Metal-Organic Framework Derived Catalysts for Electrochemical Energy Conversion

Thesis submitted in partial fulfillment for the

Award of Degree

Doctor of Philosophy

By

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ABBREVIATION

AC	Active catalyst
AFM	Atomic force microscopy
BA	Benzyl alcohol
BDC	Benzene dicarboxylic acid
CA	Chronoamperometry
CC	Carbon cloth
C_{dl}	Double-layer capacitance
cm	Centimeter
CP	Chronopotentiometry
CV	Cyclic voltammetry
ECSA	Electrochemical surface area
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
EXAFS	Extended X-ray absorption fine structure
FE	Faradaic efficiency
FTO	Fluorinated tin oxide
HC	Hydroxide carbonate
HER	Hydrogen evolution reaction
^{1}H NMR	Proton nuclear magnetic resonance
HRTEM	High-resolution transmission electron microscopy
HS	High spin

iR	Internal resistance
IR	Infrared spectroscopy
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
J	Joule
kJ	kiloJoule
LDH	Layered double hydroxide
LS	Low spin
LSV	Linear sweep voltammetry
mA	Milliampere
MJ	Megajoule
MOF	Metal-organic framework
mV	Millivolt
NF	Nickel foam
OER	Oxygen evolution reaction
O_h	Octahedral
PB	Prussian blue
PBA	Prussian blue analogue
PC	Precatalyst
PXRD	Powder X-ray diffraction pattern
R_s	Solution resistance
R_{ct}	Charge transfer resistance
RHE	Reversible hydrogen electrode
RT	Room temperature

$	Dollar
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
Γ	Number of active sites
TEM	Transmission electron microscopy
TOF	Turn-over frequency
TW	TeraWatt
UK	United Kingdom
USA	United States of America
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence
ZIF	Zeolitic imidazolate framework

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PREFACE

The oxygen evolution reaction (OER) acts as a bottleneck for the electrochemical water splitting because of the four-electron and four-proton transfer involving high-energy reaction intermediates. Hence, OER is kinetically sluggish and also a thermodynamically uphill reaction. Therefore, OER demands an extra input of energy. Recently, plenty of transition metal-based electrocatalysts has been demonstrated for outstanding electrochemical OER activity. Interestingly, the transition metal-based catalysts experience steady structural reconstruction to form a metal hydroxide-(oxy)hydroxide [$M(OH)_2$-M(O)OH] active catalyst during OER under the effect of anodic potential in an alkaline medium.

The transition metal-based catalyst acts as a precatalyst for electrochemical OER and undergoes electrochemical surface reconstruction to form active $M(OH)_2$-M(O)OH catalysts. Interestingly, when meta-stable metal-organic frameworks (MOFs) are used directly for electrochemical OER, they undergo bulk reconstruction to form active $M(OH)_2$-M(O)OH ultrathin nanosheets.

Looking at this point, we have utilized a series of self-supported CoFe-PBAs (a sub-class of MOF) as the precatalysts to form the active catalysts Fe-$Co(OH)_2$-Co(O)OH by electrochemical anodic activation. In this respect, this thesis evaluates the following points: (i) electrochemical bulk reconstruction of CoFe-PBAs into active catalysts under varying potential and time, (ii) the role of structure, coordination, and electronic properties of the PBA precatalyst on the electrochemical reconstruction, active catalyst structure, and OER activity, (iii) bulk reconstruction of PBA precatalyst under the applied anodic and cathodic potential and (iv) the replacement of anodic OER by benzyl alcohol oxidation to improve the energy efficiency and H_2 production efficiency at very low cell voltage. The objectives of chapters 1-6 are given as:

Chapter 1 describes the origin of the thesis work. In this chapter, we have explained the basics of electrochemical water splitting and its fundamental parameters. The previous literature reports and the lacunae in this field have also been discussed. Further, the specific objectives of the thesis work have been presented at the end of the chapter.

Chapter 2 explains the electrochemical bulk reconstruction of self-supported CoFe-PBA@CC into active Fe-$Co(OH)_2$-Co(O)OH catalysts. The effect of variation of the potentials (1.45 V, 1.55 V, 1.65 V *vs* RHE) and time (12 h and 24 h) on the structure, morphology, and activity of the ultrathin Fe-$Co(OH)_2$-Co(O)OH nanosheets has been investigated. The optimum reaction condition for the complete reconstruction and best OER activity has been established. The improved electrochemical activity of ultrathin nanosheets has also been demonstrated compared to the pristine PBA and hydrothermally developed bulk CoHC and CoFe-LDH. In addition, the superiority of electrochemically generated Fe-$Co(OH)_2$-Co(O)OH nanosheets over the noble metal RuO_2 catalyst has been described.

Chapter 3 demonstrates the effect of ligands in CoFe-PBA@CC precatalyst to modulate the structural features, electronic properties, and electrochemical stability. The tuning of the structural and electronic properties, as well as electrochemical reconstruction of the PBA precatalyst, has been established by replacing the –CN group with the –NO group in PBA. The facile electrochemical reconstruction of PC-2 (in 15 CV cycles) and PC-1 (in 600 CV cycles) into the corresponding active catalysts have been explained. The spectroscopic (X-ray absorption spectroscopy, X-ray photoelectron spectroscopy), microscopic and analytical studies have been utilized to realize the variation in the local atomic and electronic structure, Co/Fe ratio, and electronic properties of the active catalysts AC-1 and AC-2. The outstanding electrochemical OER activity and stability have also been investigated.

Chapter 4 describes the design of precatalyst CoFeCo-PBA@CC and their chronoamperometric reconstruction under applied anodic and cathodic potential. The bulk reconstruction of CoFeCo-PBA@CC precatalyst into Fe-$Co(OH)_2$-Co(O)OH nanosheets at anode and Fe-$Co(OH)_2$ at cathode having different Fe-content has been described with the help of spectroscopic and microscopic studies. Further, the excellent electrochemical OER, HER, and overall water splitting activities have been established with outstanding stability.

Chapter 5 describes the designing of a self-supported precatalyst CoFe-PBA@NF and its electrochemical bulk reconstruction into an active Fe-$Co(OH)_2$-Co(O)OH catalyst by cyclic voltammetry. The implementation of the active catalyst for anodic electrochemical BA oxidation reaction replacing OER has been established in this chapter. The active catalyst Fe-$Co(OH)_2$-Co(O)OH has been utilized for the industrial current density BA oxidation with ~100% selectivity and ~98.3% Faradaic efficiency. The improvement in the hydrogen evolution efficiency and effect of applied potential on the BA oxidation, its conversion, and selectivity have also been demonstrated.

Chapter 6 summarizes the overall work of the thesis. The utilization of self-supported PBA precatalysts and their electrochemical bulk reconstruction under applied anodic potential and cathodic potential have been summarized. Moreover, PBA-derived active catalysts have also been employed for the anodic organic oxidation reaction. Further, the future scope and perspective of the thesis work have been described.