

**UNDERSTANDING DEFECTS IN
ADVANCED ENERGY MATERIALS
FROM FIRST-PRINCIPLES
CALCULATIONS**

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OCTOBER-2021**

**UNDERSTANDING DEFECTS IN
ADVANCED ENERGY MATERIALS
FROM FIRST-PRINCIPLES
CALCULATIONS**

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

October-2021

Dedicated to
my parents and husband

Certificate

This is to certify that the thesis entitled “**Understanding Defects in Advanced Energy Materials from First-Principles Calculations**” being submitted by **Ekta Arora**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics is a record of bonafide research work carried out by her under my supervision and guidance. She has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard. The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Acknowledgements

I wish to express my sincere gratitude to my thesis advisor, Dr. Saswata Bhattacharya, for his continuous guidance in my research work, patience, and motivation. His immense expertise in the subject has helped me throughout, from the research related work to the thesis writing. I would like to thank my student research committee (SRC) members, Prof. Bodh Raj Mehta, Prof. Varsha Banerjee, and Prof. Ali Haider, for being generous with their expertise and precious time. The discussions held with them from time to time helped me hugely improve my research work quality. I also thank my colleagues for the countless hours of discussions and the assistance they provided. I sincerely acknowledge the High-Performance Computing (HPC) facility at IITD for providing the computational assistance necessary for my research work.

Ekta Arora

Abstract

With the world's growing energy needs and the exhausting supply of fossil fuels, it has become crucial to shift to renewable energy sources. The renewable energy sources that are cost-effective, environmentally friendly, and abundant in nature are the solution to the current situation. The advanced solid-state materials used for addressing environmental issues have drawn significant research attention. In this thesis, advanced energy materials and their crystal defects are investigated with state-of-the-art Density Functional Theory (DFT) and *ab-initio* thermodynamics. The thesis mainly addresses the three classes of advanced energy materials, viz., hydrogen-storage materials, electrocatalyst materials used in electrochemical reduction of CO₂ to CO, and solid-state electrolyte materials for the all-solid-state batteries.

Hydrogen is considered a clean, abundant, and thus, a promising alternative for fossil fuels. Complex metal hydrides are referred to as a suitable medium for the storage of hydrogen. The release of hydrogen from such materials is possible only in the presence of an appropriate catalyst. Transition metal (TM) atom dopants improve the desorption kinetics and environmental condition requirements. The mechanism of dehydrogenation from catalyzed complex metal hydrides involves the diffusion of hydrogen-related intrinsic defects. We emphasize the role of environmental conditions and doping on the relative stability of the H-related defects in NaAlH₄, a prototypical system widely studied for the application of hydrogen storage. Firstly, we examine the effect of temperature and pressure on H-related defects' stability and concentration by incorporating *ab initio* thermodynamics. Next, the most suitable TM atom dopants are selected based on various factors like stability, structural distortion, and change in concentration of intrinsic defects in dopants' presence.

Another way to solve environmental concerns is to lower the concentration of CO₂ in the atmosphere by chemically reduce CO₂ to various other critical industrial feedstocks. Electrochemical reduction (ECR) of CO₂ to CO is carried out in a cell where the cathode material works as an electrocatalyst. The Electrocatalyst is required to have high

Faradaic efficiency and product selectivity. Cu-based alloys and compounds are known to have sufficiently high Faradaic efficiency. Experimentally, it is observed that Cu-In-O nanocomposites exhibit very high electrocatalytic activity and product selectivity. Cu-In-O nanocomposites efficiently suppress competitive hydrogen evolution reactions. We validate the experimental findings through our computational investigations. We study the effect of point defects on the Cu-In-O nanocomposites' catalytic activity by inducing various vacancy defects in the nanocomposite. Further, we explain the role of In-atoms in enhancing the product selectivity by suppressing the competitive hydrogen evolution reactions.

Li-ion batteries are the leading energy storage technology with a wide range of applications in portable electronics and automobiles. The use of flammable liquid electrolytes inhibits their realization in large scale energy applications. Replacing liquid electrolytes with solid-state electrolytes as in all-solid-state batteries ensures safety with improved battery design. However, achieving high ionic conductivity and appropriate mechanical properties for a solid-state candidate material is a challenge. We determine the mechanical stability of various sulfide materials for electrolytic applications. We also investigate the role of point defects, viz. halide doping, in improving the candidate materials' mechanical properties. We perform *ab-initio* molecular dynamics simulations to estimate the materials' diffusional properties and select the best-suited material based on the diffusional properties. We also elucidate the role of Li-vacancy in enhancing the diffusion of Li-ions through the bulk of such materials.

सार

दुनिया की बढ़ती ऊर्जा जरूरतों और जीवाश्म ईंधन की थकाऊ आपूर्ति के साथ, नवीकरणीय ऊर्जा स्रोतों में स्थानांतरित करना महत्वपूर्ण हो गया है। नवीकरणीय ऊर्जा स्रोत जो लागत प्रभावी, पर्यावरण के अनुकूल और प्रकृति में प्रचुर मात्रा में हैं, वर्तमान स्थिति का समाधान हैं। पर्यावरणीय मुद्दों को संबोधित करने के लिए उपयोग की जाने वाली उन्नत ठोस-अवस्था सामग्री ने महत्वपूर्ण शोध ध्यान आकर्षित किया है। इस थीसिस में, उन्नत ऊर्जा सामग्री और उनके क्रिस्टल दोषों की जांच अत्याधुनिक घनत्व कार्यात्मक सिद्धांत (डीएफटी) और एब-इनिटियो थर्मोडायनामिक्स के साथ की जाती है। थीसिस मुख्य रूप से उन्नत ऊर्जा सामग्री के तीन वर्गों, हाइड्रोजन-भंडारण सामग्री, CO_2 से CO की विद्युत रासायनिक कमी में उपयोग की जाने वाली इलेक्ट्रोकेटलिस्ट सामग्री और सभी ठोस-राज्य बैटरी के लिए ठोस-राज्य इलेक्ट्रोलाइट सामग्री को संबोधित करती है।

हाइड्रोजन को स्वच्छ, प्रचुर मात्रा में, और इस प्रकार, जीवाश्म ईंधन के लिए एक आशाजनक विकल्प माना जाता है। जटिल धातु हाइड्राइड को हाइड्रोजन के भंडारण के लिए उपयुक्त माध्यम के रूप में संदर्भित किया जाता है। ऐसे पदार्थों से हाइड्रोजन का उत्सर्जन एक उपयुक्त उत्प्रेरक की उपस्थिति में ही संभव है। ट्रांज़िशन मेटल (टीएम) परमाणु डोपेंट desorption कैनेटीक्स और पर्यावरण की स्थिति की आवश्यकताओं में सुधार करते हैं। उत्प्रेरित जटिल धातु हाइड्राइड से डिहाइड्रोजनीकरण के तंत्र में हाइड्रोजन से संबंधित आंतरिक दोषों का प्रसार शामिल है। हम NaAlH_4 में एच-संबंधित दोषों की सापेक्ष स्थिरता पर पर्यावरणीय परिस्थितियों और डोपिंग की भूमिका पर जोर देते हैं, एक प्रोटोटाइप प्रणाली जिसका व्यापक रूप से हाइड्रोजन भंडारण के अनुप्रयोग के लिए अध्ययन किया गया है। सबसे पहले, हम *ab initio* ऊष्मप्रवैगिकी को शामिल करके एच-संबंधित दोषों की स्थिरता और एकाग्रता पर तापमान और दबाव के प्रभाव की जांच करते हैं। इसके बाद, स्थिरता, संरचनात्मक विकृति, और डोपेंट की उपस्थिति में आंतरिक दोषों की एकाग्रता में परिवर्तन जैसे विभिन्न कारकों के आधार पर सबसे उपयुक्त टीएम परमाणु डोपेंट का चयन किया जाता है। पर्यावरणीय चिंताओं को हल करने का एक और तरीका है कि वातावरण में CO_2 की सांद्रता को रासायनिक रूप से CO_2 को विभिन्न अन्य महत्वपूर्ण औद्योगिक फीडस्टॉक्स में कम किया जाए। सीओ 2 से सीओ की विद्युत रासायनिक कमी (ईसीआर) एक सेल में की जाती है जहां कैथोड सामग्री इलेक्ट्रोकेटलिस्ट के रूप में काम करती है। इलेक्ट्रोकेटलिस्ट को उच्च फैराडिक दक्षता और उत्पाद चयनात्मकता की आवश्यकता होती है। Cu -आधारित मिश्र धातुओं और यौगिकों को पर्याप्त रूप से उच्च फैराडिक दक्षता के लिए जाना जाता है। प्रायोगिक तौर पर, यह देखा गया है कि Cu-In-O नैनोकंपोजिट्स बहुत उच्च इलेक्ट्रोकेटलिटिक गतिविधि और उत्पाद चयनात्मकता प्रदर्शित करते हैं। Cu-In-O नैनोकंपोजिट्स प्रतिस्पर्धी हाइड्रोजन विकास प्रतिक्रियाओं को कुशलतापूर्वक दबा देते हैं। हम अपनी कम्प्यूटेशनल जांच के माध्यम से प्रयोगात्मक निष्कर्षों को मान्य करते हैं। हम नैनोकंपोजिट में विभिन्न रिक्ति दोषों को उत्प्रेरण करके Cu-In-O नैनोकंपोजिट्स की उत्प्रेरक गतिविधि पर बिंदु दोषों के प्रभाव का अध्ययन करते हैं। इसके अलावा, हम प्रतिस्पर्धी हाइड्रोजन विकास प्रतिक्रियाओं को दबाकर उत्पाद चयनात्मकता को बढ़ाने में इन-परमाणुओं की भूमिका की व्याख्या करते हैं।

पोर्टेबल इलेक्ट्रॉनिक्स और ऑटोमोबाइल में अनुप्रयोगों की एक विस्तृत श्रृंखला के साथ ली-आयन बैटरी अग्रणी ऊर्जा भंडारण तकनीक है। ज्वलनशील तरल इलेक्ट्रोलाइट्स का उपयोग बड़े पैमाने पर ऊर्जा अनुप्रयोगों में उनकी प्राप्ति को रोकता है। लिक्विड इलेक्ट्रोलाइट्स को सॉलिड-स्टेट इलेक्ट्रोलाइट्स से बदलना, जैसा कि ऑल-सॉलिड-स्टेट बैटरी में होता है, बेहतर बैटरी डिज़ाइन के साथ सुरक्षा सुनिश्चित करता है। हालांकि, एक ठोस राज्य उम्मीदवार सामग्री के लिए उच्च आयनिक चालकता और उपयुक्त यांत्रिक गुणों को प्राप्त करना एक चुनौती है। हम इलेक्ट्रोलाइटिक अनुप्रयोगों के लिए विभिन्न सल्फाइड सामग्री की यांत्रिक स्थिरता का निर्धारण करते हैं। हम बिंदु दोषों की भूमिका की भी जांच करते हैं, अर्थात्। उम्मीदवार सामग्री के यांत्रिक गुणों में सुधार के लिए हैलाइड डोपिंग। हम सामग्री के प्रसार गुणों का अनुमान लगाने के लिए *ab-initio* आणविक गतिकी सिमुलेशन करते हैं और विसरणीय गुणों के आधार पर सबसे उपयुक्त सामग्री का चयन करते हैं। हम ऐसी सामग्री के थोक के माध्यम से ली-आयनों के प्रसार को बढ़ाने में ली-रिक्ति की भूमिका को भी स्पष्ट करते हैं।

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