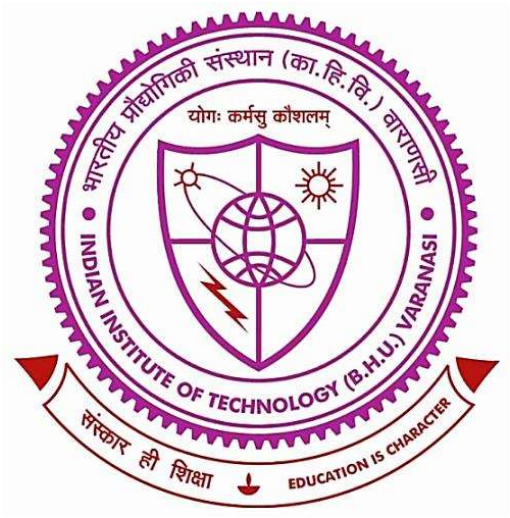
Zeolitic Imidazolate Framework-Derived Layered Double Hydroxides for Electrochemical Water Oxidation



Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

by

Priyanka Maurya

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI-221005

INDIA

Roll No. 18051012 **Year 2025**

COPYRIGHT TRA

Title of the Thesis: **Zeolitic Imidazolate F**

for Electrochemical Water Oxidation.

Name of the Student: **Priyanka Maurya**

COPYRIGHT

CER

It is certified that the work contained in

Derived Layered Double Hydroxides f

Maurya has been carried out under m

elsewhere for a degree.

It is further certified that the studen

Examination, Candidacy, and SOTA for

DECLARATION

I, "**Priyanka Maurya**", certify that

bonafide work and carried out by me under t

"**July-2018**" to " **June-2024**", at the **Dep**

Technology, (BHU), Varanasi. The matter em

the award of any other degree/diploma. I decla

credits to the research workers wherever their

I further declare that I have not willfully copie

CERT

Certified that the work contained in the thesis
Layered Double Hydroxides for Electro
Maurya has been carried out under my supe
mandatory requirement of TWO quality publi

It is further certified that the two publicati
Maurya have been published in the Journals

(a) SCI
(b) SCI Extended
(c) SCOPUS
(d) Non-indexed journals-
(Only in special cases)
(* Please enclose DPGC resolution in this

Contents

Preface

The electrochemical oxygen evolution reaction (OER), an anodic half-reaction of water electrolysis, has attained enormous attention in the field of energy conversion. However, OER is a bottleneck for the large-scale production of hydrogen gas due to the involvement of high energy reaction intermediate following a four-proton and four-electron transfer mechanism. Therefore, the OER kinetics is sluggish and it becomes a thermodynamically unfavorable reaction. OER requires additional energy input to cross the high energy barrier. Recently, efforts have been provided to develop transition metal-based electrocatalysts for efficient electrochemical OER. Among different OER active materials, layered double hydroxides (LDHs) have emerged as one of the most outstanding electrocatalysts because of the flexibility in their composition and structure and facile fabrication techniques. In this reference, Co-LDHs have been considered to show promising OER activity but their OER activity is constrained due to the low Gibbs free binding energy of *O on Co-sites and their low electronic conductivity.

Recently, MOF-derived self-supported LDHs have come out as one of the most promising groups of electrocatalysts because of their unique layered structure and potent electrocatalytic activity. In this context, we have utilized self-supported ZIF-67 (zeolitic imidazolate framework, a subclass of metal organic framework, MOF) as the precatalyst to form the active catalysts. ZIF-67-derived LDHs have high surface area and tunable pore structure, which make them suitable OER catalysts.

In addition to this, the incorporation of high-valent metals in Co-LDHs can greatly enhance the OER performance. Simultaneously, the use of a self-supported catalyst on a conductive substrate can enhance the electronic conductivity and strengthen the interaction between catalysts

and support which improves the activity and stability. Therefore, in this thesis, we have explored the self-supported and heterometal-doped Co-LDHs to attain the required OER catalytic activity.

Chapter-1 demonstrates the objectives of the thesis work looking at progress in this field. In this chapter, we have covered the principles of electrochemical water oxidation, its significance in the field of energy conversion and storage, and its evaluation parameters. Further, we have discussed the previously reported MOF-derived LDHs for OER along with various shortcomings in this field. We have discussed the advantages of using ZIF-67 as the precursor for the synthesis of OER catalysts.

Chapter-2 demonstrates the synthesis of noble-metal free V-doped Co-LDHs (V_xCo-LDH) hollow nanocages, synthesized from ZIF-67. ZIF-67 was converted into LDH along with the incorporation of vanadium when treated with VCl_3. The V doping has been found to be crucial to enhance the OER activity of Co-LDH in the alkaline medium. The effect of changing the amount of V on the activity of V_xCo-LDH was also studied and it was observed that all V_xCo-LDH exhibited better OER activity than Co-LDH while the activity of $V_{0.2}$Co-LDH was found to best among all the synthesized V_xCo-LDHs. $V_{0.2}$Co-LDH required only 280 mV of overpotential to produce 100 mA cm^{-2} of current density with stability for 24 h.

Chapter-3 explains the Lewis acid-assisted hydroxylation of ZIF-67 to form Fe_xCo-LDH nanosheets via hydrothermal technique. The most appropriate reaction condition for the complete reconstruction and optimal OER activity has been determined. The effect of variation in the quantity of Fe(III) on the OER activity of Fe_xCo-LDH has been explored where it was found that

$Fe_{0.4}$Co-LDH exhibited the best OER activity. The enhanced electrochemical OER activity of ultrathin nanosheets has also been compared with Co-LDH, ZnCo-LDH, and hydrothermally synthesized $Fe_{0.4}$Co-HC.

In **Chapter-4**, we have shown electrochemical reconstruction of ZIF-67 during anodic water oxidation resulting in the formation of FeCo-LDH-x [Fe-$Co(OH)_2$/Co(O)OH] (where x = 1, 2, 3, 4, 5). The Fe(III)-ions, present in the electrolyte solution, are introduced in the structure of the active catalyst during the anodic reconstruction of ZIF-67. Electrochemically derived FeCo-LDH-x demonstrates high electrochemical surface area, exposed active sites, atomic-level thickness, and adjusted structural and electronic features to improve the OER activity. The activity of all FeCo-LDH-x was found to be better than that of as synthesized Co-LDH-3. Among the synthesized catalysts, FeCo-LDH-3 exhibited the best OER activity generating 50 mA cm^{-2} current density at 180 mV overpotential and with the lowest Tafel slope value and charge transfer resistance.

Chapter-5 demonstrates a facile technique for the synthesis of a self-supported heterostructure catalyst system CeO_2/Ce-Co-LDH (CeCo-x, where, x= 1, 2, 3) using nickel foam supported ZIF-67. The precursor was treated with various amount of $Ce(NO_3)_3.9H_2O$ by hythrothermal technique. During hydrothermal treatment, the insertion of Ce into Co-LDH resulted in 4f-2p-3d orbital overlap along with the formation of heterojunction between CeO_2 and CeCo-LDH. Out of all synthesized CeCo-x catalysts, CeCo-2 demonstrated excellent OER activity as it produces 50 mA cm^{-2} current density at a very low overpotential of 220 mV. 4f-2p-3d orbital overlap modulated the electronic structure and the heterostructure regulated the transportation of charges during the OER process. The 4f-2p-3d orbital overlap demonstrated the more proficient delocalization of π-

electron density over metal center via oxide bridging in comparison to 3d-2p-3d overlap. Thus, CeO_2/Ce-Co-LDH heterostructures exhibited excellent OER performance and stability.

In Chapter-6 we have presented a succinct overview of the scientific contributions made in this thesis and summarized our findings, which provide valuable insights for the development of ZIF-67 derived new efficient electrocatalysts for electrochemical energy conversion. We have also explored the future prospects of these research endeavors.

Acknowledgment

In this moment of reminiscence, I would like to thank everyone who has helped me during my Ph.D. journey at IIT (BHU). I see it as a happy and modest act, in addition to my moral duty, to express my genuine gratitude to everyone.

First and foremost, I would like to express my gratitude to my esteemed supervisor, Dr. Arindam Indra, whose invaluable supervision, unwavering support, patience, motivation, profound knowledge and expert guidance have been proved as cornerstones throughout my pursuit of Ph.D. degree. His guidance served as a beacon to guide me and improved the quality of my research and thesis writing. I am incredibly grateful for the chance to have such a dedicated mentor and advisor.

I am incredibly grateful to HOD, Prof. Sundaram Singh, and Ex-HOD, Prof. Y. C. Sharma, Department of Chemistry, IIT (BHU), for providing me the resources and their constant support during my research period. My special appreciation goes to my RPEC members, Prof. Kamdeo Mandal, Department of Chemistry, IIT (BHU) and Prof. Pralay Maiti, Department of School of Material Science and Technology, IIT (BHU), for their perceptive advice, constant guidance, and considerate assistance during my research work. I express my sincere gratitude to all the faculty members of my department, for their encouragement and assistance. I extend my sincere gratitude to all non-teaching staff (Mr. Rambish, Mr. Neeraj, Mr. Abhishek and Mr. Amit) of the Chemistry Department of IIT(BHU), because this work could not be accomplished without their technical assistance.

I also gratefully acknowledge the DST-INSPIRE for the financial support in the form of JRF and SRF. I express my gratitude to CIFC, IIT (BHU), Varanasi, for providing the resources required to do several sample characterisations.

I am indebted to my lab mates, Dr. Ved Vyas, Mr. Deepak Kumar, Mr. Vishesh Kumar, Mr. Toufik Ansari, Deepak Kumar Ray, Vijay Patel and Harshit Gupta for their intellectually

fascinating conversations and the camaraderie that enriched the last five years. I feel incredibly fortunate to offer my heartfelt gratitude to my friend, mentor, and senior, "Dr. Abhay Narayan Singh", Department of School of Material Science and Technology, IIT (BHU), for all his support and insightful advice.

I would like to thank my friends Ms. Garima Pandey, Ms. Aditi, and Dr. Swati Chauhan for their companionship, constant motivation and love. I am deeply grateful to my beloved husband, Mr. Rohit Kumar Maurya, for his unwavering support, love, laughter, and motivation. His encouragement has kept me focused and made this project possible, especially during the challenging times. I wish to express my heartfelt gratitude to everyone who has offered their support in various ways during my time at the Indian Institute of Technology (Banaras Hindu University), Varanasi, India. I am also grateful for the negative experiences, as they have taught me valuable life lessons and contributed to my growth.

I express my heartfelt thanks to my most loving and caring Grandmother, Smt. Kamla Devi and my grandfather, Late Ram Adhar Maurya, for being the best storytellers, inspiring me to study and teaching me about life. I am extremely thankful to my loving mother, Smt. Asha Maurya and father Sri Panna Lal Maurya for their unconditional love and sacrifices. I am also very grateful to my loving and caring brothers, Mr. Pradip Kumar Maurya, Mr. Prashant Kumar Maurya, Mr. Piyush Kumar Maurya and Mr. Praveen Kumar Maurya, for their unwavering support and love that helped me many times in many ways.

I am also grateful to my loving and supportive sisters-in-law, Mrs. Nisha Maurya, Mrs. Arti Maurya, and Mrs. Pooja Maurya, for their love, blessings, support and motivation.

I am also blessed with my loving nieces, Avisha, Kashvi, and Pravya, who bring immense joy to my life.

Date: 08/07/2025 **Priyanka Maurya**

Place: Varanasi

List of Figures

List of Schemes

List of Table

θ	Angle (degree)
a.u.	Atomic Unit
BE	Binding Energy
eV	Electron Volt
EDX	Energy Dispersive X-ray
HR-SEM	High Resolution-Scanning Electron Microscopy
MOF	Metal-Organic Framework
SAED	Selected Area Electron Diffraction
s	Second
HR-TEM	High Resolution-Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
λ	Wavelength
ZIF	Zeolitic Imidazolate Framework
η	Overpotential
Ω	Ohm
j	Current Density
ECSA	Electrochemical Active Surface Area
S_{Ageo}	Geometrical Surface Area
C_{dl}	Double-Layer Capacitance
LDHs	Layered Double Hydroxides
R_{ct}	Charge Transfer Resistance
TOF	Turn Over Frequency

NF	**Nickel foam**
EIS	**Electrochemical Impedance Spectroscopy**
CV	**Cyclic Voltammetry**
LSV	**Linear Sweep Voltammetry**
RHE	**Reversible Hydrogen Electrode**
OER	**Oxygen Evolution Reaction**
HER	**Hydrogen Evolution Reaction**
CA	**Chronoamperometry**
PBA	**Prussian Blue Analogue**
MIL	**Materials of Institute Lavoisier**
SDS	**Sodium Dodecyl Sulfate**
AFM	**Atomic Force Microscopy**