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

A Thesis

submitted by

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Doctor of Philosophy

School of Engineering

Indian Institute of Technology, Mandi

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Dedicated

To

My

Champions

Mom and Dad !!

To,

My Mentor

Dr. Aditi Halder,

Dear Madam,

गुरुर्ब्रह्मा ग्रुरुर्विष्णुः 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

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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.

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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

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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 ($CaCu_3Ti_4O_{12}$ (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-MnO_2 lattice and study the effect on ORR, OER and rechargeable Zn-air battery performance. Different amount of iron was doped in α-MnO_2 and amount of dopant was also optimized.

Chapter 5: As δ-MnO_2 displays better energy storage activity than α-MnO_2, 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-MnO_2. Fe and Ni has been carefully doped in the in-planar sites as well as in the interlayer space of MnO_2. The ternary complex of Ni-Fe-Mn was found to be suitable for performing ORR and OER catalysis, much better than the single δ-MnO_2 or binary Fe doped δ-MnO_2. **Chapter 5** describes the effect of Fe and Ni co-doped δ-MnO_2 (Ni-FeMnN). The activity towards ORR, OER was compared with only Ni doped δ-MnO_2 (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-MnO_2 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-MnO_2 possess layered structure, it was proved both in-plane and inter-planar doping of cobalt in δ-MnO_2 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 MnO_2 and efficacious utilization in fabricating PEZAB.

As MnO_2 contain primarily either tunnels or layers which act as active site for catalysis, we have explored α and δ phases of MnO_2. α-MnO_2 have well-defined (2×1) and (1×1) tunnels to trap smaller ions into it. On the other hand, δ-MnO_2 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 MnO_2 towards ORR and OER performance. Furthermore, a composite of these two phases in varying ratios was prepared and compared with parent MnO_2 phases towards fabrication of PEZAB. The composite (α+δ)-Mn11 with equal amount of α- and δ-MnO_2 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.

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1. L. Sharma, H. S. Kushwah, A. Mathur and A. Halder, "Role of molybdenum in Ni-MoO_2 catalysts supported on reduced graphene oxide for temperature dependent hydrogen evolution reaction," *Journal of Solid State Chemistry*, vol. 265, pp. 208–217, 2018.
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