

**EXPLORING PRUSSIAN BLUE ANALOGUES FOR ENHANCED
BIFUNCTIONAL OXYGEN ELECTROCATALYSIS**

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by

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Submitted

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to the



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DEDICATED TO
MY FAMILY

CERTIFICATE

This is to certify that the thesis entitled, “**Exploring Prussian Blue Analogues for Enhanced Bifunctional Oxygen Electrocatalysis**” being submitted by **Miss Priya Jain** to the **Indian Institute of Technology, Delhi** for the award of degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The results contained in this thesis have not been submitted to any other university or institute wither in part or full for the awards of any other degree or diploma.

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Priya

ABSTRACT

The rising global energy demands and the depletion of fossil fuels, along with environmental concerns, have thrust renewable energy sources into the spotlight. However, the intermittent nature of these renewable energy sources presents a significant challenge to their effective utilization. Electrochemical energy conversion and storage devices, such as water electrolyzers, fuel cells, and metal-air batteries, have emerged as promising alternatives for energy harvesting. Yet, they face a common hurdle: the lack of suitable bifunctional oxygen electrodes with high activity and stability. The sluggish kinetics of the Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR) lead to high overpotentials, diminishing energy efficiency and stability of these devices. Moreover, the reliance on precious metal-based electrocatalysts aggravates the cost and sustainability issues. This thesis seeks to investigate non-precious metal-based materials, particularly Prussian Blue analogues (PBA) or Metal Hexacyanoferrates (MHCFs), as bifunctional oxygen electrocatalysts. PBAs, a class of coordination polymers, offer a cost-effective alternative for electrocatalysis due to their structural versatility and suitable properties such as high surface area, abundant metal sites, tuneable morphology, and ease of synthesis. Furthermore, understanding the structure-activity relationships is vital for advanced electrocatalyst design using these PBA based catalyst. Thus, this work focuses on developing highly active and stable PBA-based bifunctional oxygen electrocatalysts by exploring potential strategies, including structural modifications, doping, and hybridization with carbon supports. The thesis comprises eight chapters, each outlined briefly below.

Chapter 1 provides a brief introduction to bifunctional oxygen electrocatalysis, its mechanisms, and its significance in electrochemical energy conversion and storage devices. It addresses the major challenges in catalyst design, performance, cost, and durability, discussing the scope of Prussian Blue Analogues (PBAs) as bifunctional catalysts, along with associated advantages, disadvantages, and opportunities. A detailed literature survey highlights gaps in current research, exploring various strategies to enhance the performance of MHCFs-based catalysts. The chapter concludes by outlining the scope and objectives of the thesis focused on the development of MHCF-based electrocatalysts for bifunctional OER/ORR.

Chapter 2 delves into the methodologies employed in this thesis, including nanomaterial synthesis, physicochemical characterization, and electrochemical analysis. It elaborates on the important techniques and parameters for evaluating bifunctional oxygen electrocatalysis using PBAs as catalyst materials.

In **Chapter 3**, the strategy of introducing carbon support to address the challenges associated with the low stability and conductivity of copper hexacyanoferrates (CuHCF) was introduced. A novel approach was employed to create 1D/3D hybrid nano-heterostructures of 3D CuHCF functionalized with multi-walled carbon nanotubes (f-MWCNTs). The resulting electrocatalyst (CuHCF/f-CNT) demonstrates a remarkable improvement in both OER and ORR due to the synergistic effects of CuHCF and f-MWCNTs. Specifically, the CuHCF catalytic sites facilitate mass transport, while the f-MWCNTs boost electron conduction and enlarge the surface area. Additionally, the strong metal support interactions (SMSI) between CuHCF and f-CNT enhances charge transfer at the electrochemical interface, elevating the electro-positivity of Cu catalytic centers and defect sites for efficient adsorption of reaction intermediates. Furthermore, the formation of a thin layer of $\text{Cu}(\text{OH})_2$ on the CuHCF surface was identified as a key contributor to the enhanced electrocatalytic performance.

In **Chapter 4**, to further enhance the activity and address the limitations of the previous study, we used a nanocomposite of cobalt-hexacyanoferrate onto a 3D network of interconnected graphene oxide and functionalized carbon nanotubes support (referred to as CoHCF/GO/f-CNT). The high OER activity of Co centres due to stability at high oxidising potentials and the synergistic effect of high surface area of GO and high conductivity of f-CNT helped in enhanced OER/ORR activity. Further, the SMSI induced electro-positivity of the Co^{2+} metal center, facilitated the surface reconstruction and formation of CoOOH film under alkaline conditions, serving as an active site. It was observed that the CoHCF primarily contributes to OER through in-situ formation of CoOOH/FeOOH, while GO/f-CNT maximizes active site density and electronic conductivity. For ORR. Efficient O^{2-} adsorption and faster electron transfer resulting in excellent bi-functional activity with low overvoltage (0.8 V) and high stability (100 hrs. for OER, 24 hrs. for ORR).

In **Chapter 5**, we demonstrate a strategy to concurrently engineer the coordination sphere vacancies and Lewis acid sites, via atomically dispersed Zn^{2+} dopants in CoFe PBA that makes Co^{n+} more electropositive, to boost the bi-functional oxygen electrocatalysis on PBA surfaces. The optimal Zn-doping (3 mole%) not only enhances oxygen evolution reaction activity of CoFe PBAs to the comparable level of IrO_2 catalyst, but also depicts an

impressive bi-functional oxygen activity with low reversible overvoltage of 0.84 V. This work also demonstrated that an in-situ formation of Co^{3+} (CoOOH) and Fe^{3+} (FeOOH) during the OER plays a crucial role for the boosted activity in bifunctional oxygen electrocatalysis.

In **Chapter 6** we utilized the strategy of tuning the metal centres/d-band centres in PBA based catalyst for enhanced OER/ORR activity. The d-band center has been used as a promising descriptor to understand trends in electrocatalysis for PBAs. Herein, we present our systematic study aimed at developing a mini-volcano plot demonstrating dependence of bi-functional oxygen electrocatalytic activity of Prussian blue analogues (PBAs) on their d-band center. Our results from ex-situ core level and valence band XPS, Raman, and FTIR spectroscopy suggest that the tuning of d-band center via modulated N and C-coordinated metal centers dictates their electrocatalytic OER and ORR activities. Among PBAs, the CoCo PBA exhibits highest activity due to its optimal position of d-band center and abundant Co^{3+} active sites. Moreover, M-Co PBAs showcased superior performance than M-Fe PBAs, attributed to facile formation of surface-active sites, i.e., metal oxy(hydroxide).

Chapter 7 focuses on synthesizing CoFe PBA with two distinct precursor ratios (3:2 and 1:1), to tune the FeCN vacancy in PBAs to understand their impact on catalytic performance. An investigation encompassing synthesis and anodic activation studies reveals intriguing insights. The 3:2 precursor ratio exhibits enhanced activity facilitated by the presence of Co^{3+} and V_{FeCN} than 1:1 CoHCF. Further, the 3:2 also shows facile surface reconstruction as evident from the analysis post anodic activation. The increased defect sites elevate the coordination number of Co and Fe, facilitating surface reconstruction in CoHCF (3:2) and enhancing catalyst performance towards OER and ORR, while also suppressing Fe leaching for improved OER activity. Operando Raman and ex-situ X-ray photoelectron spectroscopy analyses further unveil the role of anodic potential in altering Co valence, thereby strengthening the adsorption of oxygen-containing species and enhancing activity.

Finally in **Chapter 8**, the thesis work is summarised and concluded. It is concluded that the various strategies utilized in the work directly influence the surface reconstruction in PBAs in alkaline medium leading to different activities. Furthermore, the future scope of the thesis has been discussed.

संक्षेप

पर्यावरणीय चिंताओं के साथ-साथ वैश्विक ऊर्जा की बढ़ती मांग और जीवाश्म ईंधन की कमी ने अक्षय ऊर्जा स्रोतों को सुर्खियों में ला दिया है। हालांकि, इन नवीकरणीय ऊर्जा स्रोतों की दिन के हर समय उपस्थित नहीं प्रकृति उनके प्रभावी उपयोग के लिए एक महत्वपूर्ण चुनौती प्रस्तुत करती है। विद्युत रासायनिक ऊर्जा रूपांतरण और भंडारण उपकरण, जैसे कि जल इलेक्ट्रोलाइजर, ईंधन सेल और धातु-वायु बैटरी, ऊर्जा संचयन के लिए आशाजनक विकल्पों के रूप में उभरे हैं। फिर भी, उन्हें एक आम बाधा का सामना करना पड़ता है: उच्च गतिविधि और स्थिरता के साथ उपयुक्त द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोड की कमी। ऑक्सीजन इवोल्यूशन रिएक्शन (OER) और ऑक्सीजन रिडक्शन रिएक्शन (ORR) के सुस्त गतिकी से इन उपकरणों की उच्च क्षमता, ऊर्जा दक्षता और स्थिरता कम हो जाती है। इसके अलावा, कीमती धातु-आधारित विद्युत उत्प्रेरक पर विश्वसनीयता लागत और स्थिरता के मुद्दों को बढ़ाती है। यह शोध प्रबंध गैर-कीमती धातु-आधारित सामग्रियों, विशेष रूप से प्रशियाई ब्लू एनालाॅग (PBA) या मेटल हेक्सासियानोफेरेट्स (MHCF) की द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोडकैटलिस्ट के रूप में जांच करना चाहता है। PBA समन्वय पॉलिमर का एक वर्ग, अपनी संरचनात्मक बहुमुखी प्रतिभा और उच्च सतह क्षेत्र, प्रचुर मात्रा में धातु स्थलों, ट्यूनेबल मॉर्फोलॉजी और संश्लेषण में आसानी जैसे उपयुक्त गुणों के कारण इलेक्ट्रोडकैटालिसिस के लिए एक लागत प्रभावी विकल्प प्रदान करता है। इसके अलावा, इन पीPBA आधारित उत्प्रेरक का उपयोग करके उन्नत विद्युत उत्प्रेरक डिजाइन के लिए संरचना-गतिविधि संबंधों को समझना महत्वपूर्ण है। इस प्रकार, यह कार्य संरचनात्मक संशोधनों, डोपिंग और कार्बन समर्थन के साथ संकरण सहित संभावित रणनीतियों की खोज करके अत्यधिक सक्रिय और स्थिर पीबीए-आधारित द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोडकैटलिस्ट विकसित करने पर केंद्रित है। थीसिस में आठ अध्याय हैं, जिनमें से प्रत्येक का संक्षिप्त विवरण नीचे दिया गया है।

अध्याय 1 द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोडकैटालिसिस, इसके तंत्र और विद्युत रासायनिक ऊर्जा रूपांतरण और भंडारण उपकरणों में इसके महत्व का संक्षिप्त परिचय प्रदान करता है। यह उत्प्रेरक डिजाइन, प्रदर्शन, लागत और स्थायित्व में प्रमुख चुनौतियों को संबोधित करता है, संबंधित लाभ, नुकसान और अवसरों के साथ-साथ द्वि-कार्यात्मक उत्प्रेरक के रूप में प्रशिया ब्लू एनालाॅग (पीबीए) के दायरे पर चर्चा करता है। एक विस्तृत साहित्य सर्वेक्षण MHCF-आधारित उत्प्रेरकों के प्रदर्शन को बढ़ाने के लिए विभिन्न रणनीतियों की खोज करते हुए वर्तमान अनुसंधान में कमियों पर प्रकाश डालता है। अध्याय का समापन द्वि-कार्यात्मक OER/ORR के लिए एमएचसीएफ-आधारित इलेक्ट्रोडकैटलिस्ट के विकास पर केंद्रित थीसिस के दायरे और उद्देश्यों को रेखांकित करके किया गया है।

अध्याय 2 इस थीसिस में नियोजित कार्यप्रणाली पर प्रकाश डालता है, जिसमें नैनोमटेरियल संश्लेषण, भौतिक रासायनिक लक्षण वर्णन और विद्युत रासायनिक विश्लेषण शामिल हैं। यह उत्प्रेरक सामग्री

के रूप में PBA का उपयोग करके द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोकेटलिसिस का मूल्यांकन करने के लिए महत्वपूर्ण तकनीकों और मापदंडों पर विस्तार से बताता है।

अध्याय 3 में, कॉपर हेक्सासियानोफरेट्स (CuHCF) की कम स्थिरता और चालकता से जुड़ी चुनौतियों का समाधान करने के लिए कार्बन समर्थन शुरू करने की रणनीति पेश की गई थी, बहु-दीवार वाले कार्बन नैनोट्यूब के साथ कार्यात्मक 3डी सीयूएचसीएफ के 1डी/3डी संकर नैनो-हेटरोस्ट्रक्चर बनाने के लिए एक नए दृष्टिकोण का उपयोग किया गया था (f-MWCNTs). परिणामस्वरूप विद्युत उत्प्रेरक (CuHCF/f-CNT) सीयूएचसीएफ और एफ-एमडब्ल्यूसीएनटी के सहक्रियात्मक प्रभावों के कारण ओईआर और ओआरआर दोनों में उल्लेखनीय सुधार दर्शाता है। विशेष रूप से, CuHCF उत्प्रेरक स्थल बड़े पैमाने पर परिवहन की सुविधा प्रदान करते हैं, जबकि f-MWCNT इलेक्ट्रॉन चालन को बढ़ावा देते हैं और सतह क्षेत्र को बढ़ाते हैं। इसके अतिरिक्त, CuHCF और f-CNT के बीच मजबूत धातु समर्थन अंतःक्रिया (SMSI) विद्युत रासायनिक इंटरफेस पर आवेश अंतरण को बढ़ाता है, प्रतिक्रिया मध्यवर्ती के कुशल अवशोषण के लिए सी. यू. उत्प्रेरक केंद्रों और दोष स्थलों की विद्युत-सकारात्मकता को बढ़ाता है। इसके अलावा, CuHCF सतह पर Cu(OH)_2 की एक पतली परत के गठन को विद्युत उत्प्रेरक प्रदर्शन में वृद्धि के लिए एक प्रमुख योगदानकर्ता के रूप में पहचाना गया था।

अध्याय 4 में, गतिविधि को और बढ़ाने और पिछले अध्ययन की सीमाओं को संबोधित करने के लिए, हमने परस्पर जुड़े ग्राफीन ऑक्साइड और कार्यात्मक कार्बन नैनोट्यूब समर्थन (CoHCF/GO/f-CNT के रूप में संदर्भित) के 3D नेटवर्क पर कोबाल्ट-हेक्सासियानोफरेट के नैनोकंपोजिट का उपयोग किया। उच्च ऑक्सीकरण क्षमता पर स्थिरता के कारण सह केंद्रों की उच्च ओईआर गतिविधि और जीओ के उच्च सतह क्षेत्र के सहक्रियात्मक प्रभाव और एफ-सीएनटी की उच्च चालकता ने ओईआर/ओआरआर गतिविधि को बढ़ाने में मदद की। इसके अलावा, SMSI ने Co^{2+} धातु केंद्र की विद्युत-सकारात्मकता को प्रेरित किया, क्षारीय परिस्थितियों में सतह के पुनर्निर्माण और CoOOH फिल्म के निर्माण की सुविधा प्रदान की, जो एक सक्रिय स्थल के रूप में कार्य करता है। यह देखा गया कि CoHCF मुख्य रूप से CoOOH/FeOOH के इन-सीटू गठन के माध्यम से OER में योगदान देता है, जबकि GO/f-CNT सक्रिय साइट घनत्व और इलेक्ट्रॉनिक चालकता को अधिकतम करता है। ओआरआर के लिए। कुशल O_2 -अवशोषण और तेज इलेक्ट्रॉन हस्तांतरण जिसके परिणामस्वरूप कम ओवरवोल्टेज (0.8 V) और उच्च स्थिरता के साथ उत्कृष्ट द्वि-कार्यात्मक गतिविधि होती है।

अध्याय 5 में, हम CoFe PBA में परमाणु रूप से फैले Zn^{2+} डोपेंट के माध्यम से समन्वय क्षेत्र रिक्तियों और लुईस एसिड साइटों को समवर्ती रूप से इंजीनियर करने की रणनीति प्रदर्शित करते हैं, जो PBA सतहों पर द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोकेटलिसिस को बढ़ावा देने के लिए Co^{2+} को अधिक इलेक्ट्रोपोजिटिव बनाता है। इष्टतम Zn-डोपिंग (3 मोल%) न केवल CoFe PBAs की ऑक्सीजन विकास प्रतिक्रिया गतिविधि को IrO_2 उत्प्रेरक के तुलनीय स्तर तक बढ़ाता है, बल्कि 0.84

V के कम प्रतिवर्ती ओवरवोल्टेज के साथ एक प्रभावशाली द्वि-कार्यात्मक ऑक्सीजन गतिविधि को भी दर्शाता है। इस कार्य ने यह भी प्रदर्शित किया कि ओईआर के दौरान $\text{Co}^{3+}(\text{CoOOH})$ और $\text{Fe}^{3+}(\text{FeOOH})$ का इन-सीटू गठन द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोकेटलिसिस में बढ़ी हुई गतिविधि के लिए महत्वपूर्ण भूमिका निभाता है।

अध्याय 6 में हमने बढ़ी हुई ओईआर/ओआरआर गतिविधि के लिए पीबीए आधारित उत्प्रेरक में धातु केंद्रों/डी-बैंड केंद्रों को ट्यून करने की रणनीति का उपयोग किया। डी-बैंड केंद्र का उपयोग PBA के लिए विद्युत उत्प्रेरण के रुझानों को समझने के लिए एक आशाजनक वर्णनकर्ता के रूप में किया गया है। यहाँ, हम अपने डी-बैंड केंद्र पर प्रशिया ब्लू एनालॉग (पीबीए) की द्वि-कार्यात्मक ऑक्सीजन विद्युत उत्प्रेरक गतिविधि की निर्भरता का प्रदर्शन करने वाले एक मिनी-ज्वालामुखी भूखंड को विकसित करने के उद्देश्य से अपना व्यवस्थित अध्ययन प्रस्तुत करते हैं। एक्स-सीटू कोर स्तर और वैलेंस बैंड एक्सपीएस, रमन और एफटीआईआर स्पेक्ट्रोस्कोपी के हमारे परिणाम बताते हैं कि मॉड्युलेटेड एन और सी-समन्वित धातु केंद्रों के माध्यम से डी-बैंड केंद्र की ट्यूनिंग उनकी विद्युत उत्प्रेरक ओईआर और ओआरआर गतिविधियों को निर्धारित करती है। CoCoPBA में डी-बैंड केंद्र और प्रचुर मात्रा में Co^{3+} सक्रिय स्थलों की अपनी इष्टतम स्थिति के कारण उच्चतम गतिविधि प्रदर्शित करता है। इसके अलावा, M-Co PBAs ने M-Fe PBAs की तुलना में बेहतर प्रदर्शन किया, जिसका श्रेय सतह-सक्रिय साइटों, मेटल ऑक्सी के आसान गठन को दिया जाता है।

अध्याय 7 उत्प्रेरक प्रदर्शन पर उनके प्रभाव को समझने के लिए PBAs में FeCN रिक्ति को ट्यून करने के लिए दो अलग-अलग अग्रदूत अनुपात (3:2 और 1:1) के साथ CoFe PBA को संश्लेषित करने पर केंद्रित है। संश्लेषण और एनोडिक सक्रियण अध्ययनों को शामिल करने वाली एक जांच दिलचस्प अंतर्दृष्टि का खुलासा करती है। 3:2 पूर्ववर्ती अनुपात 1:1 CoHCF की तुलना में Co^{3+} और VFeCN की उपस्थिति द्वारा सुगम गतिविधि को प्रदर्शित करता है। इसके अलावा, 3:2 भी आसान सतह पुनर्निर्माण दिखाता है जैसा कि विश्लेषण पोस्ट एनोडिक सक्रियण से स्पष्ट है। बढ़ी हुई दोष साइटें Co और Fe की समन्वय संख्या को बढ़ाती हैं, CoHCF (3:2) में सतह पुनर्निर्माण की सुविधा प्रदान करती हैं और OER और ORR की ओर उत्प्रेरक प्रदर्शन को बढ़ाती हैं, जबकि बेहतर OER गतिविधि के लिए Fe लीचिंग को भी दबाती हैं। ऑपेरांडो रमन और एक्स-सीटू एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी विश्लेषण को वैलेंस को बदलने में एनोडिक क्षमता की भूमिका का खुलासा करते हैं, जिससे ऑक्सीजन युक्त प्रजातियों के अवशोषण को मजबूत किया जाता है और गतिविधि को बढ़ाया जाता है।

अंत में **अध्याय 8** में, शोध प्रबंध कार्य को संक्षेप में प्रस्तुत किया गया है और समाप्त किया गया है। यह निष्कर्ष निकाला गया है कि काम में उपयोग की जाने वाली विभिन्न रणनीतियाँ क्षारीय माध्यम में पीबीए में सतह के पुनर्निर्माण को सीधे प्रभावित करती हैं जिससे विभिन्न गतिविधियाँ होती हैं। इसके अलावा, शोध प्रबंध के भविष्य के दायरे पर चर्चा की गई है।

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SYMBOLS AND ABBREVIATIONS

BV	Butler–Volmer
BET	Brunauer-Emmett-Teller
C _{dl}	Differential Capacitance
CE	Counter Electrode
CNTs	Carbon Nanotubes
CV	Cyclic Voltammetry
ECSA	Electrochemically Active Surface Area
EDS	Energy Dispersive Spectrometer
EIS	Electrochemical impedance spectroscopy
FESEM	Field-Emission Scanning Electron Microscopy
FTO	Fluorine-Doped Tin Oxide
FTIR	Fourier Transform Infrared
FWHM	Full width half maxima
GC	Glass Carbon
GCE	Glass Carbon Electrode
GO	Graphene Oxide
HRTEM	High Revolution Transmission Electron Microscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
K-L	Koutecky–Levich
LSV	Linear Sweep Voltammetry
FC	Fuel Cell
MOFs	Metal–Organic Frameworks
MWCNTs	multiwalled CNTs
M-Fe PBA	Metal Hexacyanoferrates
M-Co PBA	Metal Hexacyanocobaltates
NC	N-doped carbon
NF	Ni foam
OCP	Open circuit potential
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
Oh	Octahedral
PBAs	Prussian Blue Analogues
PVP	Polyvinylpyrrolidone
RDEs	Rotating Disk Electrodes
RE	Reference Electrode
RHE	Reversible Hydrogen Electrode
RRDE	Rotating Ring-Disk Electrode
rGO	Reduced Graphene Oxide
SAED	Selected Area Electron Diffraction
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SOFCs	Solid Oxide Fuel Cells
SMSI	Strong Metal Support Interactions
Td	tetrahedral

TOF	Turnover Frequency
TGA	Thermogravimetry analysis
WE	Working Electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction