Synergistic and compositional modulation of advanced transition metal oxide based electrocatalysts for alkaline water oxidation

Examiner Comments

Examiner 1

General Comments

The overall objective of the thesis was to investigate the Oxygen Evolution Reaction (OER) and its role in the electro-catalysts. However, the author has investigated efficient catalyst materials and composite materials to enhance the process of oxygen evolution reaction.

I suggest the author to make following corrections:

1. He should change the sentence "This thesis seeks to deepen our understanding....." Instead, he has investigated the.....

   Response: We appreciate the examiner's observation. The sentence has been revised accordingly to reflect the actual scope of the work. Instead of "This thesis seeks to deepen our understanding …", it now reads as "The thesis presented the understanding of the OER mechanism…." to provide a more precise description of the study. Changes are made in preface (page no. xxiii).
2. Again, sentences like "This thesis is an attempt to contribute meaningfully" should be written as "The objective (or overall goal) of the thesis is....." It makes clear his goals and achievements.

   Response: We thank the examiner for this valuable suggestion. The sentence "This thesis is an attempt to contribute meaningfully …" has been revised to "The overall objective of the thesis is …" to clearly state the goals and achievements of the work in a more precise and formal manner. Changes are made in preface (page no. xxv).

The thesis is divided into six chapters describing (1) literatures, (2) Background of experimental work, (3) experimental methods, (4) explores the electrocatalytic performance of cobalt tungstate nanoparticles, (5) electro-catalyst materials, metal oxides and their composites, and (6) summary of key results of the thesis.

Specific Comments:

The specific comments are summarized in following sections:

3. In my opinion the headings of the chapters do not do justice with the materials described in the chapters. Especially words like "understanding" "Investigating", and "Synergistic" causes some uncertainties. For example, chapter describes electro-catalytic role of magnesium doped bismuth copper titanate in OER. The author had synthesized, characterized and demonstrated the parameters relevant to OER. So, in my opinion, a better title may be something like" Development of electro-catalytic role of magnesium doped bismuth copper titanate in OER or Synthesis, characterization and performance of magnesium doped bismuth copper titanate for electro-catalytic role for OER" Similarly, author may think about chapter 4 and 5 also.

   Response: We sincerely thank the examiner for this insightful suggestion regarding the chapter headings. We agree that certain words, such as “understanding,” “investigating,” and “synergistic” may cause ambiguity. Accordingly, the chapter titles have been revised to better align with the content. For example, the title of the chapter 3 has been modified to “Synthesis, characterization, and electro-catalytic performance of magnesium-doped bismuth copper titanate (BCTO) for oxygen evolution reaction.” Similar revisions have been made for chapters 4 and 5 to ensure that the headings more accurately reflect the synthesis, characterization, and electrochemical performance presented in each case. Changes have been made in the separator of the chapters and contents section.

Chapter 1: General Introduction and Literature Survey (pages 1-42)

Chapter 1 summarizes the introduction to the literature describing the previous investigation reported on page 34. materials will be this field. The author has given relevant reasons and some literature to justify the project.

4. On page 34 author wrote "The objective is to develop a non-precious, durable, and efficient material suitable.... " It may be changed to “low-cost durable.....” After successful demonstration the process or materials will be precious.

   Response: We thank the examiner for this suggestion. The sentence has been revised from “non-precious, durable, and efficient material …” to “low-cost, durable, and efficient material …” as recommended. Changes have been made on page 34.

Chapter 2: Characterization Techniques (pages 43-73)

Chapter 2 described the general experimental procedure used for the preparation and characterization of doped $Bi_{2/3}Cu_3Ti_4O_{12}$ systems. He indicated that the semi-wet route was used for the preparation of materials and used XRD for size determination. He used typical characterization methods including Transmission electron microscope (TEM), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) etc. X-ray photoemission spectroscopy (XPS) used to characterize materials have been described in detail. He used a high-performance frequency LCR meter (E4980A/AL, for the dielectric and conductivity measurements for temperatures range of 303 K-503K.)

If there is any new process/novelty in his procedure, he should clearly mention in the text. Also, few lines on the mechanism of changes on dielectric constant as function of frequency may be added in this section.

Since all characterization XRD, SEM, EDS etc are shown to confirm the materials, these satisfactory explain the compounds and needs no comments on these observations in all chapters.

Chapter 3: Understanding the electrocatalytic role of magnesium doped bismuth copper titanate (BCTO) in oxygen evolution reaction (pages 73-115)

5. On page 117, it is mentioned, it is essential to alter the electronic structure of transition metal oxides and enhance their electrical conductivity as mentioned in reference 20 and 21. They explained based on Te doped materials. There is no mention of Fe, Cr. Mn ions by them. So, this statement may not be 100 % true for their dopants.

   Response: We thank the reviewer for this insightful comment. The statement has been revised to clarify that references 20 and 21 specifically discuss Te-doped systems. We have further highlighted that our work adopts a similar strategy and is employed to tune the electronic structure and improve conductivity, thereby enhancing catalytic activity. Changes have been made in page no. 117.

WO_3 exhibits a reversible surface oxygen ion exchange aptitude and an exception ($Bi_{(2/3)-x}Nd_xCu_3Ti_4O_{12}$ (BNCTO, x = 0.05, 0.10, 0.20) (Pages 78-106) (Please see the general comment for the heading).

6. Chapter III describes the synthesis, characterization, and Mg-BCTO ceramic with composition (x = 0.05, 0.1, and 0.2) prepared by semi wet route and sintered at 1173 K. for 8 h. It is very good that author used as sullied materials as listed "Copper acetate $Cu(CH_3COO)_2.H_2O$ (99 % Merck, India), bismuth nitrate $Bi(NO_3)_3.5H_2O$ (purity around 98 % Marek, India), titanium oxide TiO_2 (purity around 98.5 % Merck, India), citric acid (99.5 % Merck, India), magnesium acetate $Mg(CH_3COO)_2.H_2O$ (purity around 98.5 % Merck, India)". No need to write analytical grades since sometimes analytical grades can be 99.99999% pure.

   Response: We thank the reviewer for this observation. The mention of "analytical grade" has been removed, and only the purity percentages and suppliers of the chemicals have been provided, as suggested. Changes have been made on page no. 77.

7. In the Raman spectra shown in Fig. 3.3 author wrote that presence of the modes at 432, and 511 cm^{-1} confirms the phase of bismuth titanate in the synthesized catalysts using reference [27]. There is a low order peak at 263 cm^{-1} wavenumbers. It is important, reference 27 does not explain clearly. If you think as LO and TO modes, it will enhance the quality of your discussion.

   Response: We thank the examiner for this valuable comment. In the revised discussion of Fig. 3.3, we have clarified that the Raman modes at 432 and 511 cm^{-1} confirm the presence of the bismuth titanate phase, consistent with reference [27]. Additionally, the low-order peak observed at 263 cm^{-1}, though not explicitly explained in reference [27], has now been discussed in terms of possible longitudinal optical (LO) and transverse optical (TO) phonon mode contributions. This interpretation provides a more complete explanation of the vibrational features and enhances the quality of the Raman analysis. The revised discussion is added on page no. 83 and 84.

8. SEM morphologies in Fig. 3.8. are extremely important. As one can see, 3.8(a) is almost unfaceted and Mg-doped showed faceted microstructures. In spite of low temperature processing, even in undoped materials faceted structures were observed. However, Mg doped showed even more faceting indicating that grains containing Mg have higher anisotropy. The average grain size is found to be 0.83 µm, 0.65 µm, and 0.641 µm, respectively Author may want to write a sentence because sizes differ.

   Response: We thank the examiner for highlighting the importance of SEM analysis. In the revised thesis, we have expanded the discussion of Fig. 3.8 to emphasize the role of Mg doping in enhancing grain faceting and anisotropy. We have also included a

sentence discussing the variation in average grain size, which provides additional insight into the microstructural evolution. The changes are made on page no. 86.

The stoichiometry, purity, and the presence of elements (Bi, Cu, Nd. Ti, and O) of synthesized samples were confirmed by EDX studies. They claim that the FM analysis shows a reduction in surface root mean square roughness as the proportion of Nd ions increases, with corresponding values of 255 nm, 158 nm, and 125 nm, respectively, and average grain size also decreases which validates the SEM result. He may want to add his opinion why ion changed the size. Nd doping can result in an exceptionally low dielectric loss (tan δ), with a minimum value of 0.05 at 1 kHz and 303 K. for BNCTO-0.2. These findings show that Nd doping is more favourable to dielectric characteristics, introducing increased grain boundary resistance, activation energy, and lower conductivity. I assume that overall resistivity decreased since conductivity of grains may have increased.

9. Author mentions that literature shows an increase in oxygen vacancies correlates with enhanced OER performance and oxygen vacancies provide an abundance of electrons, which enhance the attachment of adsorbates to the catalyst surface via interactions between the surface and the adsorbate. He may want to mention one sentence that Mg doping then increases vacancies in the end of that discussion.

Response: We thank the examiner for this valuable insight. The discussion has been updated by adding a clarifying statement that highlights Mg doping contributes to the generation of oxygen vacancies, thereby reinforcing the link between material modification and enhanced OER activity. The changes are made on page no. 92.

Chapter 4: Investigating the electrochemical performance of cobalt tungstate $Co_xW_{2-x}O_4$; x = 0.5, 1.0, 1.5 catalysts for alkaline water oxidation: Tailoring (page 116-154).

10. Author may want to change the heading.

Response: As per the suggestion, the chapter heading has been revised to: "Development and evaluation of electrochemical Performance of cobalt tungstate ($Co_xW_{2-x}O_4$; x = 0.5, 1.0, 1.5) catalysts for alkaline water oxidation: Tailoring composition for optimal activity." Corresponding changes have also been incorporated in the chapter separator and table of contents.

11. Cobalt tungstate is a good material system. The topics such as 4.3.3 Working electrode fabrication does not look good. Just "Electrode Fabrication" may be better.

Response: Thank you for the suggestion. The subsection title “Working electrode fabrication” has been revised to “Electrode Fabrication” for improved clarity. The changes are made on page no. 120.

Characterization results show the intended synthesis and are good enough. The thermodynamic explanation for FTO/ $CoWO_4$ justify (parameters of Table 4.3) that the initiation of adsorption during the electrochemical oxygen evolution process is most pronounced for the FTO/$CoWO_4$ electrode, suggesting a higher density of active sites accessible for the adsorption of reactive intermediate species. This observation aligns well with the significantly negative value of ASO, which indicates a more ordered transition state and a strong interaction between the electrode surface and the reacting species. The thermodynamic parameters associated with this process are comprehensively presented in Table 4.3 to explain thermodynamic predictions.

Chapter 5: Synergistic electrocatalysis for oxygen evolution reaction using novel polypyrrole integrated $CoWO_4$ in alkaline solution (page 154-196).

12. I can see the use of the topic as we know that synergistic means relating to the interaction or cooperation of two or more substances, or other agents to produce a combined effect greater than the sum of their separate effects, but he has investigated this effect. So, he may want to write "Investigation of...

Response: We appreciate the observation. The term “Synergistic” in the title may create ambiguity. Since the chapter primarily involves examining this effect rather than presuming it, the heading has been revised to “Synthesis, characterization, and OER activity of polypyrrole integrated $CoWO_4$ nanoparticles in alkaline solution” to more accurately reflect the scope of the work. Changes are made on chapter separator and contents.

This is an interesting chapter since cobalt-based tungstate have been studied for other applications also. Also, effect of transition metal cobalt in optical emission has been less studied. Cobalt based compounds are highly efficient electrocatalysts for water splitting (oxygen reduction range of water) because of their high stability and strong catalytic activity towards OER.

13. Author has used a low temperature synthesis using sodium tungstate dihydrate, pyrrole, cobalt chloride hexahydrate, ferric chloride and sodium hydroxide. This itself can be listed as good and unique process including Polypyrrole synthesis and author may want to mention this.

Response: Thank you for the valuable suggestion. The uniqueness of the adopted low-temperature synthesis route, which involves sodium tungstate dihydrate, pyrrole, cobalt chloride hexahydrate, ferric chloride, and sodium hydroxide, has now been highlighted in the revised text. In particular, the incorporation of in situ polypyrrole synthesis has been mentioned as a noteworthy aspect of the process. Changes are made on page no. 160.

14. Characterization and confirmation of compounds are very similar to that described earlier, so I do not have any comments on the materials characterization. However, again P cobalt tungstate/ppy are extremely faceted as shown in Figures 5.4 and 5.5. a small explanation on faceted structure will enhance the quality of discussion.

Response: Thank you for pointing this out. While the general characterization and confirmation of the compounds follow similar procedures as described earlier, additional explanation has now been included in the discussion of Figures 5.4 and 5.5. Specifically, the highly faceted morphology observed in the $CoWO_4$/ppy samples has been elaborated upon. Faceted structures generally indicate anisotropic growth, which can expose a higher density of catalytically active sites and thereby contribute positively to electrochemical performance. Changes are made on page no. 167.

15. A question arises which may be beyond this thesis, does morphology affect the OER? If so, catalytic effects should be more on non-faceted micromorphology. This may not apply to water splitting. May be Fig. 5.7 beyond P/Po for one may explain this.

Response: Generally, non-faceted morphologies with rougher and more irregular surfaces are expected to provide a higher density of active sites due to their increased surface irregularity, which can enhance catalytic effects in some systems. However, in water splitting reactions, especially OER, the situation is more complex. Faceted morphologies, such as those observed in the $CoWO_4$/ppy composites, often expose specific crystallographic planes that are intrinsically more active for oxygen evolution, thus enabling improved electron transfer and adsorption of intermediates. Therefore, while non-faceted morphologies may enhance site density, faceted structures can promote site selectivity and catalytic efficiency [1].

$CoWO_4$/ppy composite, when compared to other transition metal-based compounds, appears to be extremely good. The data presented here showed that $CoWO_4$/ppy has a lower Tafel slope, and hence superior catalytic kinetics and an efficient OER process. The Thesis claims that the $CoWO_4$/ppy composite also exhibited excellent surface adherence to the FTO plate which is favourable for practical applications in energy conversion devices. The finding here is clear that $CoWO_4$/ppy composite shows superior performance as an electrocatalyst for OER compared to its individual counterparts.

16. Author may want to mention that his results are better than other similar materials/PPY such as reported in reference 10 etc.

Response: We thank the examiner for this valuable suggestion. In the revised discussion, we have now included a comparative statement highlighting that the obtained OER activity of our $CoWO_4$/ppy composite is superior to other reported ppy based hybrid catalysts. The changes are made on page no. 188 and 189.

Chapter 6. Summary and Conclusion (pages 197-200)

Author summarised the results of all experiments and discussion in this chapter.

The summary shows that the author investigated the catalytic performance of mixed metal oxide systems incorporating the conducting polymer polypyrrole. The author started with metal oxides, followed by metal doping within the crystal lattice to enhance electrocatalytic activity. His results indicated that doping and polymer integration significantly improved the catalytic performance and stability.

17. It may be better if he mentions the number/or percentage improvements compared to $CoWO_4$/ppy or other materials to show excellent properties of Co based tungstate in this section which will enhance his argument of increase in performance and uniqueness.

Response: We thank the examiner for this valuable suggestion. Accordingly, we have now included a quantitative comparison highlighting the percentage improvements in overpotential for Mg-doped BCTO, $CoWO_4$, and $CoWO_4$/ppy. The conclusion section has been revised to emphasize the superior performance and uniqueness of Co-based tungstate/ppy composites over other reported materials. The changes are made on page no. 200.

Examiner 2

The thesis of Sarvatej Kumar Maurya deals with the development of non-noble oxide-based electrocatalysts by design. The multimetallic oxide materials are structurally tuned by doping and by varying the ratios of the metal contents. Polypyrrole polymer is chosen to improve the conductivity of the oxide composite. The main focus of this thesis is to employ the designed materials to address the barrier in the complex electrochemical oxygen evolution reaction and improve its efficiency for the benefit of electrochemical energy systems. The materials designed and evaluated include Mg-doped BiCuTiO, CoWO with varying Co/W ratio, and $CoWO_4$/ppy composite. It turns out that the studies on Mg0.1-BiCuTiO, $Co_xW_{2-x}O_4$ x=1.0, $CoWO_4$/ppy materials show consistent electrocatalytic activity improvement. Working electrodes of the materials are fabricated using standard-sized FTO plates, and measurements are done consistently using the three-electrode system at room temperature under alkaline conditions on the CHI-608C workstation.

Chapter 3 is on Mg-doped BiCuTiO for OER. This system is chosen as a potential multi-metallic doped material sparsely explored for OER. Mg-doping seems to help improving the activity.

1. Can you ensure that Mg is doped from XRD in Fig.3.1? Can it be confirmed by the Vegard's law?

   Response: The presence of Mg in the doped BCTO sample cannot be directly confirmed solely from the XRD patterns. Although no discernible peak shift is observed in the XRD pattern of Mg-doped BCTO (Fig. 3.1), this does not necessarily indicate the absence of Mg incorporation. At low doping levels, the substitution of Mg^{2+} ions can cause only very subtle lattice distortions that are often below the detection limit of conventional XRD. While Vegard's law can be applied in principle to correlate lattice parameters with dopant concentration, the negligible change in lattice constants here suggests that XRD alone cannot conclusively confirm Mg doping. Therefore, the presence of Mg in the lattice is further supported by complementary techniques such as EDX and XPS, which provide direct evidence of elemental incorporation and the oxidation state of Mg, ensuring a more reliable confirmation of successful doping.

2. In figure 3.3, there is only one spectrum, so write spectrum in the caption.

   Response: We acknowledge the observation. Since only a single spectrum is presented in Figure 3.3, the caption has been revised to read "Raman spectrum of $Mg_{0.1}$BCTO" to accurately reflect the content. Changes are made on page no. 82, 83, and 84.

3. It is interesting that Raman signal at 606 cm^{-1} is missing in sample (b), not in (c) in figure 3.4. Any specific reason?

   Response: The Raman band at 606 cm^{-1} in BCTO corresponds to the Ti–O stretching vibration in the perovskite lattice. Its negligible presence in the $Mg_{0.05}$BCTO sample, while substantial presence in BCTO, $Mg_{0.1}$BCTO, and $Mg_{0.2}$BCTO, can be attributed to the interplay between Mg doping concentration and lattice dynamics. At low doping levels, the substitution of Mg^{2+} ions at the Ti^{4+} sites may be insufficient to induce significant lattice distortions detectable by Raman spectroscopy. This subtle incorporation might not perturb the Ti–O bond vibrations enough to manifest as a distinct Raman peak. Conversely, at higher doping concentrations (0.1–0.2 mol fraction), the increased presence of Mg^{2+} ions can lead to more pronounced lattice distortions or local structural changes, which can enhance or activate specific vibrational modes, making the 606 cm^{-1} band detectable.

   Additionally, the presence of secondary phases or variations in crystallinity at different doping levels can influence the Raman spectrum. Secondary phases or amorphous regions might not exhibit the same Raman features as the primary crystalline phase, leading to the absence or alteration of specific peaks [2].

4. Fig. 3.11(c) Cu 2p spectrum is interpreted wrongly. The peak at 933.2 eV is 2p3/2 and at 953.1 eV is 2p1/2.z

   Response: We acknowledge the observation regarding the Cu 2p XPS spectrum in Figure 3.11(c). Upon re-evaluation, the peak at 933.2 eV corresponds to Cu $2p_{3/2}$, and the peak at 953.1 eV corresponds to Cu $2p_{1/2}$. The figure caption and discussion have been corrected accordingly to accurately reflect the proper assignment of the Cu 2p spin–orbit components. Changes are made on page no. 90 and 91.

5. You have reported potentials in figure 3.12 with respect to RHE. Is there any difference between RHE, NHE and SHE electrodes?

   Response: There is a difference between RHE and SHE, mainly related to reference conditions and pH dependence. The standard reduction potential of Standard Hydrogen Electrode (SHE) is defined at 0 V under standard conditions (1 M H^+, 1 atm H_2, 25 °C) and is independent of pH. The Normal Hydrogen Electrode (NHE) is practically

identical to SHE and often used interchangeably in literature. In contrast, the Reversible Hydrogen Electrode (RHE) accounts for the solution pH, with its potential shifting according to the Nernst equation: $E_{RHE}=E_{SHE}+0.059\times pH$ (at 25 °C).

Reporting potentials with respect to RHE is particularly useful in aqueous electrochemistry, as it reflects the actual proton activity in the electrolyte and allows direct comparison of OER performance across different pH conditions.

6. The Nyquist plots in fig.3.14 show two semicircles, one smaller and another larger. What does it indicate?

Response: In a Nyquist plot, the semicircles appear in order of increasing time constant and decreasing relaxation frequency. Parallel RC circuits with smaller RC time constants (smaller products) will appear first at higher frequencies, while processes with larger time constants will appear later at lower frequencies. In Figure 3.14, the first semicircle in the EIS spectrum originates from the impedance of the film resistance which forms at the interface between the electrode and electrolyte surface. The second semicircle in the EIS results is associated with the charge transfer resistance (R_{ct}), which is related to the kinetics of an electrochemical reaction and is affected by factors such as surface coating, phase transition, bandgap structure, and particle size [3].

7. The Z' and Z" units are different in figures 3.14, 3.15, 3.16. What should be the units of Z' and Z"? What is Z, resistance or impedance? Any difference between these two?

Response: In Figures 3.14 and 3.16, the impedance values are reported in Ω-cm², as they are normalized by the geometric surface area of the electrode, whereas in Figure 3.15, the values are reported in Ω-mg, since they are normalized by the mass loading of the catalyst. In the original version of Figure 3.16, the unit was incorrectly written as $\Omega\cdot cm^{-2}$, which has been corrected in the revised thesis (Page 99).

Impedance (Z) represents the overall opposition of the system to alternating current (AC) and is a complex quantity consisting of a real part (Z′) and an imaginary part (Z″). The real part, Z′, corresponds to energy dissipation and is analogous to resistance, while the imaginary part, Z″, represents energy storage in capacitive or inductive elements. Both Z′ and Z″ are expressed in ohms (Ω), which is the generic unit for these quantities.

The major difference between impedance (Z) and resistance (R) is that resistance measures the opposition to direct current (DC) and is purely real, whereas impedance accounts for both resistive and reactive effects under AC. In essence, resistance can be considered a special case of impedance under DC conditions [4].

8. Is the proposed OER mechanism consistent with the activity?

Response: The proposed OER mechanism is well-aligned with the observed catalytic activity of the material. The stepwise sequence involving the adsorption of OH^- ions at the metal active sites (M), followed by the formation of surface-bound intermediates OH^*, O^*, and OOH^*, provides a mechanistic rationale for the efficient electron transfer observed during OER. Each electrochemical step, involving a single electron transfer, is energetically feasible and contributes to the overall low overpotential and high current density recorded experimentally.

The formation of $O*$ and $OH*$ intermediates at the active sites is particularly significant, as these species facilitate the subsequent O-O bond formation, a key rate-determining step in oxygen evolution. The strong adsorption of intermediates at the metal sites ensures proper stabilization of these transient species, thereby lowering activation barriers and enhancing reaction kinetics.

9. Chapter 4 title is incomplete. Check it. This chapter is on water oxidation using $Co_xW_{2-x}O_4$.

Response: We thank the examiner for pointing this out. The chapter title has been updated to accurately reflect the content. The revised title is:

"Development and evaluation of electrochemical performance of cobalt tungstate $Co_xW_{2-x}O_4$; x = 0.5, 1.0, 1.5 catalysts for alkaline water oxidation: Tailoring composition for optimal activity." Changes are made on separator and contents.

10. Multiple oxidation states of metal ions in metal tungstites would be helpful for this reaction. However, does variation in the Co/W ratio have any effect on this reaction?

Response: We thank the examiner for this important observation. Variation in the Co/W ratio in $Co_xW_{2-x}O_4$ has a pronounced effect on the OER activity due to its impact on the electronic structure and redox behavior of the catalyst. Changing the Co/W ratio alters the relative concentration of Co^{2+}/Co^{3+} and W^{6+} species, which are critical for the formation and stabilization of surface-adsorbed intermediates (OH^*, O^*, and OOH^*) during water oxidation. An optimized Co/W ratio enhances the density of catalytically active sites and facilitates efficient electron transfer between the metal centers and adsorbed species, thereby reducing the overpotential and improving the reaction kinetics.

11. LSV curves in figure 4.6(a) show that the activity of $CoWO_4$ is better. It means that the stoichiometric 1:1 compound is more active for water oxidation. The reason seems to be elusive.

Response: We appreciate the examiner's comment. The enhanced OER activity of the stoichiometric $CoWO_4$ (1:1 Co:W ratio) can be attributed to its optimal electronic structure and balanced distribution of active sites. In this composition, the Co^{2+}/Co^{3+} redox couple is maximized, providing efficient charge transfer and stabilizing the surface-adsorbed intermediates (OH^*, O^*, and OOH^*) essential for water oxidation.

Deviations from the 1:1 ratio can lead to either excess Co or W, which may disrupt the electronic interactions within the lattice, reduce the number of catalytically active sites, or affect the adsorption energetics of reaction intermediates. Consequently, the stoichiometric $CoWO_4$ exhibits the most favorable combination of electronic structure, active site density, and intermediate stabilization, resulting in superior OER performance.

12. Chapter 5 is electrocatalysis study of $CoWO_4$/ppy composite. The idea of adding ppy seems to be to increase the conductivity. The XRD pattern of $CoWO_4$/ppy, composite in fig.5.2 becomes intense after heating. Why does it happen? Compare figures 5.1 and 5.2.

Response: We thank the examiner for this observation. The increased intensity of the XRD peaks in the $CoWO_4$/ppy composite after heating (Figure 5.2) compared to the as-synthesized sample (Figure 5.1) can be attributed to improved crystallinity and phase stabilization induced by thermal treatment. Heating reduces structural defects and residual strains in the lattice, leading to sharper and more intense diffraction peaks.

Additionally, the thermal treatment may enhance the interaction between CoWO4 and polypyrrole (ppy), promoting better adhesion and uniform distribution of the composite, which can further improve the structural ordering.

13. The BET isotherm in fig.5.7 does not show any porosity. It only shows condensation after 0.9. Nevertheless, the $CoWO_4$/ppy, composite shows improved electrocatalytic activity.

Response: We thank the examiner for the comment. A detailed BET analysis of the $CoWO_4$/ppy nanostructures (Figure 5.7) indicates that the material exhibits a Type IV isotherm with H2-type hysteresis, characteristic of mesoporous materials. Although the condensation occurs at high relative pressures ($P/P_0 > 0.9$), the BJH pore size distribution confirms the presence of mesopores with sizes predominantly in the 2–40

nm range. The specific surface area (12.8 $m^2\ g^{-1}$) and total pore volume (0.1061 $cm^3\ g^{-1}$) suggest a well-developed porous architecture.

This mesoporosity, combined with the conductive ppy network, facilitates rapid ion transport, efficient electrolyte penetration, and enhanced charge transfer at the active sites. Therefore, the improved OER performance of the $CoWO_4$/ppy composite is not solely dependent on apparent high porosity but arises from the synergistic effect of moderate mesoporosity, high surface area, and enhanced electronic conductivity provided by ppy.

14. The OER mechanisms in all three-chapter studies are identical.

Response: We thank the examiner for the comment. Although the three studies, Mg-doped BCTO, cobalt tungstate with varying stoichiometries, and $CoWO_4$/ppy composite, investigate different materials, the fundamental OER mechanism remains consistent because the reaction in alkaline media universally follows the $OH^*/O^*/OOH^*$ mediated pathway. This involves sequential adsorption of OH^- ions at the metal active sites, formation of surface-bound intermediates, and eventual evolution of O_2. The similarity in mechanism does not imply identical activity; rather, each material exhibits distinct electrocatalytic performance due to differences in electronic structure, active site density, metal oxidation states, and conductivity. For instance, Mg doping in BCTO optimizes intermediate adsorption and charge transfer, varying the Co/W ratio in cobalt tungstate tunes the Co^{2+}/Co^{3+} redox distribution, and incorporating polypyrrole in $CoWO_4$ enhances electronic conductivity and stabilizes intermediates. Therefore, while the core mechanistic steps are same, material-specific properties govern the kinetics and overall efficiency, providing a coherent yet differentiated understanding of OER across the three systems.

Additional comments:

15. What is the change in Gibbs free energy for the water splitting reaction?

Response: The change in Gibbs free energy (ΔG) for the overall water splitting reaction can be calculated from the standard thermodynamics of the reaction:

The overall reaction in water splitting is:

$$\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$$

Under standard conditions (25 °C, 1 atm, pH = 0):

The standard Gibbs free energy change for water splitting is:

$$\mathbf{\Delta G^\circ = 237.2\ kJ/mol\ of\ H_2O}$$

This corresponds to 1.23 V per electron in electrochemical terms, using the relation:

$$\Delta G = -nFE^{\circ}$$

Where:

n=2 electrons per H_2 molecule,

F=96485 C/mol (Faraday's constant),

E°=1.23V (standard potential for water splitting).

So, ΔG for the full water splitting reaction (producing 2 mol H_2 and 1 mol O_2) is:

$$\Delta G = 2\times 96485\times 1.23 \approx 237.2 kJ/mol\ H_2O$$

This is the minimum thermodynamic energy required to split water under standard conditions.

16. Compare OER in alkaline and acidic media. Which is more favourable kinetically?

Response: The oxygen evolution reaction (OER) differs significantly in alkaline and acidic media due to variations in reaction kinetics, thermodynamics, and electrode stability. In alkaline media, OH^- ions are the primary reactants, and the OER proceeds via adsorption of OH^- on the catalyst surface, formation of intermediates (OH^*, O^*, OOH^*), and eventual release of O_2. In acidic media, water molecules are directly oxidized to form O_2, generating H^+ ions.

Kinetically, OER is generally faster in alkaline media for most transition-metal-based catalysts. This is because OH^- ions are more reactive and facilitate faster electron transfer, and the abundance of OH^- lowers the energy barrier for intermediate formation. In contrast, acidic OER requires more robust catalysts (e.g., noble metals like IrO_2 or RuO_2) due to slower kinetics and corrosion of non-noble metal oxides.

In summary, while both media follow the same fundamental OER mechanism, alkaline media is more favorable kinetically for earth-abundant transition-metal catalysts, whereas acidic media demands higher catalyst stability and often exhibits slower reaction rates.

17. What is the principle of XPS?

Response: The principle of X-ray Photoelectron Spectroscopy (XPS) is based on the photoelectric effect, where incident X-ray photons irradiate a material and eject core-level electrons from its atoms. When an X-ray photon of known energy (hν) strikes a sample, it can transfer energy to a core electron, causing the electron to be emitted with a kinetic energy (E_k) that depends on the binding energy (E_b) of that electron:

$$E_b = h\nu - E_k - \phi$$

Here, ϕ is the work function. By measuring the kinetic energy of the emitted electrons, XPS allows the determination of binding energies, which are characteristic of specific elements and their oxidation states. This provides detailed information about the elemental composition, oxidation states, and chemical environment of atoms on the surface (typically the top 5–10 nm) of the material.

18. Why Hg/HgO reference electrode is chosen in these studies? Is it stable in alkaline solutions?

Response: The Hg/HgO reference electrode is chosen in these studies because it is particularly stable and reliable in alkaline media. Its potential is well-defined in basic electrolytes, such as 1 M KOH, and it provides reproducible and accurate reference measurements for electrochemical experiments like OER.

Yes, the Hg/HgO electrode is stable in alkaline solutions because the Hg/HgO redox couple ($Hg + 2OH^- \rightleftharpoons HgO + H_2O + 2e^-$) does not undergo corrosion or decomposition under typical OER operating potentials. This makes it an ideal reference for evaluating overpotentials, Tafel slopes, and other electrochemical parameters in alkaline electrolytes.

19. What is meant by capacitive current in CV in fig.2.10?

Response: In cyclic voltammetry (CV), the capacitive current refers to the non-faradaic current that arises from the charging and discharging of the electrical double layer at the electrode–electrolyte interface, rather than from any redox reaction. When a potential is applied, ions in the electrolyte reorganize near the electrode surface, forming a double layer, and this results in a current proportional to the scan rate ($i_c = C \cdot \nu$, where, C is the double-layer capacitance and ν is the scan rate).

In Fig. 2.10, the capacitive current manifests as the background current in the CV curve, producing a roughly rectangular shape in the absence of faradaic peaks. It does not involve electron transfer via chemical reactions, but it is important because it contributes to the overall current and can be used to estimate the electrochemically active surface area (ECSA) of the catalyst.

20. How is CV different from LSV?

Response: Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) are both electrochemical techniques, but they differ in potential application and the information they provide. In CV, the potential is swept linearly forward and backward between two set limits, forming a cyclic waveform, which allows observation of both anodic and

cathodic peaks. This provides insights into the redox behavior, reversibility, and reaction kinetics of the system, while also capturing both faradaic and non-faradaic (capacitive) currents. In contrast, LSV involves a unidirectional potential sweep, producing a forward current–potential curve that is primarily used to determine onset potentials, overpotentials, and catalytic activity. Therefore, while CV is ideal for mechanistic studies and evaluating electron transfer processes, LSV is better suited for assessing electrocatalytic performance.

21. How do you calculate the d-values using XRD profile?

Response: The d-values (interplanar spacings) in X-ray diffraction (XRD) are calculated using Bragg's law:

$$n\lambda = 2d\sin\theta$$

Where,

n = order of diffraction (usually 1),

λ = wavelength of the X-ray source (e.g., Cu Kα = 1.5406 Å),

d = interplanar spacing,

θ = Bragg angle (half of the 2θ value from the XRD peak).

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