

**FUNCTIONAL MATERIALS FOR ENERGY STORAGE
AND CONVERSION DEVICES: INSIGHTS FROM
FIRST-PRINCIPLES AND MOLECULAR DYNAMICS
SIMULATIONS**

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**Functional Materials for Energy Storage and
Conversion Devices: Insights from First-Principles
and Molecular Dynamics Simulations**

by

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*This thesis is dedicated to my parents
for their endless love, support, and encouragement.*

Certificate

This is to certify that the thesis entitled **Functional Materials for Energy Storage and Conversion Devices: Insights from First-Principles and Molecular Dynamics Simulations** submitted by **Jyotsana Kala** to the Indian Institute of Technology Delhi for the award of the degree of the Doctor of Philosophy, 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 requisite standard.

The material contained in this thesis has not been submitted, either in part or in full, to any other university or institute for the award of any degree or diploma.

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“It takes a village to raise a child.”

- African Proverb

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Abstract

The increasing urgency of climate change and energy crises demand the development of sustainable energy technologies. Energy conversion and storage devices are key in reducing dependence on fossil fuels and addressing geopolitical and environmental concerns. Improving the performance of such devices requires the use of advanced materials. Among energy conversion systems, solid oxide fuel cells (SOFCs) are attractive due to their versatility in portable, stationary, and backup applications. However, high operating temperatures necessitate costly materials, and reducing the temperature leads to sluggish oxygen reduction reaction (ORR) kinetics. In addition, the cathode part also suffers from the degrading cation segregation phenomena. For example, the benchmark cathode $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) suffers from Sr-cation segregation and the formation of insulating surface phases like SrO and SrCO_3 , which degrade ORR activity. This highlights the need for innovative cathode materials, which motivates the first three projects of this thesis. The first project investigates the layered double perovskite oxide $\text{NdBaCo}_2\text{O}_{6-\delta}$ (NBCO). Its ordered oxygen vacancies and layered structure promote mixed ionic and electronic conduction, expanding the ORR-active area. Density Functional Theory (DFT) and Molecular Dynamics (MD) simulations show that NBCO exhibits high oxygen vacancy concentration and oxygen anion diffusivity at intermediate temperatures (<1073 K). However, a strong tendency for Ba-cation surface segregation was observed. Surface energy calculations predict Ba/Co-terminated surfaces to be energetically favorable, leading to surface enrichment of Ba. A metric called “degree of cation segregation” was proposed using MD to quantify segregation. Two mitigation strategies were explored: (1) Compressive strain, e.g., 4% compressive strain reduces surface cation segregation; and (2) A'-site doping with smaller cations (e.g., Sr^{2+} , Ca^{2+}) reduces ionic size mismatch between A and A'-site cations and segregation. Notably, 50% Ca-doping led to a significant reduction in segregation and enhanced oxygen transport properties. The second project focuses on the double perovskite $\text{Sr}_2\text{CoNbO}_{6-\delta}$ (SCNO).

DFT results indicate low oxygen vacancy formation energies, suggesting high vacancy concentrations. The redox-active Co^{3+} at B-site boosts oxygen vacancy formation, while the high-oxidation state Nb^{5+} at B'-site reduces Sr^{2+} cation segregation tendencies. Oxygen vacancies are more abundant at the surface than in the bulk, indicating high surface exchange coefficients. Compressive strain imposed by a Gd-doped ceria (GDC) substrate further reduces Sr-cation segregation, consistent with the trend seen in NBCO. The third project explores high-entropy perovskite oxides (HEPOs) based on the LSM perovskite oxide. A systematic approach was developed to identify synthesizable single-phase HEPOs using tolerance factors and enthalpy of mixing. Theoretical study identified $\text{La}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Gd}_{0.2}\text{Pr}_{0.2}\text{MnO}_{3-\delta}$ (LSCGP) as single-phase synthesizable HEPO. LSCGP was further successfully synthesized. LSCGP exhibits significantly enhanced oxygen vacancy concentration and diffusivity (10^{-8} cm^2/s at 873 K), several orders higher than parent $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$. MD and DFT studies reveal negligible cation segregation, unlike conventional LSM-based materials. This study demonstrates the promise of entropy-stabilized materials for enhancing performance and stability in SOFCs.

For a sustainable future, there is also a need of advance high-performance energy storage technology along with energy conversion devices. Current electrochemical energy storage technologies primarily rely on lithium-ion and metal-air batteries. For efficient and rechargeable battery operation, electrocatalysts play a critical role, particularly in facilitating the oxygen evolution reaction (OER). However, state-of-the-art OER electrocatalysts are typically based on precious metal oxides such as ruthenium and iridium, which are costly and scarce. This thesis investigates the OER activity of alternative, earth-abundant spinel oxide based on cobalt. With this, the fourth project examines Fe-doped spinel Co_3O_4 for electrocatalysts for metal-air batteries. DFT simulations were used to study adsorption energies of OER intermediates (O^* , OH^* , OOH^*) at Co and Fe octahedral sites. Adsorption was stronger at Fe sites, increasing reaction barriers. Explicit water models were used to simulate acidic environments. The O^* adsorption to OOH^* adsorption step was identified as rate-limiting with a high barrier of 87.80 kJ/mol. These insights into electronic structure and binding behavior inform catalyst design for OER. Furthermore, lithium-based electrode materials present resource and sustainability challenges, highlighting the need for alternative materials that are tunable, flexible,

and both cost and resource-efficient. In this context, redox-active organic conjugated polymers are explored as promising electrode materials for battery applications. The final project explores redox-active conjugated polymers as potential battery electrode materials, focusing on diketopyrrolopyrrole (DPP)-thiophene-based p-type polymers using MD simulations. Methoxy-functionalization of the thiophene rings was found to enhance backbone planarity, leading to improved volumetric charge density. To quantify backbone conformational dynamics, an “end-to-end distance” metric was introduced. The influence of counter-anions, varying in size, shape, and symmetry, was also investigated, revealing their significant impact on polymer planarity and hence, expected to influence charge densities. Notably, counter-anions showed preferential interactions with the polymer backbone, particularly with thiophene sites. An alchemical transformation-based approach was used to simulate polymer charging and discharging via changes in counter-anions, enabling the estimation of redox potentials directly from MD simulations. The calculated values showed good agreement with experimental trends, highlighting the potential of this framework to inform the design of high-performance polymer electrodes.

Together, these five projects contribute to the development of advanced materials for efficient, stable, and scalable energy conversion and storage systems.

सारांश

निरंतर बढ़ते जलवायु परिवर्तन और ऊर्जा संकट की तात्कालिकता, सतत ऊर्जा प्रौद्योगिकियों के विकास की आवश्यकता को रेखांकित करती है। जीवाश्म ईंधन पर निर्भरता कम करने, भू-राजनीतिक एवं पर्यावरणीय चिंताओं के समाधान में ऊर्जा रूपांतरण और संचयन उपकरण महत्वपूर्ण भूमिका निभाते हैं। इन उपकरणों के प्रदर्शन में सुधार के लिए उन्नत पदार्थों का उपयोग आवश्यक है। ऊर्जा रूपांतरण प्रणालियों में, ठोस ऑक्साइड ईंधन सेल (SOFCs) अपनी स्थानांतरणीयता, स्थायी, और बैकअप अनुप्रयोगों में बहुविज्ञता के कारण आकर्षक हैं। हालांकि, उच्च तापमान पर संचालन के लिए महंगे पदार्थों की आवश्यकता होती है, जबकि तापमान कम करने पर ऑक्सीजन अपचयन अभिक्रिया (Oxygen Reduction Reaction, ORR) की गतिशीलता धीमी हो जाती है। इसके अतिरिक्त, कैथोड भाग की सतह पर धनायन पृथक्करण SOFC के प्रदर्शन को और कम करता है। उदाहरण स्वरूप, मानक कैथोड $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) में Sr-धनायन का पृथक्करण के कारण SrO तथा SrCO_3 जैसे निरोधी सतही अवस्थाओं का निर्माण होता है, जिससे ORR गतिविधि घटती है। यह समस्या उन्नत कैथोड पदार्थों की आवश्यकता को दर्शाता है, जो इस शोध की पहली तीन परियोजनाओं की प्रेरणा है। पहली परियोजना बहुस्तरीय डबल पेरोव्स्काइट ऑक्साइड $\text{NdBaCo}_2\text{O}_{6-\delta}$ (NBCO) की जांच करता है। इसकी व्यवस्थित ऑक्सीजन रिक्तियाँ और बहुस्तरीय संरचना मिश्रित आयनिक एवं इलेक्ट्रॉनिक चालकता को बढ़ावा देती हैं, जिससे ORR-सक्रिय क्षेत्र का विस्तार होता है। घनत्व कार्यात्मक सिद्धांत (Density Functional Theory, DFT) और आणविक गतिकी (Molecular Dynamics, MD) अनुगणना दर्शाते हैं कि NBCO में मध्यवर्ती तापमान (<1073 K) पर उच्च ऑक्सीजन रिक्ति सांद्रता और ऑक्सीजन ऋणायन विसरणशीलता होती है। हालांकि, Ba-धनायन के सतही पृथक्करण की प्रवृत्ति देखी गई। DFT से की गयी सतही ऊर्जा गणनाओं के अनुसार Ba/Co-अंतित सतहें ऊर्जा की दृष्टि से अधिक अनुकूल हैं, जिससे सतह पर Ba की प्रचुरता होती है। MD के माध्यम से "धनायन पृथक्करण की सीमा (Degree of cation segregation)" नामक मापदंड प्रस्तावित किया गया। दो शमन रणनीतियाँ जांची गईं: (1) संपीड़न तनाव, जैसे कि 4% संपीड़न तनाव सतही धनायन पृथक्करण को कम करता है; और (2) A'-साइट पर छोटे धनायनों (जैसे Sr^{2+} , Ca^{2+}) की डोपिंग, जिससे A और A' साइट धनायनों के बीच आयनिक आकार असंगति से पृथक्करण और कम होता है। विशेष रूप से, 50% Ca-डोपिंग से पृथक्करण में उल्लेखनीय कमी और ऑक्सीजन परिवहन गुणों में वृद्धि हुई। दूसरी परियोजना डबल पेरोव्स्काइट $\text{Sr}_2\text{CoNbO}_{6-\delta}$ (SCNO) पर केंद्रित है। DFT अनुगणना कम ऑक्सीजन रिक्ति निर्माण ऊर्जा दर्शाते हैं, जिससे उच्च रिक्ति सांद्रता का

संकेत मिलता है। B-साइट पर अपचय-ऑक्सीकरण-सक्रिय Co^{3+} ऑक्सीजन रिक्ति निर्माण को बढ़ाता है, जबकि B'-साइट पर उच्च ऑक्सीकरण अवस्था वाला Nb^{5+} सतह पर Sr-धनायनों की पृथक्कीकरण को कम करता है। सतह पर ऑक्सीजन रिक्तियाँ बल्क की तुलना में अधिक पायी गयी, जिससे उच्च सतही विनिमय गुणांक का संकेत मिलता है। गैडोलिनियम-डोपित सेरिया (GDC) आधारपरत द्वारा लगाया गया संपीड़न तनाव Sr-धनायन पृथक्करण को और कम करता है, जो NBCO में देखी गई प्रवृत्ति के अनुरूप है। तीसरी परियोजना LSM पेरोव्स्काइट ऑक्साइड आधारित उच्च-एंट्रॉपी पेरोव्स्काइट ऑक्साइड्स (High Entropy Perovskite Oxides, HEPOs) की खोज करता है। एक व्यवस्थित पद्धति द्वारा सहनशीलता (टॉलरेंस) गुणक और मिश्रण की एन्थैल्पी का उपयोग कर एक-चरणीय HEPOs की पहचान की गई। सैद्धांतिक अध्ययन से $\text{La}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{Gd}_{0.2}\text{Pr}_{0.2}\text{MnO}_3$ (LSCGP) को एक-चरणीय HEPO के रूप में चिह्नित किया गया, जिसे सहयोगी शोधकर्ताओं द्वारा सफलतापूर्वक संश्लेषित भी किया गया। LSCGP में ऑक्सीजन रिक्ति सांद्रता और विसरणशीलता ($10^{-8} \text{ cm}^2/\text{s}$, 873 K तापमान) पारंपरिक $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ और $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ की तुलना में कई गुणा अधिक पाई गई। MD और DFT अध्ययन दर्शाते हैं कि इसमें धनायन पृथक्करण नगण्य है, जो पारंपरिक LSM-आधारित पदार्थों से भिन्न है। यह अध्ययन SOFCs में प्रदर्शन और स्थिरता के संयोजन के लिए एंट्रॉपी-स्थिरित पदार्थों की संभावना को दर्शाता है।

सतत भविष्य के लिए, ऊर्जा रूपांतरण उपकरणों के साथ-साथ उच्च-प्रदर्शन ऊर्जा संचयन तकनीकों की भी आवश्यकता है। वर्तमान वैद्युत-रासायनिक ऊर्जा संचयन तकनीकें मुख्यतः लिथियम-आयन और धातु-वायु बैटरी पर निर्भर हैं। कुशल और पुनः-आवेशणीय बैटरी संचालन के लिए वैद्युत-उत्प्रेरक, विशेष रूप से ऑक्सीजन उत्सर्जन अभिक्रिया (Oxygen Evolution Reaction, OER) को सुगम बनाने में, महत्वपूर्ण भूमिका निभाते हैं। हालांकि, वर्तमान OER वैद्युत-उत्प्रेरक सामान्यतः महंगे और दुर्लभ धातु ऑक्साइड्स (जैसे रुथेनियम और इरिडियम) पर आधारित हैं। यह शोध कोबाल्ट आधारित, पृथ्वी में प्रचुर मात्रा में उपलब्ध स्पिनल ऑक्साइड्स की OER गतिविधि की जांच करता है। इसी के तहत, चौथी परियोजना Fe-डोपेड स्पिनल Co_3O_4 को धातु-वायु बैटरियों के लिए वैद्युत-उत्प्रेरक के रूप में अध्ययन करता है। DFT अनुगणना द्वारा OER मध्यवर्ती (O^* , OH^* , OOH^*) के Co और Fe षट्मुखीय साइट्स पर अवशोषण ऊर्जा का अध्ययन किया गया। Fe साइट्स पर अवशोषण अधिक मजबूत पाया गया, जिससे अभिक्रिया अवरोध बढ़ा। अम्लीय वातावरण की अनुगणना करने के लिए स्पष्ट जल मॉडल्स का उपयोग किया गया। O^* से OOH^* अवशोषण चरण को 87.80 kJ/mol की उच्च बाधा के साथ दर-सीमित पाया गया। यह कार्य इलेक्ट्रॉनिक संरचना और

बंधन व्यवहार में OER विश्लेषण के लिए वैद्युत्-उत्प्रेरक की रचना को सूचित करता है। इसके अतिरिक्त, लिथियम-आधारित इलेक्ट्रोड पदार्थ संसाधन और स्थिरता संबंधी चुनौतियाँ प्रस्तुत करती हैं, जिससे वैकल्पिक, अनुकूलनशील, लचीली, लागत और संसाधन-कुशल पदार्थों की आवश्यकता है। इस संदर्भ में, अपचय-ऑक्सीकरण-सक्रिय कार्बनिक संयुग्मित बहुलक बैटरी अनुप्रयोगों के लिए संभावित इलेक्ट्रोड पदार्थों के रूप में उभर रहे हैं। अंतिम परियोजना में अपचय-ऑक्सीकरण-सक्रिय संयुग्मित बहुलक, विशेष रूप से डाइकेटोपाइरोलोपाइरोल (DPP)-थियोफीन-आधारित p-प्रकार बहुलक का MD अनुगणना द्वारा अध्ययन किया गया। थियोफीन रिंग्स की मेथॉक्सी-फंक्शनलाइजेशन से बैकबोन की समतलता बढ़ी, जिससे आयतनी आवेश घनत्व में सुधार हुआ। बैकबोन संरचनात्मक गतिकी को मापने के लिए "अंत से अंत तक की दूरी (End-to-End distance)" मापदंड पेश किया गया। विभिन्न आकार, आकृति, और समरूपता वाले प्रति-ऋणायनों के प्रभाव का भी अध्ययन किया गया, जिससे उनकी बहुलक समतलता पर महत्वपूर्ण भूमिका सामने आई, जो आवेश घनत्व को प्रभावित कर सकती है। उल्लेखनीय है कि प्रति-ऋणायनों ने विशेष रूप से थियोफीन साइट्स पर बहुलक बैकबोन के साथ प्राथमिक परस्पर क्रिया दिखाया। बहुलक के आवेशन और निर्वेशन की अनुगणना करने के लिए एक रसायनिक-परिवर्तनात्मक (alchemical transformation)-आधारित दृष्टिकोण प्रयोग किया गया, जिससे MD अनुगणना से सीधे अपचय-ऑक्सीकरण विभव का अनुमान संभव हुआ। गणना किए गए मान प्रयोगात्मक प्रवृत्तियों के साथ अच्छी तरह मेल खाते हैं, जिससे उच्च-प्रदर्शन बहुलक इलेक्ट्रोड रचना के लिए इस रूपरेखा की संभावनाएँ उजागर होती हैं।

सामूहिक रूप से, ये पाँचों परियोजनाएं कुशल, स्थिर और बड़े पैमाने पर लागू किए जा सकने वाले ऊर्जा रूपांतरण एवं संचयन प्रणालियों के लिए उन्नत पदार्थों के विकास में योगदान करते हैं।

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