

**DECIPHERING STRUCTURE-ACTIVITY
CORRELATION IN BIMETALLIC METAL
OXIDE CATALYSTS DURING
ELECTROCHEMICAL WATER SPLITTING**

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Deciphering Structure-Activity Correlation in Bimetallic Metal Oxide Catalysts During Electrochemical Water Splitting

by

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*Dedicated to my Grandfather and
(Late) Grandmother*

Certificate

This is to certify that the thesis entitled **“Deciphering Structure-Activity Correlation in Bimetallic Metal Oxide Catalysts During Electrochemical Water Splitting”**, submitted by **Ms Anubha Rajput** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of the original, bonafide research work carried out by her under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results of this thesis have not been submitted in part or in whole to any other university or institute for awarding any degree or diploma to the best of our knowledge.

Date:

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Abstract

Owing to the ever-increasing global energy demand, the utilization of non-renewable and non-sustainable fossil fuels has increased manifold. The combustion of fossil fuels has a severe negative environmental impact. According to the sixth assessment report by IPCC (Intergovernmental Panel on Climate Change), published in 2021, the global temperature has increased by nearly 1.1°C since 1850-1900 due to the release of heat-trapping gases into the atmosphere, which is anticipated to grow further in a few years. Hydrogen gas is a sustainable, energy-dense, and carbon-neutral energy carrier, which is the most suitable alternative to fossil fuels to realize global energy demands. Solar energy is one of the most abundant natural resources, and it can be converted into electricity energy and used further for hydrogen production. However, regional or seasonal factors make solar energy sources generally discontinuous and variable. Electrochemical water splitting to produce hydrogen and oxygen is one of the most sustainable and non-carbonaceous strategies for converting electrical energy to chemical energy, thus overcoming the intermittent nature of solar energy. Out of the two composite reactions of overall water-splitting (OWS), i.e. oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the OER is inherently sluggish owing to the involvement of four proton-coupled-electron-transfer (PCET) steps.

To increase the efficiency of the OWS process, the transition metal-based oxides have emerged to be effective in facilitating the water-splitting reaction and speeding up the kinetics. The incorporation of high-valent 4d or 5d metals like W or Mo into metal oxides leads to the formation of stable oxides (ABO_4) where W and Mo are present as an oxy anion, $[\text{BO}_4]^{-2}$ ($\text{B} = \text{Mo/W}$) and A represent the transition metal. These bimetallic oxides possess such an electronic structure that the surface adsorption-desorption kinetics of the reaction intermediate for these ternary oxides would be optimum. However, bimetallic oxides (BMOs) like transition metal molybdates (TMMs) and transition metal tungstates (TMTs) are found to undergo structural transformation to metal oxides, hydroxides, or

oxyhydroxides under alkaline conditions. The unique electronic properties of the BMOs can directly affect their electrochemical stability. However, the BMOs lack bifunctionality and stability. In this regard, the spinel ferrite materials have been found to exhibit bifunctionality towards water splitting as well as structural robustness during the alkaline electrolysis. In this thesis entitled **“Deciphering Structure-Activity Correlation in Bimetallic Metal Oxide Catalysts During Electrochemical Water Splitting”**, the electrocatalytic transformation of wolframite-like TMMs/TMTs and spinel ferrites towards in-situ evolved electroactive species has been studied, and the structure-activity has been established to decipher the water splitting mechanism, coupled with the DFT study. The experimental electrokinetic study of the activation energy, rate-limiting step, reaction order, charge transfer coefficient, etc., is also essential to study the comprehensive water splitting mechanism.

Therefore, in the first work chapter, the study on the hydrothermally synthesized Fe-based TMM/TMT, i.e., FeMoO_4 and FeWO_4 , has been carried out experimentally and theoretically to study the influence of Fe on the electronic structure and the energetics of the electroactive species formation. The greater activity of the molybdate analogue was evident from the low overpotential of 244 (± 5) mV compared to 282 (± 3) mV for FeWO_4 at 10 mA cm^{-2} . FeMoO_4 also showed a higher TOF of $2.7 \times 10^{-3} \text{ s}^{-1}$. The time-dependent quasi-in situ Raman analyses (Raman analyses performed immediately after the electroanalysis) reveal a potential-driven hydrolytic dissolution of $[\text{MoO}_4]^{-2}$ from FeMoO_4 to form $\alpha\text{-FeO(OH)}$ as the electroactive species, while FeWO_4 remains relatively stable. The higher ionic character of the Fe-O-Mo bond and low decomposition enthalpy (ΔH_D) of FeMoO_4 favour the electrocatalytic decomposition of FeMoO_4 . The peroxo (O-O) bond formation is found to be rate-limiting with a minimum potential barrier of 38 kJ mol^{-1} in the case of FeMoO_4 . This chapter combines the experimental and theoretical study of the effect of electronic structure and bonding in the catalyst on its in-situ transformation during electrocatalytic OER.

In the following work chapter, NiMoO₄ and NiWO₄ have been studied as bimetallic metal oxide catalysts as the OER electrocatalysts, and their in-situ structural transformation during alkaline electrolysis has been studied. Through the quasi-in-situ Raman examination of the electrodes, it is found that after a few CV cycles, the NiMoO₄ transformed to NiO(OH)_{ED} (ED: electrochemically derived), while NiWO₄ stays stable. NiMoO₄ first transforms to the isolable NiO phase in the absence of potential, which then transforms into NiO(OH)_{ED} when subjected to a potential bias. At the same time, such transformation is absent in NiWO₄. The conversion of NiMoO₄ into NiO(OH)_{ED} is due to the more ionic nature of the Ni-O-Mo bond, contrary to the Ni-O-W bond, which has more covalent characters. The in-situ evolved NiO(OH)_{ED} showed a lower overpotential and lower Tafel slope of 238 (±6) mV and 26 mV dec⁻¹, respectively. This study explains that monoclinic NiMoO₄ is an inherently unstable electro(pre)catalyst that undergoes structural transformation to NiO(OH)_{ED} as the real catalytic phase.

The following work chapter investigates the in-situ transformation of MnMoO₄ to the final active phase during OER in alkaline pH. It was observed that MnMoO₄ undergoes alkaline dissolution to form α-MnO₂, which further transforms to δ-MnO₂ as the final active phase under potential bias. While transforming from α-MnO₂ to δ-MnO₂ phase, an intermediate thermally stable mixed-phase α/δ-MnO₂ is formed after 10 CV cycles. This mixed phase has the overpotential of 239 mV at 333 K. Anodic transfer coefficient (α_a) of 0.7 and unimolecular reaction order for [OH]⁻ are obtained from temperature-dependent OER investigation. The enhanced OER activity on α/δ-MnO₂ is due to the rapid electrokinetics owing to a low activation barrier of 9.77 k J mol⁻¹ and a high exchange current density (j_0) of 0.095 mA cm⁻². The DFT study on δ-MnO₂ shows that the cleavage of the OH_{ad} (ad = adsorbed) bond to generate the O_{ad} is the rate-limiting step for OER. Here, the OER process is elucidated by tracking the reactive phases produced by the MnMoO₄ pre-catalyst, comprehensive electrokinetics, and theoretical analysis.

The subsequent chapter deals with a comparative OER study of a series of 3d TMTs, $A^{II}W^{VI}O_4$ ($M = Mn/Fe/Co/Ni$), correlating their electronic structure with their electrochemical stability by experimental and theoretical studies. The variation of 3d metal atoms in $[AO_6]_{Oh}$ helps to understand the role of 3d metals in controlling the electronic structure and stability of the tungstate lattices under anodic potential. Among all the examined TMTs, $MnWO_4$ shows the most labile structure, whereas $NiWO_4$ is stable up to a high anodic potential of ~ 1.68 V (vs RHE). Potential-dependent hydrolytic $[WO_4]^{-2}$ dissolution to form AO_x active species depends on the electronic properties of the lattice-like crystal field splitting energy (CFSE), formation enthalpy (ΔH_f), decomposition enthalpy (ΔH_d), and Madelung energy. The analysis of the magnitude of the Löwdin and Bader charges on A of the A- μ_2 -O-W bond confirmed the highest degree of ionic characters in the Mn-O-W bond, which gradually decreased on moving from Mn to Ni in the 3d series. The degree of ionicity or covalency in the MWO_4 lattice directly influences the catalysts' electronic structure, stability, and activity.

The last work chapter studies the electrocatalytic bifunctional performance of structurally stable bimetallic spinel oxide. The ca. 5 nm $SnFe_2O_4$ nanoparticles have been prepared, and their electrocatalytic activity is compared with that of the parent ferrite, Fe_3O_4 . $SnFe_2O_4$ nanoparticles behaved as a bi-functional electrocatalyst under alkaline conditions, with a fair OER and HER activity and appreciable long-term stability at lower cathodic/anodic potentials. After a 12 h OER-CA at a high potential of 1.64 V (vs. RHE), $SnFe_2O_4$ transformed to a mixed phase of $Fe(O)OH$, indicating the participation of Fe in the OER process. The higher activity was evident from a low activation energy of $28.71 \text{ kJ mol}^{-1}$ for OER performed by $SnFe_2O_4$, which is threefold less than Fe_3O_4 . However, understanding the reaction mechanism on an atomic scale is crucial to studying the role of heteroatom (here, p-block Sn) doping in improving catalyst activity. The density functional theory (DFT) study of the OER mechanism on the (001) plane of the inverse spinel $SnFe_2O_4$ and Fe_3O_4 shows the formation of OOH_{ad} is the RDS for $SnFe_2O_4$, while O_{ad} formation is found to be the RDS for Fe_3O_4 . It is discovered that a synergy between Fe^{III}_{Oh} and the nearby Sn^{II}_{Oh} atoms is

responsible for stabilizing the OER intermediates, thereby enhancing the catalytic OER activity of SnFe_2O_4 as compared to the parent Fe_3O_4 catalyst.

सारांश

लगातार बढ़ती वैश्विक ऊर्जा मांग के कारण, गैर-नवीकरणीय और गैर-टिकाऊ जीवाश्म ईंधन का उपयोग कई गुना बढ़ गया है। जीवाश्म ईंधन के दहन से पर्यावरण पर गंभीर नकारात्मक प्रभाव पड़ता है। 2021 में प्रकाशित IPCC (जलवायु परिवर्तन पर अंतर-सरकारी पैनल) की छठी मूल्यांकन रिपोर्ट के अनुसार, वायुमंडल में ऊष्मा-फँसाने वाली गैसों के निकलने के कारण 1850-1900 से वैश्विक तापमान में लगभग 1.1°C की वृद्धि हुई है, जिसके कुछ वर्षों में और बढ़ने का अनुमान है। हाइड्रोजन गैस एक टिकाऊ, ऊर्जा-घनी और कार्बन-तटस्थ ऊर्जा वाहक है, जो वैश्विक ऊर्जा मांगों को पूरा करने के लिए जीवाश्म ईंधन का सबसे उपयुक्त विकल्प है। सौर ऊर्जा सबसे प्रचुर प्राकृतिक संसाधनों में से एक है जिसे बिजली ऊर्जा में परिवर्तित किया जा सकता है, जिसका उपयोग हाइड्रोजन उत्पादन के लिए किया जा सकता है। हालाँकि, क्षेत्रीय या मौसमी कारकों के कारण सौर ऊर्जा स्रोत आम तौर पर असंतत और परिवर्तनशील होता है। हाइड्रोजन और ऑक्सीजन का उत्पादन करने के लिए विद्युत रासायनिक जल विभाजन विद्युत ऊर्जा को रासायनिक ऊर्जा में परिवर्तित करने के लिए सबसे टिकाऊ और गैर-कार्बोनेसियस रणनीतियों में से एक है, इस प्रकार सौर ऊर्जा की आंतरायिक प्रकृति पर काबू पाया जा सकता है। समग्र जल-विभाजन (OWS) की दो मिश्रित प्रतिक्रियाओं में से, यानी ऑक्सीजन विकास प्रतिक्रिया (OER) और हाइड्रोजन विकास प्रतिक्रिया (HER), OER चार प्रोटॉन-युग्मित-इलेक्ट्रॉन-स्थानांतरण (PCET) चरणों की भागीदारी के कारण स्वाभाविक रूप से सुस्त है।

OWS प्रक्रिया की दक्षता बढ़ाने के लिए, संक्रमण धातु-आधारित ऑक्साइड जल-विभाजन प्रतिक्रिया को सुविधाजनक बनाने और गतिज को गति देने में प्रभावी साबित हुए हैं। उच्च-संयोजक 4d या 5d धातुओं जैसे W या Mo को धातु ऑक्साइड में शामिल करने से स्थिर ऑक्साइड (ABO_4) का निर्माण होता है इन द्विधात्विक ऑक्साइड में ऐसी इलेक्ट्रॉनिक संरचना होती है कि इन त्रिधात्विक ऑक्साइड के लिए प्रतिक्रिया मध्यवर्ती की सतह अधिशोषण-विशोषण गतिकी इष्टतम होगी। हालाँकि, संक्रमण धातु मोलिब्डेट

(TMM) और संक्रमण धातु टंगस्टेट (TMT) जैसे द्विधात्विक ऑक्साइड (BMO) क्षारीय परिस्थितियों में धातु ऑक्साइड, हाइड्रॉक्साइड या ऑक्सीहाइड्रॉक्साइड में संरचनात्मक परिवर्तन से गुजरते पाए जाते हैं। BMO के अद्वितीय इलेक्ट्रॉनिक गुण सीधे उनकी विद्युत रासायनिक स्थिरता को प्रभावित कर सकते हैं। हालाँकि, BMO में द्विक्रियाशीलता और स्थिरता का अभाव है। इस संबंध में, स्पिनल फेराइट सामग्री क्षारीय इलेक्ट्रोलिसिस के दौरान जल विभाजन के साथ-साथ संरचनात्मक मजबूती के प्रति द्विक्रियाशीलता प्रदर्शित करती पाई गई है। **"इलेक्ट्रोकेमिकल वॉटर स्प्लिटिंग के दौरान बाईमेटेलिक मेटल ऑक्साइड उत्प्रेरकों में संरचना-गतिविधि सहसंबंध को समझना"** शीर्षक वाली इस थीसिस में, वोल्फ्रामाइट जैसे टीएमएम/टीएमटी और स्पिनल फेराइट्स के इन-सीटू विकसित इलेक्ट्रोएक्टिव प्रजातियों के प्रति इलेक्ट्रोकेटेलिटिक परिवर्तन का अध्ययन किया गया है, और डीएफटी अध्ययन के साथ मिलकर जल विभाजन तंत्र को समझने के लिए संरचना-गतिविधि स्थापित की गई है। व्यापक जल विभाजन तंत्र का अध्ययन करने के लिए सक्रियण ऊर्जा, दर-सीमित चरण, प्रतिक्रिया क्रम, चार्ज ट्रांसफर गुणांक आदि का प्रयोगात्मक इलेक्ट्रोकाइनेटिक अध्ययन भी महत्वपूर्ण है।

इसलिए, पहले कार्य अध्याय में, इलेक्ट्रॉनिक संरचना और इलेक्ट्रोएक्टिव प्रजातियों के गठन की ऊर्जा पर Fe के प्रभाव का अध्ययन करने के लिए हाइड्रोथर्मल रूप से संश्लेषित Fe-आधारित TMM/TMT, यानी FeMoO_4 और FeWO_4 पर अध्ययन प्रयोगात्मक और सैद्धांतिक रूप से किया गया है मोलिब्डेट एनालॉग की अधिक सक्रियता 10 mA cm^{-2} पर FeWO_4 के लिए $282 (\pm 3) \text{ mV}$ की तुलना में $244 (\pm 5) \text{ mV}$ के कम ओवरपोटेंशियल से स्पष्ट थी। FeMoO_4 ने $2.7 \times 10^{-3} \text{ s}^{-1}$ की उच्च टर्नओवर आवृत्ति भी दिखाई। समय-निर्भर अर्ध-इन-सीटू रमन विश्लेषण से पता चलता है कि FeMoO_4 से $[\text{MoO}_4]^{-2}$ का संभावित-संचालित हाइड्रोलिटिक विघटन इलेक्ट्रोएक्टिव प्रजाति के रूप में $\alpha\text{-FeO(OH)}$ बनाता है जबकि FeWO_4 अपेक्षाकृत स्थिर रहता है। Fe-O-Mo बॉन्ड का उच्च आयनिक चरित्र और FeMoO_4 का कम अपघटन एन्थैल्पी (ΔH_D) FeMoO_4 के इलेक्ट्रोकेटेलिटिक अपघटन का पक्षधर है। FeMoO_4 के मामले में पेरोक्सो (O-O) बॉन्ड गठन 38 kJ mol^{-1} के न्यूनतम संभावित अवरोध के साथ दर-सीमित पाया गया है। यह

अध्याय इलेक्ट्रोकेटेलिटिक ओईआर के दौरान उत्प्रेरक में इलेक्ट्रॉनिक संरचना और बंधन के प्रभाव के प्रयोगात्मक और सैद्धांतिक अध्ययन को जोड़ता है।

अगले कार्य अध्याय में, NiMoO_4 और NiWO_4 का OER इलेक्ट्रोकेटेलिस्ट के रूप में द्विधात्विक धातु ऑक्साइड उत्प्रेरक के रूप में अध्ययन किया गया है, और क्षारीय इलेक्ट्रोलिसिस के दौरान उनके इन-सीटू संरचनात्मक परिवर्तन का अध्ययन किया गया है। इलेक्ट्रोड की अर्ध-इन-सीटू रमन परीक्षा के माध्यम से, यह पाया गया है कि कुछ चक्रीय वोल्टामेट्री (CV) चक्रों के बाद, NiMoO_4 $\text{NiO(OH)}_{\text{ED}}$ (ED: इलेक्ट्रोकेमिकली व्युत्पन्न) में परिवर्तित हो गया, जबकि NiWO_4 स्थिर रहता है। NiMoO_4 पहले विभव की अनुपस्थिति में पृथक NiO चरण में परिवर्तित होता है, जो फिर विभव पूर्वाग्रह के अधीन होने पर $\text{NiO(OH)}_{\text{ED}}$ में परिवर्तित हो जाता है, जबकि NiWO_4 में ऐसा परिवर्तन अनुपस्थित है। NiMoO_4 का $\text{NiO(OH)}_{\text{ED}}$ में रूपांतरण Ni-O-Mo बंध की अधिक आयनिक प्रकृति के कारण होता है इन-सीटू विकसित $\text{NiO(OH)}_{\text{ED}}$ ने क्रमशः 238 (± 6) mV और 26 mV dec⁻¹ का निचला ओवरपोटेंशियल और निचला टैफल ढलान दिखाया। यह अध्ययन बताता है कि मोनोक्लिनिक NiMoO_4 एक स्वाभाविक रूप से अस्थिर इलेक्ट्रो(प्री) उत्प्रेरक है जो वास्तविक उत्प्रेरक चरण के रूप में $\text{NiO(OH)}_{\text{ED}}$ में संरचनात्मक परिवर्तन से गुजरता है।

अगले कार्य अध्याय में, क्षारीय pH में OER के दौरान MnMoO_4 के अंतिम सक्रिय चरण में इन-सीटू परिवर्तन की जांच की गई है। यह देखा गया कि MnMoO_4 क्षारीय विघटन से गुजरता है जिससे $\alpha\text{-MnO}_2$ बनता है, जो आगे संभावित पूर्वाग्रह के तहत अंतिम सक्रिय चरण के रूप में $\delta\text{-MnO}_2$ में बदल जाता है। इस मिश्रित चरण में 333 K पर 239 mV की ओवरपोटेंशियल है। तापमान पर निर्भर OER जांच से $[\text{OH}^-]$ के लिए एनोडिक ट्रांसफर गुणांक (α_a) 0.7 और यूनिमॉलिक्युलर प्रतिक्रिया क्रम प्राप्त किया जाता है। $\alpha/\delta\text{-MnO}_2$ पर बढ़ी हुई OER गतिविधि 9.77 k J mol⁻¹ के कम सक्रियण अवरोध और 0.095 mA cm⁻² के उच्च विनिमय धारा घनत्व (j_0) के कारण तेज़ इलेक्ट्रोकाइनेटिक्स के कारण है। $\delta\text{-MnO}_2$ पर DFT अध्ययन से पता चलता है कि O_{ad} उत्पन्न करने के लिए OH_{ad} बॉन्ड का विभाजन OER के लिए दर-सीमित चरण है। यहाँ, MnMoO_4 प्री-कैटेलिस्ट, व्यापक

इलेक्ट्रो-काइनेटिक्स और सैद्धांतिक विश्लेषण द्वारा उत्पादित प्रतिक्रियाशील चरणों की इन-सीटू टैकिंग का उपयोग करके OER प्रक्रिया को स्पष्ट किया गया है।

अगला अध्याय 3d TMTs, $A^{II}W^{VI}O_4$ ($M = Mn/Fe/Co/Ni$) की एक श्रृंखला के तुलनात्मक OER अध्ययन और प्रयोगात्मक और सैद्धांतिक अध्ययनों के माध्यम से उनके इलेक्ट्रॉनिक संरचना को उनके विद्युत रासायनिक स्थायित्व के साथ सहसंबंधित करने से संबंधित है। 3d धातु परमाणु $[AO_6]_{Oh}$ का परिवर्तन, एनोडिक विभव के तहत टंगस्टेट जालकों की इलेक्ट्रॉनिक संरचना और स्थिरता को नियंत्रित करने में 3d धातुओं की भूमिका को समझने में मदद करता है। सभी जांचे गए TMTs में, $MnWO_4$ सबसे अधिक अस्थिर संरचना दिखाता है, जबकि $NiWO_4 \sim 1.68$ V (बनाम RHE) के उच्च एनोडिक विभव तक स्थिर रहता है। AO_x सक्रिय स्पीशीज बनाने के लिए विभव-निर्भर हाइड्रोलाइटिक $[WO_4]^{2-}$ विघटन, जाली-सदृश क्रिस्टल क्षेत्र विभाजन ऊर्जा (CFSE), निर्माण एन्थैल्पी (ΔH_f), अपघटन एन्थैल्पी (ΔH_d), और मैडेलुंग ऊर्जा के इलेक्ट्रॉनिक गुणों पर निर्भर करता है। $A-\mu_2-O-W$ बॉन्ड के A पर लोवडिन और बेडर चार्ज के परिमाण के विश्लेषण ने $Mn-O-W$ बॉन्ड में आयनिक लक्षणों की उच्चतम डिग्री की पुष्टि की, जो 3d श्रृंखला में Mn से Ni की ओर बढ़ने पर धीरे-धीरे कम हो गई। MWO_4 जाली में आयनिकता या सहसंयोजकता की डिग्री सीधे उत्प्रेरक की इलेक्ट्रॉनिक संरचना, स्थिरता और गतिविधि को प्रभावित करती है।

अंतिम कार्य अध्याय अपेक्षाकृत स्थिर द्विधात्विक स्पिनल ऑक्साइड के इलेक्ट्रोकेटेलिटिक द्विकार्यात्मक प्रदर्शन का अध्ययन करता है। 5 nm. $SnFe_2O_4$ नैनोकणों को तैयार किया गया है और उनकी इलेक्ट्रोकेटेलिटिक गतिविधि की तुलना मूल फेराइट, Fe_3O_4 के साथ की गई है। $SnFe_2O_4$ नैनोकणों ने क्षारीय परिस्थितियों में एक द्विकार्यात्मक इलेक्ट्रोकेटेलिस्ट के रूप में व्यवहार किया 1.64 V (बनाम RHE) के उच्च क्षमता पर 12 घंटे के OER-CA के बाद, $SnFe_2O_4$ $Fe(O)OH$ के मिश्रित चरण में बदल गया, जो OER प्रक्रिया में Fe की भागीदारी को दर्शाता है। उच्च गतिविधि $SnFe_2O_4$ द्वारा किए गए OER के लिए $28.71 \text{ kJ mol}^{-1}$ के कम सक्रियण से स्पष्ट थी, जो Fe_3O_4 से तीन गुना कम है। हालांकि, उत्प्रेरक गतिविधि को बेहतर बनाने में हेटेरोएटम (यहां p-ब्लॉक

Sn) डोपिंग की भूमिका का अध्ययन करने के लिए प्रतिक्रिया तंत्र की परमाणु पैमाने की समझ महत्वपूर्ण है। व्युत्क्रम स्पिनल SnFe_2O_4 और Fe_3O_4 के (001) तल पर OER तंत्र के घनत्व कार्यात्मक सिद्धांत (DFT) अध्ययन से पता चलता है कि OOH_{ad} का गठन SnFe_2O_4 के लिए RDS है यह पता चला है कि $\text{Fe}^{\text{III}}_{\text{Oh}}$ और निकटवर्ती $\text{Sn}^{\text{II}}_{\text{Oh}}$ परमाणुओं के बीच सहक्रिया OER मध्यवर्ती को स्थिर करने के लिए जिम्मेदार है, जिससे मूल Fe_3O_4 उत्प्रेरक की तुलना में SnFe_2O_4 की उत्प्रेरक OER गतिविधि में वृद्धि होती है।

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= 0 V (black line), 1.23 V (red line), and 1.62 V (green line) (vs RHE). Shown below are the optimized OER intermediates on the Fe_3O_4 (001) surface.228

Abbreviations

AEM	A dsorbate E volution M echanism
BET	B runauer– E mmett– T eller
CA	C hrono a mp e rometry
CBC	C onduction B and
CC	C arbon C loth
CBM	C onduction B and M inima
CE	C ounter E lectrode
CFSE	C rystal F ield S tabilization E nergy
CV	C yclic V oltammetry
DFT	D ensity F unctional T heory
DOS	D ensity of S tates
EDX	E nergy D ispersive X -ray
EIS	E lectrochemical I mpedance S pectroscopy
ECSA	E lectrochemical S urface A rea
EPR	E lectron P aramagnetic R esonance
FE	F aradaic E fficiency
F_E	F ermi E nergy
FESEM	F ield E mission S canning E lectron M icroscopy
FTIR	F ourier T ransform I nfrared
GC	G lassy C arbon
HER	H ydrogen E volution R eaction
HRTEM	H igh R esolution T ransmission E lectron M icroscopy
ICDD	I nternational C entre for D iffraction D ata
ICPMS	I nductively C oupled P lasma M ass S pectrometry
JCPDS	J oint C ommittee on P owder D iffraction S tandards
KIE	K inetic I sotope E ffect
LSV	L inear S weep V oltammetry
LOM	L attice O xidation M echanism
NF	N ickel F oam
OER	O xygen E volution R eaction
ORR	O xygen R eduction R eaction
OWS	O verall W ater S plitting

Abbreviations

PCET	Proton Coupled Electron Transfer
PXRD	Powder X-ray Diffraction
RDS	Rate Determining Step
RE	Reference Electrode
RHE	Reversible Hydrogen Electrode
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TMM	Transition Metal Molybdates
TMT	Transition Metal Tungstates
TOF	Turnover Frequency
UV	Ultraviolet
VBM	Valence Band Maxima
VB	Valence Band

Symbols

E_a	activation energy
$^{\circ}\text{C}$	Celcius
cm	centimetre
α	charge transfer coefficient
R_{ct}	charge transfer resistance
j	current density
ΔH_d	decomposition enthalpy
C_{dl}	double-layer capacitance
eV	electron volt
j°	exchange current density
F	Faraday constant
ΔH_f	formation enthalpy
h	hour
K	Kelvin
keV	kilo electron volt
kV	kilo volt
μm	micrometre
mA	milli-Ampere
mL	milliliter
mol	mole
min	minute
nm	nanometre
η	overpotential
m	reaction order
R_s	solution resistance
C_s	specific capacitance
β	symmetry factor
b	Tafel slope
T	temperature