide range of fields, e.g. gas storage and separation, batteries and catalysts etc., benefiting from their high specific surface area, tuneable porosity and abundant active metal sites.^[175-180] Two-dimensional (2D) MOF based materials have attracted growing attention for OER catalysts with unique physicochemical features. 2D structure enables hydroxide units in the electrolyte to easily reach the active site and generated O₂ dissociate quickly, as well as shortening electron transfer pathway through the thin film to the conductive support.^[181-183] 2D MOFs possess a large number of coordinatively unsaturated metal atoms exposed as active sites.^[60, 184] Surface atom structure and bonding arrangement can be elaborately controlled to facilitate the interaction between the active site and the reaction intermediates for superior OER electrocatalysts.^[185, 186] However, 2D MOFs have a high tendency to aggregate with each other,^[187, 188] leading to decreased effective surface area. Avoiding aggregation with high active surface area and improving the integral structural stability for superior OER catalysts are thus essential.

To deal with these issues, there are increasing reports demonstrating that the introduction of functional nanoscale components (nanosheets or nanoparticles etc.) in a MOF composite could prevent the aggregation and enhance the integral structural stability during operation.^[188, 189] Meanwhile, the electronic structure of metal units in the MOFs can be optimized by incorporation with heterogeneous metal containing groups for superior OER performance.^[188-192] For example, Qiao and coworkers have synthesized 2D Ni-BDC/Ni(OH)₂ heterostructure, exhibiting a lower n of 320 mV at 10 mA cm⁻² than that of Ni-BDC nanosheets, and a good catalytic durability of 20 h. The improved OER performance is attributed to the rational design of the composition and structure, and to the mitigation of aggregation of Ni-BDC by coupling with Ni(OH)₂.^[188] Similarly, Qin et al. have reported hybrids of Fe-Co polyphenolic network wrapped Fe₃O₄ nanocatalysts for enhanced OER with an η of 260 mV at 10 mA cm⁻² and a durability over 24 h, taking advantage of strong metal-polyphenolic ligand complexation that ensures robust metal Co-Fe polyphenolic shells for prolonged operations.^[189] Inspired by these reports, 2D Ni based MOFs could be promising candidates for constructing hybrid electrocatalysts due to superior surface structure and physicochemical features. Meanwhile, considering Fe₃O₄ nanoparticles with good electrical conductivity (>100 S cm⁻¹) and fast electron transfer between Fe²⁺ and Fe³⁺ in the crystals,^[189, 193] the incorporation of Fe₃O₄ nanoparticles on the surface of 2D Ni based MOFs could be promising for OER.

Herein, I have successfully prepared ultrasmall Fe_3O_4 nanoparticles that are uniformly immobilized on 2D Ni based MOFs (Fe_3O_4/Ni -BDC). The functionalized Fe_3O_4 50

nanoparticles (6 \pm 2 nm) with abundant surface hydroxide groups are synthesized separately, and then either added directly during the synthesis of 2D Ni-BDC layers (4 \pm 1 nm) or alternatively mixed with pre-synthesized 2D Ni-BDC. We have investigated electronic structure modulation and morphology changes to tackle the aggregation issue for OER via different amounts of Fe₃O₄ immobilized on the 2D Ni-BDC layers. The optimized Fe₃O₄/Ni-BDC-4 composite demonstrates significantly enhanced OER performance with a η of 295 mV at 10 mA cm⁻², a Tafel slope of 47.8 mV dec⁻¹ and a superior catalytic durability over 40 h.

3.2 Experimental

3.2.1 Chemicals and Reagents

Iron (III) chloride hexahydrate (FeCl₃ 6H₂O, 97%), sodium bicarbonate (NaHCO₃, \geq 99.7%), L-ascorbic acid, terephthalic acid (1, 4-BDC, 98%), N,N-dimethylformamide (DMF, 99.8%), Nafion solution (10 wt%) were bought from Sigma-Aldrich. Triethylamine (TEA, 99%) was purchased from Merck (Germany). Nickel (II) chloride hexahydrate (NiCl₂ 6H₂O, 98%) was from BDH Chemicals Ltd Poole England. All chemicals were used as received without further purification. Ultrapure water (\geq 18.25 MQ cm, Sartorius arium® pro, Germany) was used to prepare all the aqueous solutions.

3.2.2 Synthesis of Fe₃O₄/Ni-BDC composites

Water-soluble Fe₃O₄ nanoparticles were synthesized as in a previous report.^[194] Briefly, a 20 ml aqueous solution of 1 mM L-ascorbic acid was added into a 60 ml mixture aqueous solution of 6 mM FeCl₃ $6H_2O$ and 18 mM NaHCO₃, under stirring for 20 min. The mixture was transferred to a 150-ml-volume Teflon-lined stainless-steel autoclave, which was kept at 150 °C for 6 h. The product was separated using a magnet, washed with ultrapure water more than three times, and leading to water-soluble Fe₃O₄ nanoparticles that could be re-dispersed in water for further using.

Ni-BDC was grown with or without the presence of water-soluble Fe₃O₄ for Fe₃O₄/Ni-BDC composites. 63 mg 1,4-BDC was first dissolved in a mixed solvent of DMF (15 ml), ethanol (1 ml), and ultrapure water (1 ml), into which 90 mg NiCl₂ \cdot 6H₂O and a certain volume of water or water-soluble Fe₃O₄ solution were added subsequently and under ultrasonication for 10 min, followed by a quick injection of 0.50 ml TEA. To optimize the ratio of Fe₃O₄ and Ni-BDC in the composite, different volumes of water-soluble Fe₃O₄ solution (12 mg ml⁻¹; 1, 2, 3, 4 or 5 ml) were used. The above mixture was sealed and continuously ultrasonicated for 6 h at room temperature. Finally, the precipitates were centrifuged and washed with ethanol three times, dried in a vacuum oven at 60 °C for 12 h. The obtained composites were collected and labelled as Fe₃O₄/Ni-BDC-n (n = 1, 2, 3, 4 and 5).

3.2.3 Materials characterization

The crystalline structure was characterized by X-ray diffraction (XRD, D8 Advance X-Ray diffractometer (Huber)). X-ray photoelectron spectroscopy (XPS) was performed by dropping samples onto silicon substrates with a Thermo-Scientific system (Al-Ka radiation, 1484.6 eV). Fourier transform infrared spectroscopy (FTIR) measurements were performed on an Alpha-P FTIR spectrometer (Bruker) in the range of 4,000–400 cm⁻¹ with a resolution of 2 cm⁻¹. The specific surface area was estimated by a Surface Area & Pore Size Analyzer (ASAP 2020, Micromeritics). Elemental analysis was performed by inductively-coupled plasma optical emission spectrometry (ICP-OES). Microstructure and composition characterization was conducted with scanning electron microscopy (SEM, Quanta FEG 200 ESEM, 15 kV), atomic-force microscopy (AFM, Agilent Technology 5500, tapping mode, a mica sheet as the substrate), and transmission electron microscopy (TEM, Tecnai G2 T20, 200 kV).

3.2.4 Electrochemical measurements

In order to prepare catalyst inks, 4 mg of active materials (Fe₃O₄/Ni-BDC-n, Ni-BDC or Fe₃O₄), 4 mg carbon black (Alfa AesarTM) and 25 µl of Nafion solution (10 wt%) were mixed with 0.75 ml 2-propanol and 0.25 ml ultrapure water for a uniform ink after 1 h sonication. Prior to use, rotating disk electrodes (RDE) using glassy carbon electrodes (GCEs, d = 5.0mm, A = 0.19625 cm²) and rotating ring disk electrodes (RRDEs, d_{disk} = 5.61 mm, A_{disk} = 0.2472 cm^2 , d_{ring} (inner) = 6.25 mm, d_{ring} (outer) = 7.92 mm, A_{ring} = 0.1859 cm²) with a GCE disk and a Pt ring were polished on a polishing pad with Al₂O₃ slurries with decreasing particle diameters (1.0, 0.3 and 0.05 μ m). Afterwards, 10 μ l of the catalyst ink was dropcast onto the surface of GCEs giving a mass loading of 0.398 mg cm⁻² and dried under room temperature. Electrochemical tests were carried out in a typical three-electrode setup with 1.0 M KOH solution as the electrolyte on an electrochemical workstation (Autolab PGSTAT12) with a graphite rod as counter electrode and a Ag/AgCl (sat. KCl) reference electrode. Rotation of RDE and RRDE were controlled on a Pine Instruments rotating system. The applied potentials were compensated with the solution resistance R_s and current I via: $E_{Ag/AgCl-corr} = E_{Ag/AgCl} - IR_s$, ^[195] where the uncompensated Ohmic solution resistance (R_s) high-frequency was measured by electrochemical impedance spectroscopy (EIS) in a frequency range from 100 kHz to 0.1 Hz at 1.525 V vs. RHE. All potentials measured were calibrated to reversible hydrogen electrode (RHE) potential according to the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl-corr}} + 0.197 + 0.059 \times \text{pH}$. To maintain the O₂/H₂O equilibrium at 1.23 V versus RHE, oxygen gas ($O_2 \ge 99.995\%$) flow was kept in the electrolyte during the test. The η for OER was defined as: $\eta = E_{RHE} - 1.23$ V. For OER test, working electrodes were initially scanned 10 cycles using cyclic voltammetry (CV) to obtain stable signals. Then, linear sweep voltammetry (LSV) curves were obtained with a slow scan rate of 5 mV s^{\cdot 1} at a rotational speed of 1,600 rpm to decrease capacitive currents and interference from generated gas bubbles. The electrode durability was 52

evaluated by chronopotentiometry at a current density of 10 mA cm⁻². Tafel slope (b) was calculated based on the Tafel equation: ^[164, 196]

$$\eta = a + b \cdot \log j \tag{3.1}$$

and compared to b = 2.303 RT/anF, where *j* is current density of samples from the LSV test, a the charge transfer coefficient, n is the number of transferred electrons during the redox reaction, F is the Faraday constant (96485 C mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (K).

The electrochemical double-layer capacitance (C_{dl}) was tested by using CVs in a narrow potential range of 1.223–1.323 V vs. RHE, with scan rates of 40, 60, 80, 100, and 120 mV s⁻¹. The plot of $\Delta j = (j_a - j_c)$, where j_a and j_c are the anodic and cathodic current, respectively, at 1.24 V vs. RHE (no faradaic reaction occurring) against the scan rate had a linear relationship, whose slope was twice of C_{dl}. The electrochemically active surface area (ECSA) relative to GCE and GCE-normalized current density were calculated according to the equations:^[197]

$$ECSA = \frac{C_{dl_samples}}{C_{dl_GCE}}$$
(3.2)

$$j_{ECSA_normalized} = \frac{j}{ECSA}$$
(3.3)

Herein, C_{dl-GCE} is the specific capacitance for a plane surface in the range of 20-60 μ F cm⁻², and C_{dl-GCE} =40 μ F cm⁻² was used.^[190] To investigate the reaction mechanism for OER, RRDE voltammograms were recorded to determine the OER reaction pathway by measuring the HO₂⁻ formation, with the ring potential held at 1.50 V vs. RHE at 1,600 rpm, and linearly scanning the potential of the disk in O₂-saturated 1.0 M KOH solution. RRDE was also used to determine faradaic efficiency (FE) reaction process as described:^[198] where I_{ring} is the oxygen reduction reaction (ORR) collection current on the Pt ring when held at 0.4 V vs. RHE in an Ar-saturated 1.0 M KOH solution at a rotation rate of 1,600 rpm, while I_{disk} is set at 300 μ A on the disk.

3.3 Results and discussion

3.3.1 Structural and component characteristics

 $\rm Fe_3O_4/Ni$ -BDC composites are synthesized through a two-step procedure as illustrated in Scheme 3.1. Water-soluble $\rm Fe_3O_4$ nanoparticles are initially prepared with a modified hydrothermal method.^[194] Dehydroascorbic acid (DHAA) is oxidized from the ascorbic acid, serving as a stabilizer and capping ligand on surfaces of $\rm Fe_3O_4$ nanoparticles interacted by carbonyl groups, ensuring a good dispersibility of $\rm Fe_3O_4$ nanoparticles in aqueous solution.^[199, 200] During the subsequent sonication process, functionalized $\rm Fe_3O_4$ nanoparticles are homogenously dispersed in an alkaline solution (pH ~ 10), immobilizing 2D Ni-BDC as surface layers with strong interactions due to abundant hydroxide groups of DHAA-Fe $_3O_4$ and terephthalate linkers of Ni-BDC layers, leading to the final Fe $_3O_4$ /Ni-BDC composites.



Scheme 3.1 Schematic illustration of the synthesis of Fe_3O_4/Ni -BDC composite. Inset shows two-dimensional Ni-BDC layer immobilized ultrasmall Fe_3O_4 nanoparticles with ball and stick mode: nickel (pink), oxygen (red), carbon (grey), hydrogen(white) and iron (blue). Not drawn to real scale.



Fig. 3.1 XRD patterns (a) and FT-IR spectra (b) of Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4. (c) High-resolution Ni 2p XPS spectra of Ni-BDC and Fe₃O₄/Ni-BDC-4. (d) High-resolution Fe 2p XPS spectra of Fe₃O₄ and Fe₃O₄/Ni-BDC-4. (e) High-resolution O 1s XPS spectra of Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4. (f) Typical nitrogen adsorption-desorption isotherms of Fe₃O₄/Ni-BDC-4 composites; inset is the corresponding pore-size distribution.

The water-soluble Fe₃O₄ nanoparticles (Fig. 3.1a) were characterized by XRD analysis, showing peaks matching well with the standard Fe_3O_4 phase (JCPDS no. 89-0688), with peaks at 18.3°, 30.0°, 35.4°, 43.0°, 56.9° and 62.5° fitting well with (111), (220), (311), (400), (511) and (440) planes of magnetite, respectively. The diffraction peaks of pure Ni-BDC (Fig. 3.1a) can be assigned based on Ni-BDC composites in literature.^[185, 201] The main diffraction peaks at 8.8°, 15.7° and 17.9° are ascribed to the (200), (201) and (-201) planes of Ni-BDC, respectively. Fe₃O₄/Ni-BDC-n composites with various amount of Fe₃O₄ are successfully synthesized, and XRD patterns of Fe_3O_4/Ni -BDC-4 (Fig. 3.1a) confirm the coexistence of the crystalline phases of Fe_3O_4 and Ni-BDC. Similar diffraction peaks are also observed on those of Fe₃O₄/Ni-BDC-1, 2, 3 or 5 (Fig. 3.2). In addition, FTIR spectra of Fe_3O_4 , Ni-BDC and Fe_3O_4 /Ni-BDC-4 are shown in Fig. 3.1b. The band at 553 cm⁻¹ is assigned to the Fe-O stretching vibration of Fe_3O_4 ,^[202] and the strong bands at 1373 and 1564 cm⁻¹ are ascribed to the stretching modes of the coordinated carboxylate (-COO⁻) of terephthalate linkers of Ni-BDC.^[203] The absorption band at 1647 cm⁻¹ is regarded as the coordination between O atom of the carbonyl group (C=O) from DHAA and Fe units from the surfaces of Fe_3O_4 nanoparticles.^[194] The broad band at 3315 cm⁻¹ is attributed to the strong stretching mode of hydroxyl groups (-OH) from the DHAA of functionalized Fe₃O₄ nanoparticles and organic ligands of Ni-BDC layers.^[194, 203]



Fig. 3.2 XRD patterns of Fe₃O₄/Ni-BDC-n (n= 1, 2, 3 and 5).

The chemical bonding states of Fe₃O₄, Ni-BDC and Fe₃O₄/Ni-BDC composites are investigated by XPS. All signals originating from expected elements (Ni, Fe, O or C) are recorded in the survey spectra (Fig. S3.1). High-resolution Ni 2p (Fig. 3.1c) and Fe 2p (Fig. 3.1d) spectra indicate the Ni $2p_{3/2}$ (856.7 eV for Ni-BDC) and Fe $2p_{3/2}$ (710.4 eV for Fe₃O₄) shift to lower and higher binding energies (Fig. 3.1c, d and 3.3; Ni 2p_{3/2} and Fe 2p_{3/2} of Fe₃O₄/Ni-BDC-4), respectively.^[201, 204] The detailed binding energy data are summarized in Table 3.1. Increasing the amount of Fe_3O_4 nanoparticles in the composite, binding energy level of Ni 2p_{3/2} decreases, while Fe 2p_{3/2} increases slightly. This indicates that there is change in the bond strength of both Fe and Ni to varying degree in the different Fe₃O₄/Ni-BDC composites. The typical O 1s spectrum of Fe₃O₄/Ni-BDC-4 (Fig. 3.1e) indicates peaks at 533.4, 532.4 and 531.6 eV, that are assigned to O-H, O=C-O and Ni-O bonding, respectively, originating from the terephthalate linker and NiO_6 octahedra in Ni-BDC.^[185] Other peaks at 531.2, 530.7 and 529.8 eV are assigned to O-H, O=C and Fe-O bonding, respectively, attributed to the surface hydroxyl and carbonyl groups from the DHAA and internal Fe-O units of the water-soluble Fe₃O₄.^[205, 206] To quantify the specific surface area and pore sizes of Fe_3O_4/Ni -BDC-4, the typical adsorption-desorption isotherm is recorded using nitrogen adsorption-desorption measurements (Fig. 3.1f). The specific surface area is determined to be $136 \text{ m}^2 \text{ g}^{-1}$, which is attributed to the slit-like structure formed by aggregation of Fe₃O₄/Ni-BDC-4.^[201] The pore size distributions of the

composite are mainly centred at 40 nm. The mesoporous center at 40 nm correlates well with the sub 100 nm structure observed in the SEM images (Fig. 3.4c and Fig. S3.2f). Besides, the pore size distribution indicates the presence of micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm), confirming a hierarchical porous structure for Fe₃O₄/Ni-BDC-4, which is beneficial for mass transport for OER. Finally, ICP-OES is conducted to check the metallic components of various Fe₃O₄/Ni-BDC composites (Table 3.2). It verified that proportional Fe in the composite increases with the added amount of Fe₃O₄. Fe₃O₄/Ni-BDC-4 is composed of 24.7 at% Ni and 75.3 at% Fe.



Fig. 3.3 High-resolution (a) Ni 2p and (b) Fe 2p XPS spectra of Fe_3O_4/Ni -BDC-n (n= 1, 2, 3 and 5).

Table 3.1 Binding energies of Fe_3O_4 , Ni-BDC and synthetic Fe_3O_4 /Ni-BDC for high-resolution Ni 2p and Fe 2p, respectively.

Sample	Ni 2p _{3/2} (eV)	Fe 2p _{3/2} (eV)
Fe_3O_4	N/A	710.4
Ni-BDC	856.7	N/A
Fe ₃ O ₄ /Ni-BDC-1	856.6	711.7
Fe ₃ O ₄ /Ni-BDC-2	856.2	710.7
Fe ₃ O ₄ /Ni-BDC-3	856.2	710.7
Fe ₃ O ₄ /Ni-BDC-4	855.9	710.7
Fe ₃ O ₄ /Ni-BDC-5	855.8	710.6

Sample	Ni (at%)	Fe (at%)
Fe ₃ O ₄ /Ni-BDC-1	60.0	40.0
Fe ₃ O ₄ /Ni-BDC-2	41.0	59.0
Fe ₃ O ₄ /Ni-BDC-3	30.6	69.4
Fe ₃ O ₄ /Ni-BDC-4	24.7	75.3
Fe ₃ O ₄ /Ni-BDC-5	19.8	80.2

Table 3.2 Atom ratios of Ni/Fe for synthetic Fe₃O₄/Ni-BDC determined by ICP-OES.

3.3.2 Morphology and microstructure

The morphologies of Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC are performed by SEM and TEM. SEM images of pure Ni-BDC (Fig. 3.4a, Fig. S3.2a and b) show a hierarchical-layer structure comprised of aggregated 2D nanosheets. After immobilizing different amounts of Fe₃O₄ nanoparticles (Fig. 3.4b, Fig. S3.2c and d), the generated Fe₃O₄/Ni-BDC composites show changes in morphology and microstructures. With increasing the ratio of Fe₃O₄, the Fe₃O₄/Ni-BDC (Fig. 3.4c, Fig. S3.2e and f, Fig. S3.3) turns from a layered structure to a smoother structure with smaller Ni-BDC grains. The observation is likely caused by Fe₃O₄ nanoparticles anchoring Ni-BDC on their surface, hindering extended growth of Ni-BDC layers. As a control to assess if any leaching Fe from could cause MOF formation, samples following the same synthetic route of Fe₃O₄/Ni-BDC-4 without the addition of NiCl₂ 6H₂O are also fabricated, but were difficult to purify and separate from solution. SEM images and the corresponding EDS spectrum (Fig. S3.4) indicate that the control sample is the water-soluble Fe₃O₄ nanoparticles with no formation of Fe based MOF. This further confirms the importance of Ni source (NiCl₂ 6H₂O) in the formation of Fe₃O₄/Ni-BDC composites. TEM image of pure Ni-BDC (Fig. 3.4d) clearly demonstrates a two-dimensional hierarchical-layer structure. The AFM image (Fig. S3.5) of partial Ni-BDC samples further indicates the thickness of Ni-BDC nanosheets is 5 ± 1 nm. TEM image of Fe_3O_4 (Fig. 3.4e) obviously shows ultrafine nanoparticles with a particle size of 6 ± 2 nm. The interplanar spacing of the lattice (Fig. 3.4f) is measured to be 0.485 nm, matching well with the (111) plane of magnetite Fe_3O_4 (JCPDS no. 89-0688).^[207] The typical TEM images of Fe_3O_4/Ni -BDC-4 (Fig. 3.4g and h) show that ultrafine Fe_3O_4 nanoparticles are homogenously immobilized on the 2D Ni-BDC layers. The highresolution TEM image of Fe₃O₄/Ni-BDC-4 (Fig. 3.4i) demonstrates a crystalline interplanar spacing of 0.297 nm, in accordance with the (220) plane of magnetite $Fe_{3}O_{4}$ (JCPDS no. 89-0688).^[208] The STEM-EDS elemental mapping images corresponding to a fragment of Fe₃O₄/Ni-BDC-4 (Fig. 3.4j-n) suggests the homogeneous distribution of nickel (cyan), iron (red), oxygen (green) and carbon (purple) elements, confirming that Fe_3O_4

nanoparticles are uniformly distributed on Ni-BDC sheets. Linear elemental distribution of Fe₃O₄/Ni-BDC-4 composite (Fig. S3.6) further verifies that ultrasmall Fe₃O₄ nanoparticles distribute on the surface of Ni-BDC.



Fig. 3.4 SEM images of (a) Ni-BDC, (b) Fe₃O₄ and (c) Fe₃O₄/Ni-BDC-4. (d) TEM images of Ni-BDC (d) and Fe₃O₄ (e). Inset of (e) is the particle size distribution. (f) High-resolution TEM image of Fe₃O₄. (g-h) TEM image of Fe₃O₄/Ni-BDC-4. (i) High-resolution TEM image of Fe₃O₄/Ni-BDC-4. (j-n) HAADF STEM image (j) and corresponded STEM-EDS mapping of elemental Ni (k), Fe (l), O (m) and C (n) for Fe₃O₄/Ni-BDC-4, respectively.

3.3.3 Electrochemical behavior and OER performance

OER performance of the proposed electrocatalysts was investigated in a conventional three-electrode cell containing O_2 -saturated 1.0 M KOH solution by LSV at a scan rate of
5 mV s⁻¹. As controls, the OER activities of pristine Ni-BDC, Fe_3O_4 and commercial RuO_2 with the same mass loading on GCE are examined. Catalytic performance of Fe₃O₄/Ni-BDC-n is tested for screening the optimal Fe ratio (Fig. 3.5a and Fig. S3.7). The best OER performance is obtained with the Fe₃O₄/Ni-BDC-4 (Ni 24.7 %, Fe 75.3 %), exhibiting the lowest η of 295 mV at a current density of 10 mA cm⁻². In comparison, large η of 369, 465 and 339 mV (Fig. 3.5b) is registered for pristine Ni-BDC, Fe_3O_4 and commercial RuO₂, respectively. It is noteworthy that introducing Fe_3O_4 nanoparticles, although themselves being poor OER catalysts, radically improves the overall water oxidation ability of Ni-BDC, decreasing n with as much as 170 mV. The enhanced OER performance of Fe₃O₄/Ni-BDC-4 is attributed to the optimal electronic structure of transition metals and hierarchical-layer structure, which are confirmed by XPS and TEM results (Fig. 3.1c and d. Fig. 3.4g-i). To illustrate the role of electronic structure change upon OER performance. the η of 337 mV at 10 mA cm⁻² of physical mixture of Fe₃O₄ and Ni-BDC (Fig. S3.8a) is significantly larger than that of Fe₃O₄/Ni-BDC-4. High-resolution Ni 2p and Fe 2p spectra (Fig. S3.8b and c) of physical mixed samples shows no shifts from the individual samples. In situ growth of Ni-BDC in the presence of Fe₃O₄ nanoparticles causes the binding energy changes of Ni 2p and Fe 2p in the composites (Table 3.1), optimizing the integral electronic structure of Fe₃O₄/Ni-BDC-4 composite for high OER performance. Tafel curves of Fe₃O₄/Ni-BDC-4, Ni-BDC, Fe₃O₄ and commercial RuO₂ are shown in Fig. 3.5c. Tafel slope of Fe₃O₄/Ni-BDC-4 (47.8 mV dec⁻¹) is considerably smaller than those of Ni-BDC (60.5 mV dec⁻¹), Fe₃O₄ (148.1 mV dec⁻¹) and commercial RuO₂ (83.5 mV dec⁻¹), revealing the significantly improved catalytic reaction kinetics on Fe₃O₄/Ni-BDC-4. The change of Tafel slope is related to the potential-determining step (PDS) of the electrochemical reaction, indicating the PDS of Fe₃O₄/Ni-BDC-4 is the second step for electron transfer (formation of O^{*}).^[196, 209] In addition, stability is also a critical parameter to evaluate the catalyst. The chronopotentiometric curve of Fe₃O₄/Ni-BDC-4 is shown in Fig. 3.5d. Compared with previously reported Fe₃O₄ or Ni-BDC based catalysts (Table 3.3), Fe₃O₄/Ni-BDC-4 demonstrates a superior durability over 40 h with a stable OER activity at a constant current density of 10 mA cm⁻². As a control, the pristine Ni-BDC exhibits a weak catalytic stability with less than 5 h (Fig. 3.6). The good catalytic stability of Fe₃O₄/Ni-BDC-4 requires active sites in the composite are maintained for the continuous interaction with the catalytic reaction intermediates for OER and also prevention of the aggregation of Ni-BDC layers during operation, and apparently that stability is achieved with the intermixing of Fe₃O₄ nanoparticles.



Fig. 3.5 (a) LSV polarization curves of OER for Ni-BDC, Fe₃O₄, Fe₃O₄/Ni-BDC-4 and RuO₂ in O₂-saturated 1.0 M KOH solution with a scan rate of 5 mV s⁻¹, respectively. (b) η for Ni-BDC, Fe₃O₄, Fe₃O₄/Ni-BDC-4 and RuO₂ at a current density of 10 mA cm⁻², respectively. (c) The corresponding Tafel plots from LSV curves (a). (d) Chronopotentiometric response of Fe₃O₄/Ni-BDC-4 at 10 mA cm⁻². (e) RRDE measurement of Fe₃O₄/Ni-BDC-4 in O₂-saturated 1.0 M KOH solution at a rotation of 1600 rpm with the ring potential fixed at 1.50 V vs. RHE. (f) FE testing of Fe₃O₄/Ni-BDC-4 using RRDE in N₂-saturated 1.0 M KOH solution.



Fig. 3.6 Chronopotentiometric response of pristine Ni-BDC at 10 mA cm⁻².

Catalyst	Overpotential @ 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Catalytic stability (h)	Ref.
Ni-BDC nanosheets	321	65	N/A	[201]
Ti ₃ C ₂ T _x -CoBDC	410	48.2	2.78	[81]
Fe ₂ Ni-MOF	365	81.8	15	[210]
Ni-MOF@Fe-MOF	265	82	N/A	[185]
Ni-BDC/Ni(OH) ₂	320	41	20	[188]
Pt-NC/Ni-MOF	292	N/A	N/A	[60]
Fe ₃ O ₄ @Co ₉ S ₈ /rGO ^a	340	54.5	6	[211]
H-Co ₉ S ₈ /Fe ₃ O ₄ @SNC	280	87	10	[212]
Fe ₃ O ₄ @NiS _x /rGO	330	33.5	6	[213]
$Ni_2P/Fe_2P/Fe_3O_4$	365	59	8	[214]
MPN@Fe ₃ O ₄	260	33.6	24	[189]
NiCo/Fe ₃ O ₄ / MOF-74	238	29	36	[192]
FeNi ₃ –Fe ₃ O ₄ NPs/MOF- CNT	234	37	20	[191]
Fe_3O_4	465	148.1	N/A	This
Ni-BDC	369	60.5	< 5	work This
Fe ₃ O ₄ /Ni-BDC-4	295	47.8	40	work This work

Table 3.3 OER activity comparison of reported MOF based catalysts on glassy carbon electrode in 1 M KOH.

^arGO: reduced graphene oxide; SNC: sulfur/nitrogen carbon; MPN: metal polyphenolic networks; CNT: carbon nanotube.

The key parameters involved during OER, including the number of transferred electrons and FE reaction process, are further investigated by a RRDE. Fig. 3.5e exhibits a low current density on the ring electrode at 1.50 V compared with that on the disk electrode during LSV. It indicates a desirable four-electron reaction paths $(4OH \rightarrow O_2 + 2H_2O + 4e)$ occurs on Fe₃O₄/Ni-BDC-4 with negligible generation of hydrogen peroxide during OER.^[201, 215] This further confirms the observed disk current density results from water oxidation rather than other side reactions (Fig. 3.5e), a constant current (300 µA) is applied on the disk for oxygen evolution (Fig. 3.5f). The ORR current on the ring is about 57.9 µA, indicating that the generated oxygen in disk electrode is stably reduced in the ring electrode.^[198, 201] The above results strongly assess Fe₃O₄/Ni-BDC-4 is an efficient OER catalyst.



Fig. 3.7 (a) CV curves of Ni-BDC and Fe₃O₄/Ni-BDC-n (n: 1, 2, 3, 4 and 5) in O₂-saturated 1.0 M KOH; scan rate: 50 mV s⁻¹. Inset is oxidation peak area ratio normalized on the basis of Ni-BDC. (b) Anodic peak potential (E_{pa}) and onset potential (E_{onset}) of Ni-BDC and Fe₃O₄/Ni-BDC-n (n: 1, 2, 3, 4 and 5) corresponded to the CV curves (a). (c) Current density as a function of the scan rate to derive C_{dl} for Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4. (d) Nyquist plots of Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4 measured at 1.525 V vs. RHE.

Electrochemical behavior of the samples were characterized by CV in O_2 -saturated 1.0 M KOH solution in a potential window of 1.123-1.573 V vs. RHE, a region without OER and

pre-oxidation peaks are generally observed. Such pre-oxidation peaks are usually related to the oxidation of transition metals (from 2^+ to 3^+), which are involved in OER process.^[60, 201] Ni-BDC (Fig. 3.7a) and Fe₃O₄ (Fig. 3.8) show anodic peaks potential (E_{pa}) at 1.406 and 1.460 V vs. RHE, respectively.^[216, 217] The oxidation peak area ratio of Fe₃O₄/Ni-BDC-4 (Fig. 3.7a) normalized on the basis of Ni-BDC in CV curves is larger than that of others synthetic samples, and such an increased oxidation peak area is believed to be significant for enhanced OER catalytic ability,^[218, 219] in good agreement with above measured η data. As summarized in Fig. 3.7b, E_{pa} of Fe₃O₄/Ni-BDC-n has a slight positive shift

trend with increasing n (n=1, 2, 3, 4), but the trend reverses when n=5, revealing that the amount of Fe₃O₄ nanoparticles could affect E_{pa} . As a control, the main E_{pa} (1.411 V vs. RHE) in the CV of physical mixture of Fe₃O₄ and Ni-BDC (Fig. 3.9) show a negligible change compared with the E_{pa} of pristine Ni-BDC, furtherly revealing that directly prepared Fe₃O₄/Ni-BDC composites modify the integral electronic structure for higher oxidation-state situations. Most importantly, there is likely a link between E_{pa} and onset potential of OER (E_{onset}). The optimal Fe₃O₄/Ni-BDC-4 composite demonstrates the highest E_{pa} (1.431 V vs. RHE) and the lowest E_{onset} (i.e. smallest η) among Fe₃O₄/Ni-BDC-n. Previous reports^[60, 220] indicate this could be due to higher-oxidation-state metal originating from the coupling effects of Ni and Fe in the composite is responsible for an enhanced OER performance. Overall, we successfully demonstrate that the modulation of the oxidation state of elemental Ni and Fe of 2D Ni-BDC by incorporating with Fe₃O₄, which is revealed by XPS, leads to a high E_{pa} and a small η .



Fig. 3.8 CV curves of Fe₃O₄ in O₂-saturated 1 M KOH with a scan rate of 50 mV s⁻¹.



Fig. 3.9 CV curve of physical mixture of Fe_3O_4 and Ni-BDC in O₂-saturated 1 M KOH with a scan rate of 50 mV s⁻¹.

ECSA is another crucial parameter, which is correlated to the number of active sites and has been determined via Cdl measurement (Fig. S3.9).[190, 197, 221] As displayed in Fig. 3.7c, the C_{dl} of Fe₃O₄/Ni-BDC-4 is 478 µF cm⁻², much higher than those of Fe₃O₄ (277 µF cm⁻²) and Ni-BDC (283 μ F cm⁻²). Although ECSA can assess the number of active sites, it is hard to ensure all active sites measured by ECSA are catalytically active,[197] we adopted ECSA value for normalizing the current density of LSV in Fig. 3.5a. Fe₃O₄/Ni-BDC-4 (Fig. 3.10) demonstrating the lower η than those of pristine Ni-BDC and Fe₃O₄ after normalization. The normalized current density of Fe₃O₄/Ni-BDC-4 is considerably large, for example, reaching 2.6 mA cm^{\cdot 2} at 1.55 V vs. RHE, in comparison to 0.19 and 0.05 mA cm^{-2} for pristine Ni-BDC and Fe₃O₄, respectively. This result strongly indicates that the incorporation of Ni-BDC and Fe₃O₄ effectively promotes the catalytic activity. Further, EIS helps to understand charge transfer kinetics at the electrolyte/electrode interface. Nyquist plots of Fe₃O₄/Ni-BDC-4, Ni-BDC and Fe₃O₄ are shown in Fig. 3.7d. Diameter of the semicircles in high-middle frequency region correspond to the charge-transfer resistance (R_{ct}).^[6] R_{ct} (10 Ω) of Fe₃O₄/Ni-BDC-4 during OER is significantly lower than those of pristine Ni-BDC (82 Ω) and Fe₃O₄ (746 Ω), implying a rapid charge transfer process on Fe₃O₄/Ni-BDC-4.



Fig. 3.10 Linear polarization curves of Fe₃O₄/Ni-BDC-4, Ni-BDC and Fe₃O₄ normalized by ESCA.

The morphology change of Fe_3O_4/Ni -BDC-4 after OER test has been evaluated. TEM images (Fig. 3.11a and b) show Fe_3O_4 nanoparticles are still tightly anchored on the surface of Ni-BDC layers. STEM-EDS mapping (Fig. 3.11c and d) demonstrates that the uniform distribution of elemental Ni, Fe, O and C. These observations confirm the structural stability of Fe_3O_4/Ni -BDC-4.



Fig. 3.11 (a, b) TEM images of Fe₃O₄/Ni-BDC-4 after OER test. (c-g) HAADF STEM image (c) and the corresponding STEM-EDS mapping of elemental Ni (d), Fe (e), O (f) and C (g) for Fe₃O₄/Ni-BDC-4 after OER test.

3.4 Conclusions

Ultrafine Fe₃O₄ nanoparticles homogeneously immobilized on 2D Ni based MOFs (Fe₃O₄/Ni-BDC) were synthesized. The functionalized Fe₃O₄ nanoparticles (\emptyset 6 ± 2 nm) with abundant surface hydroxide groups are produced by a hydrothermal method, and then mixed into 2D Ni-BDC layers during synthesis (thickness: 4 ± 1 nm) creating strong interactions not achieved by physically mixing the two components. Introduction of Fe₃O₄ modifies the electronic structure for reduced overpotential and prevents the aggregation of 2D Ni-BDC layers for enhanced OER catalytic stability. Different atom ratios of (Ni/Fe) in Fe₃O₄/Ni-BDC are tested for OER. Fe₃O₄/Ni-BDC-4 demonstrates the optimized OER performance with a η of 295 mV at 10 mA cm⁻², a Tafel slope of 47.8 mV dec⁻¹ and superior catalytic durability (40 h). The persistent stability during cycling (Fig. 3.5d) and the TEM images show that agglomeration is not occurring, indicating that this typically performance reducing effect can be handled. Such structure design methodologies for electronic structure and adsorbate modulation will inspire further development of promising catalysts for OER.

Chapter 4. Microwave assisted crystalline and morphology evolution of flower-like Fe₂O₃@ iron doped Kbirnessite composite and its application for lithium ion storage

This chapter describes the fabrication of microwave assisted Fe₂O₃@ iron doped Kbirnessite composites. The crystalline and morphology evolution of composites are systematically investigated. The synthesized Fe₂O₃@ iron doped K-birnessite composite is applied for the LIBs. And the performances of assembled LIBs as anode materials for lithium ion storage are tested and compared with other related literatures. The chapter is most of the published article "Microwave assisted crystalline and morphology evolution of flower-like Fe₂O₃@ iron doped K-birnessite composite and its application for lithium ion storage" in *Applied Surface Science* coauthored by Wei Huang, Xiaowen Zheng, Huihui Shangguan, Xinxin Xiao, Jing Tang, Hongyu Sun, Kristian Mølhave, Lijie Ci, Pengchao Si and Jingdong Zhang. Besides, the partial experimental data in this chapter are included in appendix II.

4.1 Introduction

Rechargeable lithium-ion batteries (LIBs) represent one of the most appealing and widely used clean energy storage technologies ^[222, 223]. However, the relatively low theoretical specific capacity of graphite (372 mA h g⁻¹) based anodes for LIBs could hardly meet the urgent demand for large-scale electronic devices ^[224]. The development of the next-generation anode materials for superior rechargeable LIBs with high electrochemical capacities and minimal environmental hazard is crucial ^[6, 14, 202, 225-227]. Transition metal oxides (TMOs) exhibit significant theoretical capacities based on a typical conversion-type reaction (MO_x + 2x Li⁺ + 2x e⁻ \leftrightarrow M + x Li₂O), which are typically more than twice of that of graphite with the insertion mechanism for lithium ion storage ^[13, 141, 228-231]. Among various TMO-based materials, manganese oxides (MnO_x) have attracted numerous

interests for anode materials due to the earth-abundant, cost-effective and low-toxic features ^[87, 232, 233]. MnO_x displays a lower lithium ion inserting potential (0.2 V vs. Li/Li⁺) than those of other TMOs, which could provide wider voltage range ^[234]. However, similar to other TMOs, MnO_x suffers from low electrical conductivity and a rapid capacity attenuation due to the volume expansion during lithium insertion/extraction.

To cope with the aforementioned challenge, one approach is to fabricate different nanostructured MnOx, such as Mn₃O₄ nanoparticle ^[235], Mn₃O₄ nanofiber ^[236], nanocrystalline MnO thin film^[237] etc. However, the low electrical conductivity and high surface energy of MnO_x nanomaterials lead to the drastic capacity decay (Table 4.1). Another method is to combine MnO_x with conductive carbonaceous materials (graphene ^[136, 238], carbon nanotube ^[239]), which could accommodate large volume change and promote the electrical conductivity for high lithium storage capacity. Alternatively, the incorporation of MnO_x with other transition metal based components emerges as a costefficient way to promote the lithium storage performance [146, 147, 240, 241]. For example, Svensson et al. have reported Co(OH)₂@MnO₂ nanosheet arrays as binder-free electrodes through a two-step process consisting of electrodeposition and heating ^[241]. The hybrids displayed a reasonable lithium storage capacity of 420 mA h g⁻¹ at 1000 mA g⁻¹ after 500 cycles, ascribed to the synergetic effects from the stable structure of $Co(OH)_2$ and MnO_2 ^[241]. Xiao and co-workers have fabricated Fe₂O₃@amorphous MnO₂ composites for enhanced lithium storage through sequential synthetic methods including solution-phase reaction, annealing and hydrothermal reaction, which exhibited a capacity of 555 mA h g^{-1} at 1000 mA g^{-1} after 100 cycles. The enhanced lithium storage performance is due to that the assembled amorphous MnO₂ nanosheets were *in situ* transformed into a Fe-Mn-O protection layer for better electrical conductivity and enhanced structural integration ^[146]. It has been demonstrated that introduction of the doping of other metal elements in the MnOx could effectively improve the physicochemical properties of MnOx with good electrochemical performance ^[242-245]. For example, Komaba and coworkers have reported different metal (Al, Ni or Co) dopings in K-birnessite-type manganese dioxides for enhanced lithium storage by longstanding solution-phase reaction and annealing [244]. Lee et al. have synthesized Fe-doped Mn_xO_y with hierarchical porous structure through a combined strategy of solution-phase reaction and annealing, showing a high-performance lithium capacity of 620 mA h g^{-1} at 200 mA g^{-1} after 100 cycles. The doping metal elements in the MnO_x improve the bulk conductivity and local electron transfer kinetics ^[245]. However, most of the previous reports require long-standing and elaborate synthetic procedures. It is thus promising to develop a low-cost and simple method to construct hybrid TMOs cooperating with heteroatom doped MnO_x for high-performance LIBs.

Microwave-assisted heating synthesis (MAHS) is regarded as a facile synthetic strategy with high reaction efficiency and reduced energy consumption compared with the traditional heating methods ^[246-248]. It holds the potential to be scaled up for industrial applications in case issues, such as limited penetration depth of the absorbed microwaves, can be well addressed. Besides, MAHS is surfactant-free strategy which circumvents the hinderance induced by capping agents around the nanomaterials ^[249]. Materials obtained by surfactant-free MAHS possess great potentials for energy storage and conversion by carefully tailoring the material structure and compositions through the fine control of microwave reaction ^[250, 251]. For example, Li and co-workers have demonstrated MAHS-derived birnessite-type MnO₂ nanospheres for supercapacitor electrodes, exhibiting a specific capacitance of 210 F g⁻¹ at 200 mA g⁻¹ ^[250]. Wang et al. demonstrated the morphology evolution control of Fe based metal-organic frameworks by MAHS, thus optimizing the derived Fe₂O₃ nanostructures for high-performance LIBs ^[251]. To the best of our knowledge, there is no report on controllably synthesizing homogeneous composites combining Fe doped birnessite-type MnO₂ with Fe₂O₃ by MAHS for enhanced lithium-ion storage performance.

Herein, flower-like Fe₂O₃@Fe doped K-birnessite composite has been successfully prepared with one-pot MAHS. The outer hierarchal iron doped K-birnessite type MnO_x layers containing internal Fe₂O₃ nanocrystals constitute into the flower-like structure, whose formation process is systematically investigated. Further, the composite shows a superior lithium-ion storage performance than pure K-birnessite, exhibiting a good lithium storage reversible capacity of 758 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles.

4.2 Experimental

4.2.1 Chemicals and reagents

Potassium permanganate (KMnO₄, \geq 99.9%) was purchased from Merck (Germany). Iron (II) sulfate heptahydrate (FeSO₄·7H₂O, \geq 99.0%) and manganese (II) sulfate monohydrate (MnSO₄·H₂O, meets USP testing specifications) were purchased from Sigma-Aldrich, Denmark. All chemicals were used as received without further purification. Ultrapure water (>18.25 MΩ cm, Sartorius arium® pro, Germany) was used for all the aqueous solution preparation.

4.2.2 Synthesis of flower-like Fe₂O₃@Fe doped K-birnessite composite

In a typical procedure, 0.200 g KMnO₄ and 0.100 g FeSO₄ $^{-}7H_2O$ were dissolved in 15 ml ultrapure water under stirring for 15 min to form a uniform purple solution, which was transferred to microwave reaction vials (10–20 ml, Biotage, Sweden). The vials were heated in a microwave oven (Biotage® Initiator+ Robot Eight) at 140 °C (pressure: 6 bar, power: 31 W) with different durations (30, 60, 90 and 180 min) to investigate the crystalline and morphology evolution of the Fe₂O₃@Fe doped K-birnessite composite. The obtained products were centrifuged and washed with ultrapure water for more than three times, and then dried in an oven at 110°C for 6 h. The pure K-birnessite composite was 70

fabricated as a control with the same procedure using 0.200 g KMnO₄ and 0.061 g $MnSO_4 \cdot H_2O$.

4.2.3 Materials characterization

Microstructure was analyzed by using the scanning electron microscope (SEM, Quanta FEG 200 ESEM, 15 kV) and transmission electron microscope (TEM, Tecnai G2 T20, 200 kV). Crystalline specialties of composites were tested by X-ray diffraction (XRD, Miniflex 600, Cu-Ka radiation, $\lambda = 1.5418$ Å) and X-ray photoelectron spectroscopic (XPS, Thermo-Scientific system (Al-Ka radiation, 1484.6 eV) analysis, respectively. Specific surface area was recorded by a Surface Area & Pore Size Analyzer (ASAP 2020, Micrometrics). The elemental compositions analysis of sample was performed by inductively-coupled plasma optical emission spectrometry (ICP-OES).

4.2.4 Electrochemical performance for lithium ion storage

Mixed active materials (70 wt%), super P (20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) were dissolved in N-methyl-2-pyrrolidone (NMP) as a slurry to coat on the copper foil. Then, the prepared electrode materials were dried in a vacuum oven at 80 °C for 12 h. The mass loading on a working electrode was about 1.4 mg. Lithium foil was used as the counter electrode. 1.0 M LiPF₆ dissolved in a solution composed of dimethyl carbonate, ethylene carbonate, diethyl carbonate (1:1:1 in volumetric ratio) was used as the electrolyte. Half coin cells (CR 2016) were assembled in a glove box under argon atmosphere at room temperature. Galvanostatic discharge/charge (GDC) tests in a voltage window of 0.01–3.0 V were recorded with a Neware-CT-3008 test system (Shenzhen, China). Cyclic voltammograms (CVs) in the voltage range of 0.01-3.0 V at a scan rate of 0.1 mV s⁻¹ were recorded with a CHI 660E electrochemical workstation (Shanghai, China). Electrochemical impedance spectroscopic (EIS) characterization in a frequency range of 0.01 to 100 kHz was carried out at the open circuit potential (OCP) by the Autolab instrument (Metrohm).

4.3 Results and discussion

4.3.1 Formation process and crystalline evolution with different reactive durations

The overall formation process of synthetic materials is illustrated in Scheme 4.1. Firstly, KMnO₄ (oxidizing agent) reacts with FeSO₄ (reducing agent) by one-pot microwave reaction. In order to investigate the formation process of the Fe₂O₃@Fe doped K-birnessite composites, different microwave reactive durations (30, 60, 90 and 180 min) are adopted. Fig. 4.1a shows the X-ray diffraction (XRD) patterns of corresponded synthetic samples

with a growth time of 30 and 60 min, respectively. No obvious diffraction peaks are detected, indicating the amorphous state of generated composites. When the growth time increases to 90 min, some weak peaks assigned to Hematite type Fe₂O₃ (JCPDS no. 33-0664) are observed. When the growth time is up to 180 min, distinct diffraction peaks match well with birnessite (JCPDS no. 80-1098) and some slight peaks are allocated to Fe₂O₃ (JCPDS no. 33-0664). The related diffraction peaks (Fig. S4.1) are distinguished in detail, with all recognizable peaks assigned to the corresponding crystalline planes of Kbirnessite and Fe₂O₃. Besides, the XRD patterns of synthetic samples with 360 min growth time (Fig. S4.2) are similar to those obtained with 180 min, indicative of the stable existence of synthetic composite after 180 min microwave reaction. As a control, the pure K-birnessite composite with 180 min growth time (Fig. S4.3) is also detected, showing a typical birnessite crystalline structure (JCPDS no. 80-1098). In addition, the surface elemental chemical states of synthetic samples with different growth times (30, 60, 90 and 180 min) are characterized by using X-ray photoelectron spectroscopy (XPS). The XPS spectra (Fig. S4.4) of 30, 60 and 90 min clearly show the existences of Fe, Mn and O elements on the surface of synthetic samples. High-resolution Fe 2p spectrum (Fig. 4.1b) of 30 min located at 712.5 (Fe 2p_{3/2}) and 725.8 eV (Fe $2p_{1/2}$) indicate the presence of Fe³⁺ originating from FeOOH, which is in agreement with previous reports ^[252]. When the growth time increases to 60 or 90 min, the peaks in high-resolution Fe 2p spectrum shift to lower binding energies, which are assigned to the Fe³⁺ of Fe₂O₃ due to the decomposition of FeOOH ^[253]. When the growth time is up to 180 min, high-resolution Fe 2p spectrum (Fig. 4.1b) shows a weak signal, indicating the presence of small amounts of Fe^{3+} on the surface of Fe₂O₃@Fe doped K-birnessite composite. As a control, the XPS spectra of pure K-birnessite composite have been also detected (Fig. S4.5), exhibiting the elemental Mn, O and K signals. The high-resolution Mn 2p spectra are shown in Fig. 4.1c, the binding energy of Mn 2p_{3/2} for pure K-birnessite is 642.38 eV, while it shifts to 642.57 eV with higher electron binding energy for Fe₂O₃@Fe doped K-birnessite, indicating higher state of Mn ^[254]. In addition, the peaks of Mn 2p spectra with Fe₂O₃@Fe doped K-birnessite (Fig. 4.1d) and pure K-birnessite (Fig. 4.1e) composites are deconvoluted into three kinds of valence states of Mn (Mn²⁺, Mn³⁺ and Mn⁴⁺). The manganese distributions (Mn 2p_{3/2}) of Fe₂O₃/Fe doped K-birnessite for Mn²⁺, Mn³⁺ and Mn⁴⁺ are 12.99%, 20.35% and 66.66%, respectively. In contrast, the manganese distributions (Mn 2p_{3/2}) of pure K-birnessite for Mn^{2+} , Mn^{3+} and Mn^{4+} are 11.52%, 27.03% and 61.45%, respectively. The decrease of Mn^{3+} percentage content for Fe₂O₃@Fe doped K-birnessite than pure K-birnessite is attributed to the substitution of Fe^{3+} for Mn^{3+} , validating the iron doping in the $Fe_2O_3@Fe$ doped Kbirnessite composite ^[254, 255]. Moreover, the typical nitrogen adsorption-desorption isotherms are shown in Fig. 4.1f. The specific surface area of Fe₂O₃@Fe doped K-birnessite is calculated to be 241.1 m² g⁻¹, ca. 9 times of the value of pure K-birnessite (26.4 m² g⁻¹). The higher specific surface area for Fe₂O₃@Fe doped K-birnessite is the result of the formation of finer porous structure, as well as the reduced thickness of birnessite plate

crystals and the presence unfold the stacking layers due to iron doping ^[256]. Fe₂O₃@Fe doped K-birnessite (Fig. S4.6) displays a mesoporous structure (2-50 nm) with pore-size distribution centered at 46.6 nm, while pure K-birnessite (Fig. S4.5) shows a macroporous structure (>50 nm) whose pore size is mainly located at 85.5 nm. The finer mesoporous structure and higher specific surface area for the Fe₂O₃@Fe doped K-birnessite than the pure K-birnessite could provide more active sites for lithium ion insertion/extraction.



Scheme 4.1 Schematic illustration of the growth process of the $Fe_2O_3@Fe$ doped K-birnessite composite. Inset shows $Fe_2O_3@Fe$ doped K-birnessite MnO_x layers. Not drawn to real scale.

Based on the above characterization, the overall formation process involving of several chemical reactions is proposed ^[257, 258]. In the very beginning, KMnO₄ reacts with H⁺ from the acidic mixed solution (pH = 2.3), decomposing into MnO₂ and O₂ in the microwave heating process (Eq. 4.1). The generated O₂ oxidizes the Fe²⁺ to FeOOH (Eq. 4.2), which is further decomposed into Fe₂O₃ under heating (Eq. 4.3). Fe₂O₃ reacts with the previously generated H⁺ from Eq. 4.2 with the formation of Fe³⁺ (Eq. 4.4), leading the Fe doping in the layer structure of composite. It is noteworthy that the generated H⁺ is not enough to react with the entire Fe₂O₃ (Eq. 4.2 and 4.4), thus the slight peaks of Fe₂O₃ (Fig. 4.1a) can

be observed from the XRD patterns of Fe_2O_3 @Fe doped K-birnessite composite. Moreover, the formative MnO_2 is further oxidized to layer-structural MnO_x (Mn^{2+} , Mn^{3+} and Mn^{4+}).

$$4 \operatorname{MnO}_{4} + 4 \operatorname{H}^{+} \xrightarrow{\Delta} 4 \operatorname{MnO}_{2} + 3 \operatorname{O}_{2} + 2 \operatorname{H}_{2} O$$

$$(4.1)$$

$$4 \text{ Fe}^{2+} + \text{O}_2 + 6 \text{ H}_2\text{O} \rightarrow 4 \text{ FeOOH} + 8 \text{ H}^+$$
(4.2)

$$2 \text{ FeOOH} \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$$

$$(4.3)$$

(4.4)

$$Fe_2O_3$$
+ 6 H⁺ \rightarrow 2 Fe³⁺ + 3 H₂O



Fig. 4.1 (a) XRD patterns of synthetic samples with different growth durations (30, 60, 90 and 180 min). (b) High-resolution XPS spectra of Fe 2p of synthetic samples with different growth times (30, 60, 90 and 180 min). (c-e) High-resolution XPS spectra of Mn 2p of Fe₂O₃@Fe doped K-birnessite (d) and pure K-birnessite (e) composites; insets in Fig. 4.1d and e are the manganese distribution (Mn2p_{3/2}). (f) Typical nitrogen adsorption-desorption isotherms of Fe₂O₃@Fe doped K-birnessite and pure K-birnessite composites.

4.3.2 Morphology evolution with different reactive durations

The morphology evolution of synthetic samples with different growth times are investigated by scanning electron microscopy (SEM) and transmission electron

microscopy (TEM). When the growth time is 30 min, the generated samples (Fig. 4.2a, e and i) show a uniform spherical shape. This is attributed to a rapid nucleation of high concentrations of Mn and Fe sources in the beginning, a process that a large amount of formative small nuclei aggregated into the spherical morphology with minimized surface energy ^[259]. As the growth time increases to 60 min, the generated small particles (Fig. 4.2b, f and j) gradually grow up and stack together into a spherical nanoplate shape. For 90 min, the stacked spherical nanoplates (Fig. 4.2c, g and k) further grow up and become thicker. When the growth time is 180 min, the generated Fe₂O₃@Fe doped K-birnessite composite shows a homogenous flower-like structure. The formation of MnO_x sheets on the edge of the composite is mainly due to the abundant positive cations (K⁺, Fe³⁺) or H₂O molecules which effectively maintain the stability of layer structure ^[260]. Besides, the samples of 360 min (Fig. S4.7) show similar flower-like structure of 180 min, implying the stable Fe₂O₃@Fe doped K-birnessite composite. As a control, SEM images of synthetic pure K-birnessite composites with growth durations of 30 (Fig. S4.8a-c), 60 (Fig. S4.8d-f), 90 (Fig. S4.8g-i) and 180 (Fig. S4.8j-l) min show similar thick uneven hierarchical structure. There are no significant differences between those samples in terms of morphology, indicating of a quick completion of the reaction within 30 min. This is because the presence of high concentrated MnO₄⁻ and Mn²⁺ in the solution fast generates MnO_x composite, leading to the thick inhomogeneous structure. It is noteworthy that the introduction of Fe sources (FeSO₄) for the Fe₂O₃@Fe doped K-birnessite composite effectively results in uniform MnOx layers covering the nano-sized iron oxide core (Fig. 4.2d and h).



Fig. 4.2 SEM images of synthetic samples with 30 (a, e and i), 60 (b, f and j), 90 (c, g and k) and 180 (d, h and l) min's growth time, respectively.

TEM images of the synthetic samples with different growth times (30, 60, 90 and 180 min) are shown in Fig. 4.3. The low-magnification TEM images (Fig. 4.3a-d) show clearly the morphology evolution of samples with different growth time, a process that the initial spherical shape slowly grows up to stacking spherical nanoplates, which turn to be a uniform flower-like hierarchical structure. The high-resolution TEM images with the growth time of 30 (Fig. 4.3e) or 60 min (Fig. 4.3f) show the amorphous structure, in agreement of the XRD patterns (Fig. 4.1a). The high-resolution TEM image with growth time of 90 min (Fig. 4.3g) demonstrates a crystalline interplanar spacing with 0.25 nm assigning to the (1 1 0) plane of Fe_2O_3 (JCPDS no. 33-0664), indicating the formation of Fe_2O_3 nanocrystals, which is also confirmed by previous analysis (Fig. 4.1a and Eq. 4.3). When the growth time is 180 min, the high-resolution TEM image of (Fig. 4.3h) shows a homogenous flower-like structure. In comparison, TEM images of pure K-birnessite (Fig. S4.9) show a disordered thick hierarchical structure, further confirming that the successful iron doping. The d-spacing of lattice fringes of Fe₂O₃@Fe doped K-birnessite is estimated to be 0.66 nm, smaller than the standard value (0.705 nm) of (0 0 1) plane of birnessite (JCPDS no. 80-1098) which is also found in the pure K-birnessite (Fig. S4.9b) with 180 min's growth time. This phenomenon is likely attributed to the loss of water molecule in the composite interlayer during the TEM measurement [261, 262]. In addition, no obvious lattice fringes of Fe₂O₃ in the layer surface of composite are observed, while STEM-EDS mapping images (Fig. 4.3i-m) show the uniform distribution of K, Fe, Mn and O elements. This observation confirms iron doping in the composite and a slight amount of Fe₂O₃ nanocrystals are embedded in the core of Fe₂O₃@Fe doped K-birnessite composite. Moreover, the elemental compositions are further examined by ICP-OES measurement, the chemical formulas of Fe₂O₃@Fe doped K-birnessite and pure K-birnessite composite are determined to be K_{0.14}Fe_{0.33}Mn_{0.53}O_x (H₂O) and K_{0.27}Mn_{0.73}O_x (H₂O), respectively. Thus, the hypothetical structure of flower-like Fe₂O₃@Fe doped K-birnessite composite (Scheme 1) is composed of edge-shared Fe doping 2D manganese oxide octahedra with interstitial cations/molecules (K⁺, H₂O) to balance the overall charge of the layers originating from inclusion of Mn²⁺, Mn³⁺ or Fe³⁺ sites into the Mn⁴⁺ sheets, and internal Fe₂O₃ nanocrystals.



Fig. 4.3 TEM images of synthetic samples with 30 (a), 60 (b), 90 (c) and 180 (d) min growth time, respectively. High-resolution TEM images of synthetic samples with 30 (e), 60 (f), 90 (g) and 180 (h) mins growth time, respectively. (i-m) HAADF STEM image (i) and corresponded STEM-EDS mapping of elemental K (j), Fe (k), Mn (l) and O (m) for synthetic samples with a 180 min growth time.

4.3.3 Crystalline and morphology evolution with different reactive temperatures and stoichiometric ratios

The influential factors, i.e. reactive temperature and stoichiometric ratio of $KMnO_4/FeSO_4 \cdot 7H_2O$, affecting the formation of flower-like Fe_2O_3 @Fe doped K-birnessite composite have been further investigated. Reactive temperatures either lower or higher than 140°C are evaluated. When using 120 °C for 180 min, the samples (Fig. 4.4a, c and e) show a nanoplate morphology, indicating that the low reactive temperature leads to the sluggish formative rate of flower-like structure. 160 °C for 180 min (Fig. 4.4b, d and f) results in samples showing larger size with thicker layers than the samples obtained at 140 °C, revealing the high reactive temperature causing the continuous growth of particles and layers. In addition, the samples fabricated at the optimal temperature condition (140 °C, 180 min) with autoclave reaction (Fig. S4.10) do not show a flower-like structure, emphasizing the role of microwave power for the fast formation of flower-like hierarchical-layer structure.



Fig. 4.4 SEM images of synthetic samples at 120 °C (Fig. 4.4a, c and e) and 160 °C (Fig. 4.4b, d and f) by 180 min microwave reaction.

The effect of the mass ratio of KMnO₄ and FeSO₄ ·7H₂O (140 °C, 180 min) upon the sample morphology is systematically investigated by XRD and SEM measurement. When the mass ratio (KMnO₄/FeSO₄ ·7H₂O) is 0.2/0.2, the obtained samples are confirmed by the XRD with main peaks (Fig. 4.5a) matching well with that of Fe₂O₃ (JCPDS no. 33-0664), with a stacked spherical shape (Fig. 4.5d, g and j). The vanish of MnO_x signal in the XRD pattern (Fig. 4.5a) is mainly due to the complete transform of MnO₄ to Mn²⁺ due to the enough Fe²⁺ in the reactive process, thus the generated Mn²⁺ dissolves in the solution. When the mass ratio is 0.2/0.4, the samples display (Fig. 4.5b) the Jarosite XRD patterns (KFe₃(SO₄)₂ (OH)₆, JCPDS no. 22-0827) and a mixed structure of nanoplates and nanospindles (Fig. 4.5e, h and k). For a mass ratio of 0.2/0.05, the XRD pattern (Fig. 4.5c) and SEM images (Fig. 4.5f, i and l) of synthetic samples show similar results to the composite obtained from 0.2/0.1, but with a much lower yield (ca. 60 mg) than that (ca. 120 mg) of Fe₂O₃@Fe doped K-birnessite composite (0.2/0.1). Accordingly, Fe₂O₃@Fe doped K-birnessite with an optimal ratio 0.2/0.1 is selected due to the largest yield and obtaining

a homogenous flower-like structure with a strong interaction between internal Fe_2O_3 nanocrystals and outer hierarchal MnO_x layers, originating from the comparable ionic radii between Mn and Fe cations ^[146, 245].



Fig. 4.5 XRD patterns and SEM images of synthetic samples with different mass ratios of KMnO₄ and FeSO₄ \cdot 7H₂O including 0.2: 0.2 (a, d, g and j), 0.2: 0.4 (b, e, h and k) and 0.2: 0.05 (c, f, i and l) at 140 °C for 180 min.

4.3.4 Lithium ion performance

In order to investigate the lithium ion storage performance of Fe₂O₃@Fe doped Kbirnessite and pure K-birnessite composites, half-cell configurations are assembled with active materials as the working electrodes and lithium foils as the counter electrodes. Fig. 4.6a shows cyclic voltammograms (CVs) of the first five cycles for Fe₂O₃/Fe doped Kbirnessite composite in the voltage range of 0.01-3.0 V at a scan rate of 0.1 mV s⁻¹. The small cathodic peaks at ca. 2.68 and 1.48 V in the first cycle are mainly attributed to the lithium intercalation in the iron doping K-birnessite layers and the internal Fe₂O₃ with the generation of solid electrolyte interface (SEI), formation of LiMnO_X and Li_vFe₂O₃. A broad peak at ca. 0.50 V and a sharp peak at ca. 0.19 V in the cathodic scan are mainly assigned to the conversion of Fe^{3+} to Fe^{0} and the generation of Li_2O and metallic Mn, respectively ^[141, 146]. The obvious oxidation peak at ca. 1.16 V and slight peak at ca. 1.56 V are corresponded to the electrochemical oxidative reaction of metallic Mn and Fe⁰, respectively. It is noteworthy that Fe could maintain as zero-valent iron nanoparticles during the reduction/oxidation reaction of K-birnessite typed MnOx due to the reduction of Fe³⁺ to Fe⁰ occurs early during the discharge scan, while oxidation of metallic iron takes place in the higher potential during the charge scan. The existence of zero-valent iron could efficiently improve the integral conductivity of MnO_x with fast electron transfer diffusion for good electrochemical performance ^[245]. After initial scans, the broad cathodic and anodic peaks gradually shift and become stable at ca. 0.15 and 1.35 V, respectively. The slight voltage shifts are attributed to the polarization stemming from the electrode resistance ^[263]. In comparison, the CVs of pure K-birnessite composite without Fe doping (Fig. S4.11) show a cathodic peak at ca. $0.19\ V$ and an anodic peak at ca. $1.21\ V$ after the initial cycle. The similar stable cathodic and anodic peak positions in the CVs indicate the main redox reaction is due to the reaction of MnOx and Li⁺ for lithium ion storage. Besides, previous reports show the stable cathodic peak of Fe₂O₃ for lithium ion storage after initial scan is at ca. 0.75 V [146, 147]. The weak cathodic peak assigning to Fe₂O₃ in CVs of Fe₂O₃@Fe doped K-birnessite composite indicates a slight existence of Fe₂O₃ nanocrystals. These results indicate the abundant majority of lithium storage capability of the Fe₂O₃@Fe doped K-birnessite composite is originated from the iron doping K-birnessite layers.



Fig. 4.6 (a) CVs of the first five cycles for Fe₂O₃@Fe doped K-birnessite with a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic discharge/charge profiles of the first five cycles at a current density of 100 mA g⁻¹. (c, d) Cycling performance of Fe₂O₃@Fe doped K-birnessite (c) and pure K-birnessite (d) composites at a current density of 100 mA g⁻¹. (e) Long-term cycling performance of Fe₂O₃@Fe doped K-birnessite at a current density of 500 mA g⁻¹.

The Galvanostatic discharge/charge (GDC) profiles of Fe₂O₃@Fe doped K-birnessite composite with the first five cycles at a current density of 100 mA g⁻¹ are shown in Fig. 4.6b. In the initial cycle, the gradual slope in the region of 1.0-0.45 V is associated with the broad cathodic wave starting from 1.0 V with a peak at ca. 0.50 V, assigning to the conversion of Fe³⁺ to Fe⁰. In addition, the platform starting from ca. 0. 43 V for the first discharge profile matches with the cathodic peak with a relatively sharp peak at ca. 0.19 V, corresponding to the generation of Li₂O and metallic Mn, respectively. In subsequent CVs, the platform at ca. 0.50 V in discharge profiles are attributed to the broad cathodic wave ranging from ca. 0.7 to 0.05 V with a peak at ca. 0.15 V. The potential region (0.7-0.05 V) means the main reaction of the formation of Li₂O and metallic Mn occurs in the process, in good agreement with gradual platforms in the discharge profiles. Similar phenomenon is also found in previous reports ^[245, 264]. The cycling performance of the Fe₂O₃@Fe doped K-birnessite composite at a current density of 100 mA g⁻¹ is shown in Fig. 4.6c. The initial discharge and charge capacities are 1490 and 604 mA h g⁻¹, respectively. The relatively low initial Coulombic efficiency (41%) are attributed to the escape of crystalline water molecules in the structure of composite (rather than free water). partially irreversible side reaction of the electrode materials with electrolyte and the formation of a SEI film. Then the discharge capacity deceases to 352 mA h g^{-1} after 40 cycles, after which the discharge capacity gradually increases and stabilizes to 742 mA h g^{-1} until 140 cycles, with a Coulombic efficiency of almost 100% after 15 cycles. The phenomenon is believed to the result of a range of activation processes including the longterm activation of electrode materials for structural rearrangement, offering more active sites for lithium storage in the subsequent discharge-charge cycles ^[202, 233]. Besides, the generation of higher-oxidation-state manganese in the composite by Li₂O oxidation during the charge process and the formation of electrochemically active gel-like films on the surface of Fe₂O₃@Fe doped K-birnessite electrode could improve efficiently the lithium storage capacity. This is also confirmed by previous reports about manganese-based materials for lithium ion storage ^[147, 233, 264]. As a control, the pure K-birnessite composite (Fig. 4.6d) delivers the initial discharge and charge capacity of 1373 and 430 mA h g⁻¹ at 100 mA g⁻¹, with a low Coulombic efficiency of 31 %. In addition, the discharge capacity decreases to 311 mA h g⁻¹ after 140 cycles. The higher capacity retention for Fe₂O₃@Fe doped K-birnessite is mainly attributed to the Fe doping in the K-birnessite composite decreases the size of particles and provides larger specific surface area for more exposing active sites. Fe₂O₃@Fe doped K-birnessite composite (Fig. 4.7a) demonstrates capacities of 403, 282, 177, 104 mA h g⁻¹ at current densities of 100, 200, 500, 1000 mA g⁻¹, respectively. When the current density is set back to 100 mA g^{-1} after 40 cycles, the capacity retained 346 mA h g⁻¹. As a contrast, the pure K-birnessite composite (Fig. 4.7b) exhibits capacities of 299, 200, 121, 70 mA h g^{-1} at current densities of 100, 200, 500, 1000 mA g⁻¹, respectively. When the current density is reduced back to 100 mA g⁻¹ after 40 cycles, the capacity only recovers to 239 mA h g⁻¹.



Fig. 4.7 Rate capability of Fe₂O₃@Fe doped K-birnessite (a) and pure K-birnessite (b) composites at different current densities of 100, 200, 500, 1000 and 100 mA g⁻¹.

In order to investigate further the cycling performance of Fe₂O₃@Fe doped K-birnessite composite at high current density, Fig. 4.6e shows the long-term cycling performance of Fe₂O₃/Fe doped K-birnessite at 500 mA g⁻¹. The capacities also demonstrate a long activation process for 39 cycles, then gradually increases and stabilizes to a reversible capacity of 758 mA h g⁻¹ after 200 cycles. The Coulombic efficiency is more than 94 % after the first six cycles. In converse, the pure K-birnessite composite (Fig. 4.8) exhibits interferer irreversible capacities after only 140 cycles, with a much higher charge capacity than the discharge capacity as a sign of the complete breakdown of active materials on the electrode. Therefore, the introduction of Fe source in the K-birnessite composite could effectively reinforce the flower-like structural stability for good cycling performance. Comparing with previously reported manganese oxide based composites for lithium ion storage (Table 4.1), the Fe₂O₃@Fe doped K-birnessite composite demonstrates a good electrochemical performance.



Fig. 4.8 Cycling performance of the pure K-birnessite at a current density of 500 mA g⁻¹.

Composites	Synthetic	Current	Cycle	Capability	Ref.
1	method	(mA g ⁻¹)	number	(mA h g ⁻¹)	
Mn_3O_4	Solution-phase	29.25	40	800	[235]
nanoparticles	reaction and annealing				
$Mn_{3}O_{4}$ nanofiber	Electrospinning and heating	NA	50	450	[236]
Nanocrystalline MnO thin film	Annealing and laser deposition	NA	25	472	[237]
Mn ₃ O ₄ /RGO	two-step solution-	40	NA	900	[136]
Graphene/Mn ₃ O ₄ Membrane	hydrothermal reaction, solution- phase reaction and	100	100	702	[238]
CNTs/MnO _x - Carbon hybrid nanofibers	liquid chemical redox reaction and annealing	100	100	560.5	[239]
MnO@Mn ₃ O ₄ /N- doped porous carbon	solution-phase reaction and annealing	200	270	1500	[233]
TiO ₂ -C/MnO ₂	Multiple-step hydrothermal reactions and	335	100	352	[240]
Fe ₂ O ₃ @amorphous MnO ₂	Solution-phase reaction, annealing and hydrothermal reaction	1000	100	555	[146]
$\alpha\text{-}Fe_2O_3/MnO_2$	Solution-phase reaction and annealing	500	500	494	[147]
Co(OH)2@MnO2	Two-step electrodeposition	1000	500	420	[241]
Co-25 birnessite	Solution-phase reaction and annealing	20	20	200	[244]
Fe doped Mn _x O _y	Solution-phase reaction and annealing	200	100	620	[245]
K-birnessite	One-pot microwave reaction	500	140	203	This work
Fe ₂ O ₃ @Fe doped K-birnessite	One-pot microwave reaction	500	200	758	This work

Table 4.1 Comparison on the electrochemical performances of $Fe_2O_3@Fe$ doped K-birnessite composite with previously reported manganese oxide based composites for lithium ion storage.

In order to make a good understanding of Fe₂O₃@Fe doped K-birnessite for lithium ion storage performance, electrochemical impedance spectroscopy (EIS) of fresh cells are recorded. Nyquist plots of Fe₂O₃@Fe doped K-birnessite and pure K-birnessite composites are shown in Fig. 4.9a. Semicircles in high-middle frequency region correspond to the charge-transfer resistance (R_{ct}) through the electrode/electrolyte interfaces. The R_{ct} (52 Ω) of Fe₂O₃@Fe doped K-birnessite is much lower than that of pure K-birnessite composite (210Ω) . The result indicates Fe doping in the K-birnessite composite efficiently improves the overall electrical conductivity and decreases the interface polarization of electrode. Moreover, the Fe₂O₃@Fe doped K-birnessite after testing at 100 mA g⁻¹ for 140 cycles has been evaluated by SEM and EDS (Fig. 4.9b, d-g), which clearly indicate the $Fe_2O_3@Fe$ doped K-birnessite composite stably exists in the electrode. TEM images (Fig. 4.9c) shows a corresponding flower-like structure, further confirming the structural stability. The reasons for Fe₂O₃@Fe doped K-birnessite composite showing an enhanced lithium-ion storage performance than pure K-birnessite can be summarized as: (1) the monodisperse flower-like Fe₂O₃@Fe doped K-birnessite particles with a high specific surface area provide abundant active sites for lithium insertion/extraction. (2) The synergetic effects of K-birnessite type MnO_x and Fe₂O₃ promise the improved lithium capacity with a strong interaction between MnOx and Fe₂O₃, originating from the comparable ionic radii between Mn and Fe cations [146, 245]. (3) iron doping in the K-birnessite typed MnO_x not only facilitates the bulk conductivity and promotes the electron transfer kinetics, but also provides extra active sites from the defects of iron doping. There results guarantee flowerlike Fe₂O₃@Fe doped K-birnessite composite demonstrate a good electrochemical performance and can be an alternative anode material for LIBs.



Fig. 4.9 (a) Nyquist plots of $Fe_2O_3@Fe$ doped K-birnessite and pure K-birnessite composites. SEM (b) and TEM (c) images of $Fe_2O_3@Fe$ doped K-birnessite composite based lithium storage material after 140 cycles at 100 mA g⁻¹, (d-g) EDS mapping images correspond to Fig. 4.9b.

4.4 Conclusions

Flower-like Fe₂O₃@Fe doped K-birnessite composite has been successfully fabricated using one-pot microwave reaction, and the crystalline and morphology evolution of Fe₂O₃@Fe doped K-birnessite composite related to the microwave reactive durations, reactive temperatures and stoichiometric ratios have been systematically investigated. When the designed composites are used for lithium ion storage, the comparison study indicates that the hybrid composite exhibits superior performance regarding to capacity and operational stability than that of the pure K-birnessite. Synergetic effects from the flower-like structure consisting of internal slight Fe₂O₃ nanocrystals and outer hierarchal iron doped K-birnessite type MnO_x layers with strong interaction and optimized electronic structure are believed to be responsible for the improved electrochemical behaviors. The structural design and promising performance of Fe₂O₃@Fe doped K-birnessite composite will ensure the composite could be a promising anode material of LIBs for potential practical applications and inspire the development of LIBs.

Chapter 5. Conclusions

Green energy technologies are urgently needed due to forthcoming insecurity of fossil fuel supply, increasing global energy demand as well as critical environmental and climate concerns. Exploring earth-abundant and relatively low-price transition metal-based composites as good OER electrocatalysts used for rechargeable next-generation metal-air batteries or as excellent anode materials used for high-performance LIBs are promising alternatives. In my Ph.D. project, cheap and environment-friendly iron-based composites for OER electrocatalysts and anode materials of LIBs have been explored.

Firstly, ultrafine Fe₃O₄ nanoparticles (diameter: 6 ± 2 nm) are homogeneously immobilized on 2D Ni based MOFs (Fe₃O₄/Ni-BDC) for OER. The composite is prepared through direct growth of Ni-BDC (thickness: 5 ± 1 nm) in the presence of "water-soluble" Fe₃O₄ nanoparticles with abundant surface hydroxide groups. Morphology and structural changes to tackle the aggregation issue for enhanced catalytic activity are studied via different amounts of Fe₃O₄ immobilized on the 2D Ni-BDC layers. The optimized Fe₃O₄/Ni-BDC achieves the best OER performance at an overpotential of 295 mV at 10 mA cm⁻², a Tafel slope of 47.8 mV dec⁻¹ and considerable catalytic durability (40 h). Further, the OER catalytic mechanism and how the valance state condition of oxidationstate metal affects OER performance in the composites are carefully discussed.

Secondly, a flower-like composite consisting of internal Fe₂O₃ nanocrystals and outer hierarchal iron doped K-birnessite type MnO_x layers (Fe₂O₃@Fe doped K-birnessite) is synthesized by a facile one-pot microwave-assisted heating synthesis (MAHS). The crystalline and morphology evolution of Fe₂O₃@Fe doped K-birnessite composite are studied by checking the products at various reaction durations, using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning & transmission electron microscopy (SEM & TEM). Key factors affecting the morphology such as reactive temperature and stoichiometric ratio are systematically investigated. When tested for LIBs, the optimized hybrid Fe₂O₃@Fe doped K-birnessite composite exhibits a high reversible capacity of 758 mA h g⁻¹ at 500 mA g⁻¹ after 200 cycles, outperforming the pure K-birnessite (203 mA h g⁻¹). The excellent electrochemical performance is assigned to the efficient utilization of the merits of the flower-like structure and strong interaction between MnO_x and Fe₂O₃. Further, crucial factors associated with structural stability of Fe₂O₃@Fe doped K-birnessite composite during cycling are identified.

In summary, constructing the transition metal-based composites with iron components used for oxygen evolution electrocatalysis and lithium ion storage have great potential for high-performance energy storage and conversion system, like metal-air batteries or LIBs. 88

However, more related studies are suggested to conduct. On the one hand, further exploring high-performance transition metal-based composites with scalable synthesis and bifunctional properties (such as both OER and ORR) are significantly critical. The bifunctional catalytic ability (OER/ORR) is helpful for the development of rechargeable metal air batteries. On the other hand, there are only few reports on the structural and morphological evolution of transition metal-based composites during the OER process followed by in-situ techniques (e.g. in-situ XAS, Raman, TEM etc.). In comparison to ex situ characterization, in-situ techniques combined with computational simulation is a powerful route to localizing the intrinsic active sites and understanding the reaction mechanisms. Meanwhile, high-performance anode electrode materials for LIBs with scalable and low-cost properties and high Coulombic efficiency during cycling are also strongly required. The reactive mechanism of lithium ion storage is needed to investigate carefully with combination of theoretical simulations, such as, the formation process of SEI films and their influence to the lithium ion storage. Overall, experiments incorporated with simulations including density functional theory calculations are urgent to efficiently promote the in-depth understanding among materials structure, functional properties and fundamentals in the development of next-generation energy storage and conversion system.

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Appendix I

Supporting information for chapter 3 is included.



Fig. S3.1 (a) XPS survey spectra of Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4.



Fig. S3.2 SEM images of (a, b) Ni-BDC, (c, d) Fe_3O_4 and (e, f) Fe_3O_4 /Ni-BDC-4.



Fig. S3.3 SEM images of synthetic Fe_3O_4/Ni -BDC obtained with different volumes of Fe_3O_4 (12 mg ml⁻¹; a-c: 1 ml; d-f: 2 ml; g-i: 3 ml; j-l: 5 ml).



Fig. S3.4 (a-c) SEM images of fabricated samples using the same synthetic conditions for Fe_3O_4/Ni -BDC-4 but without the addition of $NiCl_2$ 6H₂O. (d) EDS data corresponding to (c).



Fig. S3.5 Atomic-force microscopy image of partial Ni-BDC samples and the corresponding height profiles indicated as line 1, 2 and 3.



Fig. S3.6 Linear elemental distribution obtained from Fe_3O_4/Ni -BDC-4 as shown in the inset.



Fig. S3.7 Linear polarization curves of Fe₃O₄/Ni-n (n= 1, 2, 3 and 5) in O₂-saturated 1 M KOH with a scan rate of 5 mV s⁻¹.



Fig. S3.8 (a) Linear polarization curves of Fe₃O₄/Ni-BDC-4 and the physical mixture of Fe₃O₄ and Ni-BDC in O₂-saturated 1 M KOH with a scan rate of 5 mV s⁻¹. (b) High-resolution Ni 2p XPS spectra of Ni-BDC and the physical mixture of Fe₃O₄ and Ni-BDC. (c) High-resolution Fe 2p XPS spectra of Fe₃O₄ and the physical mixture of Fe₃O₄ and Ni-BDC.



Fig. S3.9 CV curves for Ni-BDC, Fe₃O₄ and Fe₃O₄/Ni-BDC-4 in a narrow potential range in O₂-saturated 1 M KOH at scan rates from 40 to 120 mV s⁻¹.

Appendix II



Supporting information for chapter 4 is included.

Fig. S4.1 XRD patterns of synthetic samples with a 180 min growth time.



Fig. S4.2 XRD patterns of synthetic samples with a 360 min growth time.

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Fig. S4.4 (a, d, g) XPS survey spectra of synthetic samples with different growth times (30, 60 and 90 min). High-resolution XPS spectra of O 1s (b, e and h) and Mn 2p (c, f and i) for synthetic samples with 30, 60 and 90 min growth time, respectively.



Fig. S4.5 (a, b) XPS survey spectra of $Fe_2O_3@Fe$ doped K-birnessite (a) and pure K-birnessite (b) composites.



Fig. S4.6 Pore-size distribution of Fe₂O₃@Fe doped K-birnessite and pure K-birnessite composites.



Fig. S4.7 SEM images of Fe₂O₃@Fe doped K-birnessite with a 360 min growth time at 140°C.



Fig. S4.8 SEM images of synthetic pure K-birnessite composites with growth durations of 30 (a, b and c), 60 (d, e and f), 90 (g, h and i) and 180 (j, k and l) min, respectively.



Fig. S4.9 (a, b) TEM images of the pure K-birnessite composite with 180 min's growth time.



Fig. S4.10 SEM images of synthetic samples under autoclave reaction at 140 $^{\circ}\mathrm{C}$ for 180 min.



Fig. S4.11 Cyclic voltammograms (CVs) of the first five cycles for pure K-birnessite at 0.1 mV s⁻¹.

Appendix III

Contributions made during the Ph.D. project are included.

Research papers included in the Ph.D. project:

1. <u>Wei Huang</u>, Xiaowen Zheng, Huihui Shangguan, Xinxin Xiao, Jing Tang, Hongyu Sun, Kristian Mølhave, Lijie Ci, Pengchao Si, Jingdong Zhang, 'Microwave-assisted crystalline and morphology evolution of flower-like Fe₂O₃/iron doped K-birnessite composite and its application for lithium storage', *Appl. Surf. Sci.*, 2020, *525*, 146513.

2. <u>Wei Huang¹</u>, Chao Peng¹, Jing Tang, Fangyuan Diao, Hongyu Sun, Christian Engelbrekt, Jingdong Zhang, Xinxin Xiao and Kristian Mølhave, 'Ultrafine Fe₃O₄ nanoparticles immobilized on two-dimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction'. (Manuscript submitted to ACS Catalysis)

3. <u>Wei Huang</u>, Jing Tang, Fangyuan Diao, Christian Engelbrekt, Jens Ulstrup, Xinxin Xiao and Kristian Mølhave, 'Recent progress of 2D metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis' (Manuscript accepted by ChemElectroChem).

Research papers in connection with the Ph.D. project:

1. Yuan Yang, Shuo Li, <u>Wei Huang</u>, Huihui Shangguan, Christian Engelbrekt, Shuwei Duan, Lijie Ci and Pengchao Si. Effective synthetic strategy for Zn_{0.76}Co_{0.24}S encapsulated in stabilized N-doped carbon nanoarchitecture towards ultra-long-life hybrid supercapacitors. J. Mater. Chem. A, 2019, 7, 14670-14680.

2. Shuo Li, Minghao Hua, Yuan Yang, <u>Wei Huang</u>, Xiaohang Lin, Lijie Ci, Jun Lou and Pengchao Si. Self-supported multidimensional Ni-Fe phosphide networks with holey nanosheets for high-performance all-solid-state supercapacitors. J. Mater. Chem. A, 2019, 7, 17386-17399.

3. Jing Tang, Rebecka Maria Larsen Werchmeister, Loredana Preda, <u>Wei Huang</u>, Zhiyong Zheng, Silke Leimkuhler, Ulla Wollenberger, Xinxin Xiao, Christian Engelbrekt, Jens Ulstrup, Jingdong Zhang. Three-dimensional sulfite oxidase bioanodes based on graphene functionalized carbon paper for sulfite/O₂ biofuel cells. ACS Catal. 2019, 9, 6543-6554.

4. Huihui Shangguan¹,<u>Wei Huang¹</u>, Christian Engelbrekt, Xiaowen Zheng, Fei Shen, Xinxin Xiao, Lijie Ci, Pengchao Si, Jingdong Zhang. Well-defined cobalt sulfide nanoparticles locked in 3D hollow nitrogen-doped carbon shells for superior lithium and sodium storage. Energy Storage Mater. 2019, 18, 114-124. (¹equal contribution)

5. Xianyi Cao, Shuai Jia, <u>Wei Huang</u>, Yingying Tang, Jens Ø Duss, Jun lou,Qijin Chi. Optimal structuring nitrogen-doped hybrid-dimensional nanocarbons for highperformance flexible solid-state supercapacitors. J. Mater. Chem. A, 2019, 7, 7501-7515.

6. Jianming Zhao, <u>Wei Huang</u>, Pengchao Si, Jens Ulstrup, Fangyuan Diao, Jingdong Zhang. General syntheses of nanotubes induced by block copolymer self-assembly. Macromol. Rapid Commun. 2018, 39, 1800125.

7. Shuo Li, <u>Wei Huang</u>, Yuan Yang, Jens Ulstrup, Lijie Ci, Jingdong Zhang, Jun Lou and Pengchao Si. Hierarchical layer-by-layer porous FeCo₂S₄@Ni(OH)₂ arrays for all-solidstate asymmetric supercapacitors. J. Mater. Chem. A, 2018, 6, 20480-20490.

8. Yuan Yang, <u>Wei Huang</u>, Shuo Li, Lijie Ci and Pengchao Si. Surfactant-dependent flower- and grass-like Zn_{0.76}Co_{0.24}S/Co₃S₄ for high-performance all-solid-state asymmetric supercapacitors. J. Mater. Chem. A, 2018, 6, 22830-22839.

9. <u>Wei Huang</u>, Hongyu Sun, Huihui Shangguan, Xianyi Cao, Xinxin Xiao, Fei Shen, Kristian Mølhave, Lijie Ci, Pengchao Si andJingdong Zhang. Three-dimensional iron sulfide-carbon interlocked graphene composites for high-performance sodium-ion storage. Nanoscale, 2018, 10, 7851-7859.

Oral presentations at national and international conferences:

1. <u>Wei Huang</u>, Huihui Shangguan, Christian Engelbrekt, Xiaowen Zheng, Fei Shen, Xinxin Xiao, Lijie Ci, Pengchao Si and Jingdong Zhang, Highly isolated cobalt sulfide nanoparticles encapsulated in 3D hollow nitrogen doped carbon shells for superior lithium and sodium storage, *Electrochemical Conference on Energy and the Environment: Bioelectrochemistry and Energy Storage*, July 2019, Glasgow, Scotland.

2. Jing Tang, Rebecka Maria Larsen Werchmeister, Loredana Preda, <u>Wei Huang</u>, Zhiyong Zheng, Silke Leimkuhler, Ulla Wollenberger, Xinxin Xiao, Christian Engelbrekt, Jens Ulstrup, Jingdong Zhang. Three-dimensional sulfite oxidase bioanodes based on graphene functionalized carbon paper for sulfite/O₂ biofuel cells. *XXV International Symposium on Bioelectrochemistry and Bioenergetics*, May 2019, Limerick, Ireland.

Poster presentations at national and international conferences:

1. <u>Wei Huang</u>, Jing Tang, Fangyuan Diao, Hongyu Sun, Christian Engelbrekt, Jingdong Zhang, Xinxin Xiao and Kristian Mølhave, Ultrafine Fe₃O₄ nanoparticles immobilized on two-dimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction, 71st Annual Meeting of the International Society of Electrochemistry, September 2020, Belgrade, Serbia.

2. <u>Wei Huang</u>, Hongyu Sun, Kristian Mølhave, Jingdong Zhang, Microwave-assisted morphology evolution of iron doped birnessite hierarchical nanosheets, *Sustain Conference*, November 2018, Kgs. Lyngby, Denmark.

3. <u>J. Tang</u>; R. M. L. Werchmeister, L. Preda, W. Huang, Z. Zheng, S. Leimkühler, U. Wollenberger, X. Xiao, J. Zhang, Graphene-sulfite oxidase bioanodes for enzymatic biofuel cells, *Sustain Conference*, November 2018, Kgs. Lyngby, Demark.

4. <u>Wei Huang</u>. Hongyu Sun, Kristian Mølhave, Lijie Ci, Pengchao Si, Jingdong Zhang, Construction of iron sulfide-carbon interconnected graphene nanocomposites for superior lithium & sodium-ion storage, *3rd Global Congress & Expo on Materials Science & Engineering*, June, 2018 Rome, Italy.

5. <u>Wei Huang</u>, Hongyu Sun, Kristian Mølhave, Jingdong Zhang, Metal-organic framework derived FeP/C interlocked graphene hybrid composite for hydrogen evolution reaction, Sustain *Conference*, December 2017, Kgs. Lyngby, Denmark.