THEORETICAL INSIGHTS INTO THE TRANSPORT, KINETICS AND ELECTRONIC PROPERTIES OF BATTERY MATERIALS FOR ENERGY STORAGE DEVICES

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by

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*Dedicated to my **family and friends….***

Certificate

This is to certify that the thesis entitled "**Theoretical Insights into the Transport, Kinetics and Electronic Properties of Battery Materials for Energy Storage Devices**" submitted by **Deepak Seth** to the Indian Institute of Technology Delhi in fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering, is a record of bona-fide research work carried out by him. He has worked under our supervision and has fulfilled the requirements, which, to our knowledge, have reached the requisite standard for the submission of the thesis. The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any other degree.

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Deepak Seth

Abstract

Advancements in technologies have led to a significant increase in energy demand, driving the need for efficient energy storage solutions. Energy storage systems such as rechargeable batteries, like lithium-ion (LIBs), sodium-ion (SIBs), and metal-air batteries (MABs), have emerged as promising candidates for energy storage due to their high energy density, long life cycle, and low cost. However, further design strategies in battery materials, including electrodes and/or electrolytes, are required to enhance their electrochemical performance.

The current study focuses on the mechanistic design of various classes of materials for energy storage systems, including aqueous metal-ion batteries, metal-air batteries, and two-dimensional (2D) materials based next-generation energy storage systems. The main objective is to tailor the battery materials and to understand the relationship between ion transport, reaction kinetics, electronic properties and their influence on electrochemical performance, using computational approaches such as density functional theory (DFT) and molecular dynamics (MD) simulations. For aqueous metal-ion batteries, the sodium superionic (NASICON)-structured $ATi_2(PO_4)_3$ (A=Na, Li) material is investigated as a potential anode in mixed electrolyte systems containing both Li^+ and Na^+ ions. MD simulations are employed to study and compare the transport properties and energetics of the Na^+ and Li^+ ions in this material. A design strategy involving lattice strain is proposed to enhance Na-ion transport properties. Additionally, the effect of grain boundaries (GB) on Na-ion conductivity and transport properties is explored using various GB structures. For metal-air batteries, the focus is on investigating the kinetic properties of electrocatalyst materials for Zn-air batteries. The performance of Zn-air batteries is limited by the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the air cathode. Molecular-level electronic structure engineering of Co_3O_4 electrocatalysts is explored to

enhance their electrocatalytic activity. The influence of factors such as the concentration of Cu-doped elements on active crystal planes, surface adsorbed intermediates, and electronic structure of the transition metal on the catalytic activity is investigated. For 2D materials, integration of reduced graphene oxide (rGO), including MoS_2 and BFO ($BiFeO_3$, $Bi_2Fe_4O_9$, and $Bi_{25}FeO_{40}$) are investigated for next-generation energy storage devices. Na-ion intercalation properties are studied in MoS_2@rGO and exhibit improved electrochemical performance due to enhanced Na-ion transport, including a reduction in the activation barrier and a corresponding increase in Na-ion diffusivity. BFO@rGO composites demonstrated enhanced electronic and photocatalytic properties, as evidenced by decreased bandgap, attributed to heteroatom (N, S) doped rGO integration.

Overall, the focus of this dissertation is to design novel battery materials for energy storage systems by tuning their ion transport, reaction kinetics, and electronic properties using computational modelling and simulations. The study aims to elucidate the relationship between the modelled structure, composition, material design strategies, and the electrochemical performance of the materials, which can be correlated with experimental observations.

सार

तकनीकी प्रगति ने ऊर्जा की मांग में महत्वपूर्ण वृद्धि की है, जिससे कुशल ऊर्जा भंडारण समाधान की आवश्यकता बढ़ गई है। ऊर्जा भंडारण प्रणालियां, जैसे रिचार्जेबल बैटरियां (लिथियम-आयन बैटरियां [LIBs], सोडियम-आयन बैटरियां [SIBs], और मेटल-एयर बैटरियां [MABs]) ऊर्जा भंडारण के लिए आशाजनक विकल्प के रूप में उभरी हैं, क्योंकि इनमें उच्च ऊर्जा घनत्व, लंबा जीवन चक्र, और कम लागत जैसे गुण मौजूद हैं। हालांकि, बैटरी सामग्रियों, जैसे इलेक्ट्रोड और/या इलेक्ट्रोलाइट्स, के डिज़ाइन में और अधिक रणनीतियां विकसित करने की आवश्यकता है ताकि उनकी इलेक्ट्रोकेमिकल प्रदर्शन क्षमता को बढ़ाया जा सके।

वर्तमान अध्ययन विभिन्न ऊर्जा भंडारण प्रणालियों के लिए तीन प्रकार की सामग्रियों के यांत्रिक डिज़ाइन पर केंद्रित है: जलीय मेटल-आयन बैटरियां, मेटल-एयर बैटरियां, और अगली पीढ़ी के ऊर्जा भंडारण उपकरणों के लिए द्वि-आयामी (2D) सामग्री। मुख्य उद्देश्य बैटरी सामग्रियों को अनुकूलित करना और आयन परिवहन, प्रतिक्रिया गतिशीलता, और इलेक्ट्रॉनिक गुणों को इलेक्ट्रोकेमिकल प्रदर्शन से जोड़ने की प्रक्रिया को समझना है, जिसके लिए घनत्व कार्यात्मक सिद्धांत (DFT) और आणविक गतिशीलता (MD) सिमुलेशन जैसे कम्प्यूटेशनल दृष्टिकोणों का उपयोग किया गया है। जलीय मेटल-आयन बैटरियों के लिए, सोडियम सुपरआयोनिक (NASICON) संरचित $ATi_2(PO_4)_3$ (A=Na, Li) सामग्री का अध्ययन मिश्रित इलेक्ट्रोलाइट प्रणालियों में संभावित एनोड के रूप में किया गया है, जिनमें Li^+ और Na^+ आयन दोनों शामिल हैं। इस सामग्री में Na^+ और Li^+-आयनों के परिवहन गुणों और ऊर्जा स्तरों का अध्ययन और तुलना करने के लिए MD सिमुलेशन का उपयोग किया गया है। Na-आयन परिवहन गुणों को बढ़ाने के लिए लैटिस तनाव के उपयोग की रणनीति प्रस्तावित की गई है। इसके अतिरिक्त, Na-आयन चालकता और परिवहन गुणों पर ग्रेन बाउंड्री (GB) के प्रभाव का अध्ययन विभिन्न GB संरचनाओं का उपयोग करके किया गया है। मेटल-एयर बैटरियों के लिए, अध्ययन का मुख्य ध्यान जिंक-एयर बैटरियों में इलेक्ट्रोकैटलिस्ट सामग्रियों के गतिशील गुणों की जांच पर है। जिंक-एयर बैटरियों का प्रदर्शन वायु कैथोड पर ऑक्सीजन रिडक्शन रिएक्शन (ORR) और ऑक्सीजन एवोल्यूशन रिएक्शन (OER) की धीमी गतिशीलता के कारण सीमित है। Co_3O_4 इलेक्ट्रोकैटलिस्ट्स की इलेक्ट्रोकैटलिटिक गतिविधि को बढ़ाने के लिए आणविक स्तर पर इलेक्ट्रॉनिक संरचना इंजीनियरिंग का अध्ययन किया गया है। सक्रिय क्रिस्टल प्लेनों पर Cu-डॉप तत्वों की सांद्रता, सतह पर अवशोषित इंटरमीडिएट्स, और संक्रमण धातु की इलेक्ट्रॉनिक संरचना जैसे कारकों के प्रभाव का विश्लेषण किया गया है। 2D सामग्रियों के लिए, अगली पीढ़ी के ऊर्जा भंडारण उपकरणों के लिए MoS_2 और BFO ($BiFeO_3$, $Bi_2Fe_4O_9$, और

$Bi_{25}FeO_{40}$) सहित रिड्यूस्ड ग्राफीन ऑक्साइड (rGO) के एकीकरण का अध्ययन किया गया है। MoS_2@rGO में Na-आयन इंटरकलेशन गुणों का अध्ययन किया गया है, जिसमें Na-आयन परिवहन में सुधार, सक्रियण अवरोध में कमी, और Na^+-आयन के प्रसार में वृद्धि देखी गई है। वहीं, BFO@rGO समग्र सामग्री ने rGO एकीकरण और हेटरोटॉम डोपिंग के कारण इलेक्ट्रॉनिक और फोटोकैटलिटिक गुणों में सुधार दिखाया है, जिसमें बैंडगैप में कमी देखी गई।

कुल मिलाकर, इस शोध का मुख्य उद्देश्य कम्प्यूटेशनल मॉडलिंग और सिमुलेशन का उपयोग करके ऊर्जा भंडारण अनुप्रयोगों के लिए नवीन बैटरी सामग्रियों को डिजाइन करना है। यह अध्ययन मॉडल संरचना, संरचना और सामग्रियों के इलेक्ट्रोकेमिकल प्रदर्शन के बीच संबंध को स्पष्ट करने का प्रयास करता है, जिसे प्रयोगात्मक अवलोकनों से जोड़ा जा सकता है।

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