

Investigations of Transition Metal Oxide-based Materials for Energy Conversion and Storage Applications

A Thesis

submitted by

Ankita Mathur (D15012)

for the award of the degree of

Doctor of Philosophy



**School of Engineering
Indian Institute of Technology, Mandi
Mandi, Himachal Pradesh- 175005**

February 2021

© Indian Institute of Technology Mandi, Kamand,
H.P.-175005, India.
All rights reserved

Dedicated

To

My

Champions

Mom and Dad !!

To,

My Mentor

Dr. Aditi Halder,

Dear Madam,

गुरुर्ब्रह्मा गुरुर्विष्णुः गुरुर्देवो महेश्वरः ।
गुरुः साक्षात् परं ब्रह्म तस्मै श्री गुरवे नमः ॥

**Whatever I am and I will be, my
failures and successes, I owe it to you !**

Yours Sincerely,

Ankita



Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis titled **“Investigations of Transition Metal Oxide- based Materials for Energy Conversion and Storage Applications”** is the result of investigations carried out by me in the **School of Engineering**, Indian Institute of Technology Mandi, under the supervision of **Dr. Aditi Halder**, for the award of the degree of Doctor of Philosophy and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

Place: Mandi, Himachal Pradesh

Signature:

Date:

Name: Ankita Mathur

Indian Institute of Technology Mandi
Mandi-175001, Himachal Pradesh, India



भारतीय प्रौद्योगिकी संस्थान मण्डी
मण्डी-175001, हिमाचल प्रदेश, भारत

Declaration by the Research Advisor

I hereby certify that the entire work in this Thesis titled “**Investigations of Transition Metal Oxide- based Materials for Energy Conversion and Storage Applications**” has been carried out by **Ankita Mathur**, under my supervision in the **School of Engineering**, Indian Institute of Technology Mandi, for the award of the degree of Doctor of Philosophy and that no part of it has been submitted elsewhere for any Degree or Diploma.

Place: Mandi, Himachal Pradesh

Signature:

Date:

Name: Dr. Aditi Halder

Acknowledgements

PhD is not a mere degree, it's a journey, full of enthusiasm, happiness, unhappiness, dilemma, stress, etc. I also experienced all these emotions during my PhD journey and when I faced them, I was not alone. There were many hands, visible and invisible, that somehow guided me to choose the right path and enlightened me with their vision.

I would sincerely like to express my heartfelt gratitude to my research supervisor **Dr. Aditi Halder**. Apart from motivating and supervising my research problem, she actually groomed me to become a better individual. Her interest and passion in material chemistry and electrochemistry imbued positive feelings in me and I feel more energetic and motivated after every discussion session with her. Her insights and directions were truly valuable and her deep sense of confidence in me encouraged me to perform better every time. The days cannot be forgotten when she was always there by my side when I was stuck in some experiments. Her trouble-shooting aptitude and always helping and caring nature inspires me the most. Her inspirational words "In tough times we must be tougher" has left a deep long-lasting impact on my mind. During my PhD, I have evolved as a better person and I owe her what I am today and for whatever I will achieve in future.

I also want to acknowledge **Dr. Viswanath Balakrishnan** for his guidance and knowledge he shared with me, not only regarding academics, also about motivational movies and general awareness. His energetic persona and time-management skills has always inspired me to excel.

I would also like to thank my Doctoral Committee members: **Dr. Satvasheel Powar, Dr. Rahul Vaish, Dr. Kunal Ghosh, Dr. Rajeev Kumar and Dr. Dhiraj Patil** for sharing their valuable time and knowledge. Their critical comments has indeed improved my research progress.

I would also like to express gratitude to IIT Mandi for giving me opportunity and funding to pursue research in my area of interest. The international trip to Dallas, Texas is one of the major opportunities I will always cherish in my life. I would also like to deeply acknowledge the help and support I received from Advanced Material Research Centre (AMRC) Staff- including Mr. Arjun Thakur, Mr. Naveen Gumra, Mr. Puneet Sood, Mr. Sunil Kumar, Mr. Dushyant Gumra and Ms. Isita Nandi, Mr. Karam and other members of AMRC and IIT Mandi. Support from School of Engineering office staff- Ms. Mamta, Mr. Sumit and Mr. Chandan is also acknowledged.

To my collaborator and senior Dr. Himmat Singh Kushwah who helped me in scientific understanding and laying a strong foundation of technical knowledge. I would also like to express gratitude to collaborator and labmate Mr. Ravinder Kaushik for sharing his knowledge and enriching the quality of my research with his experience. I am indebted to him for his company during late- night lab experiments and for proof-reading my manuscripts.

I would also like to mention and acknowledge my best friend Mr. Ashish Mishra for his constant motivation, unplanned trekking trips and dinner parties. He do justice with the saying “A friend in need is a friend indeed”. I would like to thank Ms. Deepa Thakur for not only supporting academically, but also sharing valuable information and making my PhD journey stress-free.

To my family and friends for giving me vague but innovative ideas during my mental collapse. Special mention to Manju Bisht, Mona Subramaniam A., Vyoma Singh, Prabhjot Kaur,

Paromita Dutta for giving unforgettable memories. Their logical solutions for my illogical doubts was the driving force during my PhD journey. To my friends Dr. Naina Arora, Dr. Preeti Gulia for their selfless and unwavering support as and when needed.

To my senior Dr. Davinder Singh who guided and helped me whenever required. His PhD thesis acted as a guide while framing my own. To my labmates/ colleagues Dr. Saquib, Dr. Bandhana, Lalita Sharma, Divya Verma, Trivender Kumar, Chetna Madan, Pankaj Singh, Sandeep Yadav and Nishchal Chauhan for the scientific and non-scientific discussions we had together.

Words are not enough to express my deep heartfelt gratitude to my parents Dr. Savitri Mathur and Mr. Ravindra Prakash Mathur. It was their trust, belief, blessings and selfless love that motivated me to move ahead and make them proud.

Last but not least, I would like to thank each and every one who some or the other way, directly or indirectly, supported me in this journey of PhD, including my Volleyball team and Ms. Priya Rawat.

Ankita Mathur

Preamble

With increasing environmental pollution along with population overgrowth, the energy demand has expedited enormously. Sustainable energy generation based on non-fossil fuel resources thus plays crucial role for maintaining balance in energy sector. But their stochastic nature demands utilization of alternative source of energy and its storage. Hence emphasis have been given towards electrochemical energy storage devices.

Electrochemical-based energy storage devices like Batteries and Supercapacitors have withdrawn huge attention because of their long cyclic life, minimal ecological problem, relatively cheaper cost compared to other such devices and usually independent of load and temperature. In this regard, Rechargeable Zinc-air batteries (ZABs) possess high theoretical energy density (1350 kW kg^{-1}), low cost, environmental friendliness, high safety and easy rechargeability. A rechargeable ZAB charges and discharges through oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) respectively. Thus, a bifunctional electrode is required with the capability of catalyzing ORR as well as OER in such kind of rechargeable batteries. To overcome the problem of sluggish kinetics of ORR and OER in a bifunctional electrode of ZAB, an additional thrust of renewable energy resources could be an exciting strategy. A photoactive cathode electrode that can capture photons from solar energy could also be utilized to perform photoresponsive bifunctional ORR/OER activity.

The prime objective of the thesis is to design an effective material for ORR and also a single electrode material for rechargeable Zn-air batteries, with bifunctional activity towards ORR and OER. Using strategies like doping, co-doping, allomorphous composite and photoactivity, iron oxides and MnO_2 based materials have been explored for its activity towards fabricating rechargeable Zn-air battery.

Chapter 1 deals with introduction to origin, importance and mechanism of batteries with focus on rechargeable Zinc-air batteries (ZAB). Several strategies to engineer cathode materials for ZAB are also elaborated. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are explained. Certain modifications to utilize ZAB setup for other functions are included, with focus on photo-enhanced rechargeable Zn-air battery (PEZAB).

Chapter 2 deals with brief introduction to Fe_2O_3 as ORR catalyst and MnO_2 highlighting its properties towards use as cathode material in PEZAB. Experimental procedure adopted for the synthesis for various materials are discussed. The various characterization tools used for exploring physical properties of the material are mentioned. Electrochemical characterization are also discussed.

Chapter 3 presents Fe_2O_3 as catalyst for oxygen reduction reaction. A double perovskite material- calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)) was used as support for α - Fe_2O_3 . CCTO consist of Ca^{2+} and Cu^{2+} metals at A site and Ti^{4+} at B site. Due to the optimistic synergistic interaction of Fe^{3+} , Cu^{2+} and Ti^{4+} transition metals, and Cu 3d acting as major charge carrier, improved ORR activity was observed in Fe_2O_3 - CCTO composite. Moreover, the role of Fe-N-C framework was investigated towards ORR. Nitrogen doped carbon sites causes delocalization of charge carriers and impairs O-O bond on C sites. Glucosamine hydrochloride (GA) was used as N and C precursor, reducing agent for reducing Fe^{+3} to different oxidation states and also growth promoting agent. In this work, Fe-N-C framework was prepared using Fe_2O_3 and varying quantity of GA to study the effect on ORR activity.

Chapter 4 involves doping Fe into α - MnO_2 lattice and preparing a rechargeable ZAB using it as cathode. A flexible solid-state battery was also fabricated to glow a LED and show its practicality. α - MnO_2 contains (2×2) and (1×1) tunnels which are helpful in capturing small ions. α - MnO_2 displays better ORR-OER activity than δ - MnO_2 , but poor energy storage activity. Hence, herein Fe has been doped in α - MnO_2 to enhance its energy storage property. The

objective of Chapter 4 is to study the effect of doping Fe into the α -MnO₂ lattice and study the effect on ORR, OER and rechargeable Zn-air battery performance. Different amount of iron was doped in α -MnO₂ and amount of dopant was also optimized.

Chapter 5: As δ -MnO₂ displays better energy storage activity than α -MnO₂, but poor ORR-OER activity. In this study, we have presented the synergistic interaction of doping as well as interlayer- intercalation of transition elements into δ -MnO₂. Fe and Ni has been carefully doped in the in-planar sites as well as in the interlayer space of MnO₂. The ternary complex of Ni-Fe-Mn was found to be suitable for performing ORR and OER catalysis, much better than the single δ -MnO₂ or binary Fe doped δ -MnO₂. **Chapter 5** describes the effect of Fe and Ni co-doped δ -MnO₂ (Ni-FeMnN). The activity towards ORR, OER was compared with only Ni doped δ -MnO₂ (NiMnN) and finally a rechargeable Zn-air battery was fabricated. Fe in Fe⁺³ oxidation state is very active towards ORR and Ni shows outstanding performance towards OER. Synergistic interaction of ORR and OER active material significantly enhances the rechargeable Zn-air battery performance.

Chapter 6 In this work, the augmentation of solar energy and Zn-air batteries in a single device was done to explore an effective strategy for combining energy conversion and storage. The synthesis of inexpensive cobalt doped 2D δ -MnO₂ nanosheets by one-pot hydrothermal method was done followed by spectroscopic and microscopic characterizations of all prepared catalysts. The as-prepared catalyst showed their bifunctional catalytic activity towards oxygen reduction reaction (ORR) as well as oxygen evolution reaction (OER) in presence and absence of visible light. As δ -MnO₂ possess layered structure, it was proved both in-plane and inter-planar doping of cobalt in δ -MnO₂ structure. The catalysts were explored for their activity towards ORR, OER and finally PEZAB.

Chapter 7 deals with studying the synergistic interaction between two crystallographically and morphologically different phases of MnO₂ and efficacious utilization in fabricating PEZAB.

As MnO₂ contain primarily either tunnels or layers which act as active site for catalysis, we have explored α and δ phases of MnO₂. α -MnO₂ have well-defined (2×1) and (1×1) tunnels to trap smaller ions into it. On the other hand, δ -MnO₂ has layered structure with inter-layer spacing of 7 Å, sufficient for intercalating smaller ions. This chapter deals with studying the activity of these two phases of MnO₂ towards ORR and OER performance. Furthermore, a composite of these two phases in varying ratios was prepared and compared with parent MnO₂ phases towards fabrication of PEZAB. The composite ($\alpha+\delta$)-Mn11 with equal amount of α - and δ -MnO₂ showed the best bifunctional activity. Hence it was used for fabricating PEZAB.

Chapter 8 deals with the key findings of the research work in comparison with other reported literatures, along with future scope of the findings.

Publications (related to Thesis):

1. A. Mathur, H. S. Kushwah, R. Vaish and A. Halder, “Enhanced electrocatalytic performance of perovskite supported iron oxide nanoparticles for oxygen reduction reaction,” *RSC Adv.*, vol. 6, , pp. 94826–94832, 2016.
2. A. Mathur, S. Harish and A. Halder, “Role of Nitrogen Precursor on the Activity Descriptor towards Oxygen Reduction Reaction in Iron-Based Catalysts,” *Chemistry Select*, vol. 3, , pp. 6542–6550, 2018.
3. A. Mathur and A. Halder, “One-step synthesis of bifunctional iron-doped manganese oxide nanorods for rechargeable zinc-air batteries,” *Catal. Sci. Technol.*, vol. 9, no. 5, pp. 1245–1254, 2019.
4. A. Mathur, R. Kaushik and A. Halder, “Visible-Light Driven Photo-enhanced Zinc-Air Batteries using Synergistic Effect of Different Type of MnO₂ Nanostructures”, *Catal. Sci. Technol.*, 2020, Advance Article.

5. A. Mathur, R. Kaushik and A. Halder, “Photoenhanced Performance of Co-Intercalated 2-D Manganese Oxide Sheets for Zinc-Air Battery”, *Materials Energy Today*, 2020, 100612.

Other Publications

1. L. Sharma, H. S. Kushwah, A. Mathur and A. Halder, “Role of molybdenum in Ni-MoO₂ catalysts supported on reduced graphene oxide for temperature dependent hydrogen evolution reaction,” *Journal of Solid State Chemistry*, vol. 265, pp. 208–217, 2018.
2. G. Singh, M. Sharma, A. Mathur, A. Halder and R. Vaish, “Diesel soot as a supercapacitor electrode material”, (*Under Review Journal of Electrochemical Society*).
3. D. Thakur, A. Mathur and A. Halder, “Bio-inspired Regenerative Cu_xO (x=1,2) Surface with Diverse Wetting Properties and Photocatalytic Functionality”, (*Under Review Journal of Applied Physics*).
4. U. Bhardwaj, A. Sharma, A. Mathur, A. Halder, H.S. Kushwaha, Efficacy of Sr₂TiMnO₆, as a bifunctional perovskite catalyst for durable and efficient rechargeable zinc-air batteries (*Under Review- ACS Applied Energy Materials*)

Table of Contents

Declaration by the Research Scholar	i
Declaration by the Research Advisor.....	ii
Acknowledgements	iii
Preamble	vi
Publications	ix
Chapter 1 Introduction.....	16
1.0 Renewable Energy and Energy Storage	16
1.1 History of Batteries	17
1.2 Beyond Lithium-ion Batteries	19
1.3 Metal-air batteries	20
1.4 Working Principle	22
1.4.1 Primary Zinc-air battery	22
1.4.2 Secondary (or Rechargeable) Zinc-air battery:	27
1.5 Activity Descriptor for a Primary and Secondary battery.....	30
1.6 Some examples of cathode materials for rechargeable Zinc-air battery:	37
1.7 Modifications in the conventional rechargeable Zn-air battery	40
1.7.1 Zinc-air Flow Battery	40
1.7.2 Photoenhanced Zinc-air Battery	41
1.7.3 Three-Electrode Mode:.....	43
1.7.4 Zinc-air battery based desalination device:	44
1.7.5 Hybrid Energy Storage Device by combining Zinc-ion supercapacitor and Zinc-air battery:	45
1.8 Motivation and Objective of thesis	45
1.9 Objectives.....	48
1.10 References:	50

Chapter 2 Synthesis and Characterization Techniques65

2.1 Introduction 65

2.2 Material Synthesis: 65

 2.2.1 Fe₂O₃ Synthesis 65

 2.2.2 Fe₂O₃-CaCu₃Ti₄O₁₂ composite 66

 2.2.3 Iron- Nitrogen- Carbon framework 66

 2.2.4 Synthesis of α -MnO₂: 67

 2.2.5 Synthesis of δ -MnO₂: 67

 2.2.6 Synthesis of iron doped α -MnO₂: 67

 2.2.7 Synthesis of iron doped δ -MnO₂: 67

 2.2.8 Synthesis of Ni-Fe co doped δ -MnO₂: 68

 2.2.9 Synthesis of cobalt doped δ -MnO₂: 68

 2.2.10 Synthesis of the composite of α -and δ -MnO₂: 68

2.3 Material Characterizations: 68

 2.3.1 X- Ray Diffraction 68

 2.3.2 Field Emission Scanning Electron Microscope 70

 2.3.3 Transmission Electron Microscopy 71

 2.3.4 X-Ray Photoelectron Spectroscopy 73

 2.3.5 Absorbance spectra and UV-Vis diffuse reflectance spectroscopy: 74

 2.3.6 Raman Spectroscopy 75

2.4 Electrochemical Measurements: 76

 2.4.1 Oxygen Reduction Reaction 78

 2.4.2 Oxygen Evolution Reaction 80

Chapter 3 Studying the Role of Composites Formation Between Two Oxides and N-

Doping in Carbon Supports Towards Enhancement in Oxygen Reduction Reaction81

3.1 Introduction: 82

3.2 Results and Discussion 86

 3.2.1 Synthesis of Fe₂O₃: 86

 3.2.2 Synthesis of Fe₂O₃-CaCu₃Ti₄O₁₂ composite 86

 3.2.2.1 Physical Characterization: 87

 3.2.2.2.1 Ink preparation for Fe₂O₃- CCTO: 89

 3.2.2.2.2 Electrochemical Analysis 89

3.2.3 Fe-N-C framework	95
3.2.3.1 Synthesis of Fe-N-C framework.....	95
3.2.3.2 Physical Characterization:	96
3.2.3.3 Electrochemical Studies	102
3.3 Conclusions.....	108
3.4 References:	109
Chapter 4 Hierarchical Fe doped α-MnO₂ bifunctional catalysts with tailored catalytic activity for rechargeable Zn-air batteries.....	116
4.1 Introduction	117
4.2 Results and Discussion.....	119
4.2.1 Synthesis of MnO ₂ rods:	119
4.2.2 Physical Characterization:	120
4.2.3. Electrochemical Characterization:.....	126
4.2.3.1 Oxygen Reduction Reaction:.....	127
4.2.3.2 Oxygen Evolution Reaction (OER):.....	132
4.3 Rechargeable Zinc Air Battery:.....	136
4.4 Conclusion.....	138
4.5 References:	138
Chapter 5 Synergistic Interaction of Ni and Fe in 2D Layered Manganese Dioxide for Rechargeable Zinc-Air Battery	143
5.1 Introduction:	144
5.2 Results and Discussion:.....	146
5.2.1 Synthesis of materials:.....	146
5.2.2 Physical Characterization:	146
5.2.3 Electrochemical Analysis:	154
5.3 Zinc-air Battery:	159
5.4 Conclusion:.....	161
5.5 References:	162
Chapter 6 Photoenhanced Performance of Cobalt-Intercalated 2-D Manganese Oxide Sheets for Rechargeable Zinc-Air Battery	167

6.1 Introduction	168
6.2 Results and Discussion.....	171
Synthesis protocol has been described in chapter 2.....	171
6.2.1 Physical Characterization:	172
6.2.2 Electrochemical Characterization:.....	181
6.2.2.1 Oxygen Reduction Reaction (ORR):.....	181
6.2.2.2 Oxygen Evolution Reaction (OER):.....	184
6.2.2.3 Bifunctionality of electrocatalysts:	186
6.3 Performance of Photoenhanced Zn-air battery:	187
6.3.1 Rechargeable Zinc Air Battery Assembly:.....	187
6.3.2 Photoelectrochemical Measurements:	187
6.3.3 Photoenhanced Zn-air battery (PEZAB):	187
6.3.4 Possible mechanism for PEZAB:	191
6.4 Post-activity analysis:.....	193
6.5. Conclusion.....	194
6.6 References	195

Chapter 7 Visible-Light Driven Photo-enhanced Zinc-Air Batteries using Synergistic

Effect of Different Type of MnO₂ Nanostructures.....203

7.1 Introduction	205
7.2 Results and Discussion.....	206
7.2.1. Physical Characterization:	206
7.3.2. Electrochemical Characterization:.....	214
7.3.2.1 Oxygen Reduction Reaction (ORR):.....	216
7.3.2.2 Oxygen Evolution Reaction (OER):.....	218
7.3.2.3 Bi-functionality of ($\alpha+\delta$)-MnO ₂ :	220
7.4 Zinc Air Battery:	220
7.4.1 Zinc-Air Battery Setup:.....	220
7.4.2 Solid State Zn-Air Battery Fabrication:	221
7.4.3 Zinc-Air Battery:.....	221
7.4.1 Solid State Zn-air Battery:	224
7.4.2 Photoinduced Zinc-air battery:	224
7.5 Post-battery analysis:	227
7.6 Conclusion:.....	230

7.7 References	230
Chapter 8 Conclusion and Future Scope	237
8.1 Conclusion.....	237
8.2 Future Scope.....	240
Appendix.....	242