

PROJECT REPORT
on
OXYGEN EVOLUTION REACTION USING ZINC FERRITE /
SILVER CHLORIDE NANOCOMPOSITE

Submitted by

ASWATHY SHAJI

Register No: AB23PHY005

Under the guidance of

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St. Teresa's College (Autonomous), Ernakulam

Mahatma Gandhi University, Kottayam

In partial fulfilment of the requirement for the Award of

BACHELOR'S DEGREE OF SCIENCE IN PHYSICS



ST. TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM

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CERTIFICATE

This is to certify that the project report entitle 'OXYGEN EVOLUTION REACTION USING ZINC FERRITE / SILVER CHLORIDE NANOCOMPOSITE ' is an authentic work done by ASWATHY SHAJI (AB23PHY005) of St.Teresa's College (Autonomous), Ernakulam, under my supervision at the Department of Physics for the partial requirement for the award of Degree of Bachelor of Science in Physics during the academic year 2025-2026. The work presented in this dissertation has not been submitted for any degree in this or any other university.

Supervising guide

Dr. Minu Pius
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Head of the department

Dr. Mary Vinaya
Assistant Professor

ST.TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM



B.Sc. PHYSICS

PROJECT REPORT

ASWATHY SHAJI

Register No: AB23PHY005

Year of work : 2025-2026

This is to certify that this project work entitled "OXYGEN EVOLUTION REACTION USING ZINC FERRITE / SILVER CHLORIDE NANOCOMPOSITE" is an authentic work done by Aswathy Shaji (AB23PHY005).

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Submitted for the university examination held at St.Teresa's College (Autonomous), Ernakulam.

Date: 16.04.26

Examiner:

ATHIRA PRAKASH

DECLARATION

Aswathy Shaji (AB23PH005), final year B.Sc. student, Department of Physics, St.Teresa's College, Ernakulam do hereby declare that the project work entitled "OXYGEN EVOLUTION REACTION USING ZINC FERRITE / SILVER CHLORIDE NANOCOMPOSITE " has been originally carried out under the guidance and supervision of Dr. Minu Pius, Assistant Professor and co-guidance Dr. Nisha T P, Assistant Professor, Department of Chemistry, St.Teresa's College (Autonomous), Ernakulam in partial fulfilment for the award of the degree of Bachelor of Physics.I further affirm that this project is not being presented in part or entirely for any other purpose and that the data provided in the project is accurate to the best of our knowledge.

Place :

Date :

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I would like to express our heartfelt gratitude to everyone who assisted us in reaching this stage of accomplishment. First and foremost, I thank the Lord Almighty for His abundant mercy, guidance, and blessings throughout the successful completion of this project.

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I also extend our sincere thanks to all the teaching and non-teaching staff members for their helpful advice, cooperation, and support throughout the course of this work.

Finally, I express our deep appreciation to everyone who directly or indirectly assisted me and contributed to the successful completion of this project.

PREFACE

The increasing demand for clean and sustainable energy has encouraged researchers to explore alternative fuels that can replace fossil fuels. Hydrogen is considered one of the most promising clean fuels because it produces only water as a byproduct when used. Electrochemical water splitting is an effective method for hydrogen production; however, the Oxygen Evolution Reaction (OER) involved in this process is slow and requires efficient catalysts to improve its performance.

In this project, zinc ferrite/silver chloride ($\text{ZnFe}_2\text{O}_4/\text{AgCl}$) nanocomposite was synthesized as a potential electrocatalyst for the Oxygen Evolution Reaction (OER). ZnFe_2O_4 , a spinel-structured transition metal oxide, exhibits good chemical stability and suitable electronic properties; however, its catalytic performance is often limited due to the rapid recombination of charge carriers. To overcome this limitation, silver chloride (AgCl) was incorporated to form a ternary composite, which enhances charge transfer, improves electrical conductivity, and increases catalytic efficiency. The synthesized material was characterized using X-ray diffraction (XRD) to confirm the crystalline structure and phase formation of ZnFe_2O_4 along with AgCl components, thereby verifying the successful formation and structural properties of the composite material.

By investigating $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ as a low-cost and earth-abundant catalyst, this study aims to contribute toward the development of efficient electrocatalysts for sustainable hydrogen production via oxygen evolution mechanism and clean energy applications.

OXYGEN EVOLUTION REACTION USING ZINC FERRITE / SILVER CHLORIDE NANOCOMPOSITE

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CHAPTER 1

INTRODUCTION

1.1 ENERGY CRISIS AND RENEWABLE ENERGY

The world is facing an energy crisis due to the excessive use of fossil fuels like coal and petroleum. These resources are limited and cause serious environmental problems such as pollution and global warming. As energy demand keeps increasing, it has become necessary to shift toward cleaner and sustainable energy sources.

Renewable energy sources like solar and wind energy offer a promising solution. One effective approach for storing renewable energy is the production of hydrogen via electrochemical water splitting. In this process, electrical energy derived from renewable sources is converted into chemical energy in hydrogen molecules, which can be stored and later utilized as a clean fuel.

1.1.1 HYDROGEN AS A CLEAN FUEL

Hydrogen is considered a promising clean fuel because it is sustainable, energy-efficient, and environmentally friendly. It can be produced from water through electrolysis, and when used as a fuel, it forms water again—making it a renewable and virtually unlimited energy source.

Hydrogen has a very high calorific value (about 120 MJ/kg), which is much higher than conventional fuels like CNG. This means a smaller mass of hydrogen can produce a large amount of energy. Most importantly, hydrogen contains no carbon, so its use does not release carbon dioxide or other greenhouse gases. This makes it highly beneficial in reducing global warming and pollution.

Liquified hydrogen is also being explored as a potential aviation fuel due to its high energy-to-weight ratio. Overall, hydrogen offers a clean and efficient solution to future energy demands.

However, producing hydrogen efficiently is still a challenge. Water splitting involves two reactions, OER and HER. The Oxygen Evolution Reaction (OER) is relatively slow and requires extra energy. Therefore, developing efficient and affordable catalysts, is essential to improve hydrogen production and make clean energy technologies more practical and accessible.

1.1.2 WATER SPLITTING TECHNOLOGY

Water splitting is the process of using energy (usually electricity or sunlight) to break H_2O into hydrogen and oxygen. It's the cleanest way to make hydrogen when the input electricity comes from renewables: the hydrogen can be stored, transported, and later used in fuel cells or combustion with only water as the exhaust.

There are three main technical routes people use today:

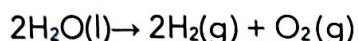
- Alkaline water electrolysis (AWE): Mature and robust, it uses alkaline electrolytes and inexpensive materials, but is less responsive to rapidly varying power.

- Proton exchange membrane electrolysis (PEM): Faster start/stop and compact (good for coupling to renewables), but requires expensive noble-metal catalysts and proton-conducting membranes.
- Solid oxide electrolysis (SOEC) and Anion exchange membrane : SOEC runs hot and can reach high efficiencies (good for co-production with heat), while anion-exchange membrane (AEM) electrolyzers and other novel cells aim to combine the best features of AWE and PEM. Each has trade-offs in cost, durability and efficiency.

Among these, OER is kinetically slow and requires efficient electrocatalysts to reduce energy loss (overpotential). Therefore, developing stable and cost-effective catalysts such is essential to improve water-splitting efficiency

1.2 WATER SPLITTING REACTION

The water splitting reaction is an electrochemical process in which water (H_2O) is broken down into hydrogen (H_2) and oxygen (O_2) using electrical energy. The overall reaction can be written as:



This process occurs through two half-reactions. At the cathode, the Hydrogen Evolution Reaction (HER) takes place, where hydrogen gas is produced. At the anode, the Oxygen Evolution Reaction (OER) occurs, where oxygen gas is formed. Among these two, OER is more complex because it involves a four-electron transfer process, making it slower and requiring higher energy (overpotential).

1.2.1 ELECTROCATALYSIS

Electrocatalysis is the process of accelerating electrochemical reactions at the surface of a catalyst by facilitating electron transfer. In systems like water electrolysis, electrocatalysts reduce the required overpotential, improve reaction kinetics, and enhance overall efficiency.

The activity of an electrocatalyst depends on factors such as adsorption of reaction intermediates, charge transfer rate, Tafel slope, and stability. According to the Sabatier principle, optimal performance occurs when intermediates bind neither too strongly nor too weakly to the catalyst surface. The OER mechanism typically begins with the adsorption of hydroxide ions (OH^-) onto metal active.

In water splitting, efficient electrocatalysts are essential for both HER and OER.

Materials like zinc ferrite are studied because their electronic structure and surface properties can promote faster reaction kinetics, especially in alkaline media.

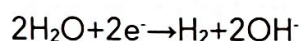
1.2.2 HYDROGEN EVOLUTION REACTION (HER)

The Hydrogen Evolution Reaction (HER) is the cathodic half-reaction in water splitting where hydrogen gas (H_2) is produced. It is a two-electron electrochemical process and plays a crucial role in hydrogen generation for clean energy applications.

In acidic media, Hydrogen Evolution Reaction (HER) occurs through the reduction of protons:



In alkaline media, water molecules are reduced



The Hydrogen Evolution Reaction (HER) mechanism generally proceeds through three fundamental steps:

1. Volmer Step (Electrochemical adsorption):

Hydrogen ions (or water molecules in alkaline medium) gain an electron and adsorb onto the catalyst surface as adsorbed hydrogen.

2. Heyrovsky Step (Electrochemical desorption):

The adsorbed hydrogen reacts with another proton (or water molecule) and an electron to form hydrogen gas.

3. Tafel Step (Chemical recombination):

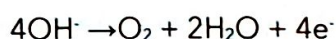
Two adsorbed hydrogen atoms combine to release hydrogen gas.

Depending on which step is rate-limiting, different reaction pathways such as Volmer-Tafel or Volmer-Heyrovsky mechanisms occur. The efficiency of Hydrogen Evolution Reaction (HER) depends strongly on the catalyst's ability to optimally bind hydrogen (neither too strongly nor too weakly).

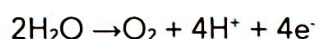
1.2.3 OXYGEN EVOLUTION REACTION (OER)

The Oxygen Evolution Reaction (OER) is the anodic half-reaction in water electrolysis where oxygen gas is generated. It is a four-electron transfer process and is considered the more challenging step in water splitting due to its complex reaction pathway and slow kinetics.

In alkaline medium, the reaction is,



In acidic medium,



The OER mechanism typically with the absorption of hydroxide ions onto metal active sites of the catalyst surface. This is followed by the formation of surface-bound intermediates such as $\ast\text{OH}$, $\ast\text{O}$, and $\ast\text{OOH}$. These intermediates undergo successive electron-transfer steps, eventually releasing molecular oxygen (O_2) and regenerating the catalyst surface.

The catalytic activity of OER materials is strongly influenced by:

- The adsorption energy of oxygen-containing intermediate.
- The scaling relationship between $\ast\text{OH}$, $\ast\text{O}$, and $\ast\text{OOH}$ species
- The Sabatier principle, which states that optimal catalytic performance occurs when the intermediates bind neither too strongly nor too weakly to the catalyst surface

Because OER involves multiple proton-coupled electron transfer steps, it requires higher overpotential compared to HER.

1.3 OXYGEN EVOLUTION REACTION (OER)

1.3.1 MECHANISM OF OER

The OER is the anodic (positive electrode) reaction in water splitting and a key process in generating molecular oxygen. It can be represented by the equation $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. It is a complex process where oxygen is generated, most commonly via the "Adsorbate evolution mechanism (AEM)", a series of electrochemical reactions on the surface of a metal catalyst. The AEM typically involves the sequential adsorption of water or hydroxide onto active metal sites, followed by deprotonation, oxidation and formation of molecular oxygen.

1) WATER/HYDROXIDE ADSORPTION

Water molecules adsorb onto the catalyst surface, often through hydrogen bonding or electrostatic interactions. This is essential for subsequent formation of surface bound oxygen species. Hydroxide ions can also adsorb onto catalyst surface. The adsorption of hydroxide ions lead to formation of surface bound oxygen species. The adsorption of water or hydroxide ions can affect the formation of key intermediates, such as $\ast\text{OH}$, $\ast\text{O}$, or $\ast\text{OOH}$ which are involved in the OER mechanism. Catalyst with optimized surface properties can facilitate the adsorption and subsequent reaction steps, leading to improved oer performance.

2) DEPROTONATION AND OXIDATION

In the deprotonation step, a proton (H^+) is removed from a surface bound species, such as $\ast\text{OH}$ or $\ast\text{OOH}$. Deprotonation can occur through various mechanisms including chemical or electrochemical pathways. In the oxidation step, concurrently with deprotonation, the surface bound species undergoes oxidation, resulting in the formation of a more oxidized intermediate. Oxidation, involves the transfer of

electrons, which can occur through the catalyst or an external circuit. This step enables the formation of oxygen-oxygen bonds and ultimately lead to release of oxygen gas. It influences oer pathway and formation of key intermediates. The energetics and kinetics of this step can significantly impact overall oer performance.

3) SECOND OXIDATION STEP IN OER

After the deprotonation and oxidation step in the Adsorbate Evolution Mechanism (AEM), the next step indeed involves another oxidation. In this step:

- **Formation of *OOH Intermediate:**
The surface-bound *O species undergoes further oxidation, leading to the formation of a *OOH intermediate. This step involves the nucleophilic attack of a water molecule or hydroxide ion on the *O species, resulting in the formation of the *OOH intermediate.

1.3.2 CATALYSTS FOR OER

Catalysts play a crucial role in facilitating the Oxygen Evolution Reaction (OER) in energy storage and conversion applications.

Let's explore the different types of OER catalysts and their properties:

1. Metal Oxides
 - Metal oxides, such as iridium oxide (IrO_2) and ruthenium oxide (RuO_2), are well-known OER catalysts.
 - They exhibit high catalytic activity and stability in acidic and alkaline environments.
2. Hydroxides
 - Metal hydroxides, such as nickel hydroxide (Ni(OH)_2) and cobalt hydroxide (Co(OH)_2), are also effective OER catalysts.
 - They often exhibit high activity in alkaline environments and can be used in various applications.
3. Perovskites
 - Perovskites, with the general formula ABX_3 , are a class of materials that can exhibit excellent OER catalytic activity.
 - They offer tunable properties and can be optimized for specific applications.
4. Ferrites (Spinel Ferrites)
 - Ferrites (MFe_2O_4 ; $\text{M} = \text{Ni, Co, Zn, etc.}$) show good electrical conductivity, stability, and abundant active sites.
 - Mixed valence states ($\text{Fe}^{2+}/\text{Fe}^{3+}$) enhance electron transfer during OER.
 - Their activity can be improved by doping or forming ternary composites.

1.3.3 KEY PARAMETERS FOR EVALUATING OER CATALYSTS

1. OVERPOTENTIAL (η):

- Water splitting requires 1.23 V theoretically to produce oxygen. But in reality, catalysts need extra voltage as OER is slow.
- This extra voltage = overpotential(η).
- The magnitude of η is a critical parameter in assessing OER electrocatalysts: Lower η values correspond to higher intrinsic catalytic activity and energy.
- Measurement Methods: Linear sweep or cyclic voltammetry

2. TAFEL SLOPE

- A measure of reaction kinetics which tells us how quickly current rises when voltage increases.
- Relationship between overpotential (η) and $\log(\text{current density})$, derived from the Tafel equation.
- Tafel Equation: (1)

$$\eta = a + b \log j$$

Where:

η = overpotential (V)

j = current density (A/cm^2)

a = intercept (related to exchange current density)

b = Tafel slope (mV/decade)

- Tafel slope: (2)

$$b = \frac{2.303RT}{\alpha nF}$$

Where:

R = gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)

T = temperature (K)

F = Faraday's constant ($96485 \text{ C} \cdot \text{mol}^{-1}$)

n = number of electrons in rate-determining step

α = charge transfer coefficient ($0 < \alpha < 1$)

3. TURNOVER FREQUENCY

- The number of O_2 molecules produced per active site per second. Measures intrinsic activity independent of surface area.
- Effective surface area accessible for reaction is called the Electrochemical Surface Area (ECSA)
- Catalysts with more surface area leads to more places for reaction.
- TOF is Oxygen molecules formed per second / Number of active sites.
- More no: of active sites leads to more oxygen production which means more efficient catalyst.

4. STABILITY AND DURABILITY

- Stability is a catalyst's ability to maintain its structure and properties during operation, while durability is its capacity to retain activity over long-term use at practical current densities..
- Several electrochemical protocols are employed to assess stability:
 - a. Chronoamperometry (CA)

The current response is recorded over time at a fixed applied potential. It shows the catalyst's ability to sustain a steady current density.
 - b. Chronopotentiometry (CP)

The electrode is operated at a constant current density while monitoring the potential drift; an increase in potential reflects catalyst degradation.
 - c. Accelerated Durability Tests (ADT)

Repeated potential cycling is applied to mimic long term operational stress and evaluate the catalyst's structural resilience.

1.4 ZINC FERRITE (ZnFe_2O_4) AS ELECTROCATALYST

Zinc ferrite (ZnFe_2O_4) is a cubic spinel material known for its versatile and adaptable nature. Its properties—whether magnetic, optical, or catalytic—largely depend on how zinc and iron ions are arranged within the crystal structure and on the particle size. Because it is chemically stable, relatively non-toxic, and easy to modify through different synthesis.

1.4.1 CRYSTAL STRUCTURE OF ZINC FERRITE (ZnFe_2O_4)

Zinc ferrite is a classic spinel ferrite widely used in magnetic, optical, and catalytic applications. Its structure is central to understanding its properties and how doping or nanosizing changes its behavior.

(i) Crystal Structure and Cation Distribution

- ZnFe_2O_4 crystallizes in a cubic spinel structure with space group $\text{Fd-}3\text{m}$, built from close-packed O^{2-} with cations in tetrahedral and octahedral interstices.
- In the ideal normal spinel, Zn^{2+} occupies A sites and Fe^{3+} B sites, i.e. $(\text{Zn})[\text{Fe}_2]\text{O}_4$
- In nanoparticles, several studies report partial inversion (some Fe^{3+} on A, some Zn^{2+} on B), inferred from XRD, Mössbauer, and magnetic behavior . This inversion is linked to surface and size effects.

(ii) Effect of Size and Doping on Structure

- Nanosizing (sol-gel, co-precipitation, combustion) preserves the cubic spinel but reduces grain size to 5-30 nm and may increase inversion, altering magnetic order.
- Substitution on Zn or Fe sites (e.g., Co, Mg, Cu, etc) generally keeps the spinel lattice but slightly changes lattice parameter, bond lengths, and force constants, reflecting cation radius and site preference.

1.4.2 ROLE AND MECHANISMS OF ZnFe_2O_4

- Active spinel ferrite catalyst:
Pure ZnFe_2O_4 spinel exhibits good alkaline OER activity ($\eta_{10} \approx 318$ mV, $Tafel \approx 50$ mV dec^{-1}) with high stability (~ 100 h at 800 mA cm^{-2}). Its spinel crystal structure and oxygen vacancies enhance electrochemical surface area and reduce charge-transfer resistance.
- Lattice Oxygen Participation Mechanism (LOM):
 ZnFe_2O_4 thin films with higher oxygen vacancies (e.g., Ar-rich sputtering) show lower bandgap, higher donor density, and improved OER activity. Here, lattice oxygen atoms directly participate in O_2 formation rather than only surface adsorbates (AEM).
- Mixed mechanism in substituted ZnFe_2O_4 :
In Al-substituted ZnFe_2O_4 (ZFAO), different sites follow different pathways:
 - (i) Al (tetrahedral sites) $\rightarrow$ Adsorbate Evolution Mechanism (AEM).
 - (ii) Fe (octahedral sites) $\rightarrow$ Lattice Oxygen Mechanism (LOM).

Oxygen vacancies facilitate fast lattice oxygen transport, giving $\eta_{10} \approx 270$ mV and stability up to 10 days.

Comparison with other composites:

- NiFe_2O_4 & CoFe_2O_4 :
Show lower theoretical energy barriers and higher turnover frequency than Fe-only spinels due to synergistic Fe-Ni or Fe-Co active sites and mixed AEM/LOM pathways, enhancing OER kinetics.
- Role of Zn in ZnFe_2O_4 :
 Zn^{2+} is mostly redox-inactive, so ZnFe_2O_4 mainly acts as a structural and defect host rather than the primary active site.
- Performance enhancement strategy:
OER activity significantly improves when ZnFe_2O_4 is coupled with redox-active Ni/Co phases or when defect-engineered interfaces increase oxygen vacancies and conductivity.

1.4.3 REPRESENTATIVE OER METRICS FOR Zn-BASED FERRITES

Zn-based spinel ferrites exhibit improved OER activity when modified through compositional tuning, defect engineering, or heterostructure formation.

1. $\text{ZnFe}_2\text{O}_4@\text{Zn}(\text{Fe})\text{OOH}$ core-shell:

Shows higher catalytic activity and stability than RuO_2 , due to synergistic interaction between the spinel core and oxyhydroxide shell, providing more active Fe sites. (7)

2. $\text{Zn}_{0.25}\text{Fe}_{2.75}\text{O}_4$ nanoparticles:

Exhibit moderate OER performance ($\eta \approx 454$ mV at 1 mA cm^{-2} , $\text{Tafel} \approx 107 \text{ mV dec}^{-1}$). Increased Fe content enhances redox-active centers but kinetics remain slower compared to doped systems. (8)

3. $(\text{Zn,Cu})\text{Fe}_2\text{O}_4 + \text{CuO}$ nanocomposite (ZCF-50):

Demonstrates significantly improved activity ($\eta \approx 280$ mV at 10 mA cm^{-2} , $\text{Tafel} \approx 80 \text{ mV dec}^{-1}$) due to synergistic Cu-Fe active sites and improved electrical conductivity. (9)

4. ZnFe_2O_4 thin film with oxygen vacancies (Z-Ar):

Shows $\sim 12.5\%$ lower overpotential compared to stoichiometric ZnFe_2O_4 , confirming that oxygen vacancies enhance charge transfer and lattice oxygen participation (LOM). (10)

1.4.4 LIMITATIONS OF PURE ZnFe_2O_4

Pure zinc ferrite (ZnFe_2O_4) is earth-abundant and can be OER-active, but it suffers from intrinsically limited activity and stability compared with optimized spinel ferrites or modified ZnFe_2O_4 , mainly due to electronic structure, poor conductivity, and the presence of OER-inactive Zn^{2+} .

1. Electronic structure and conductivity:

ZnFe_2O_4 has low electron mobility and short minority carrier diffusion length, leading to poor charge transport and recombination losses.

Its relatively small light absorption coefficient and slow surface reaction kinetics further limit utilization of generated charges in OER settings.

2. Presence of OER-inactive Zn^{2+} :

Zn^{2+} is essentially redox-inactive in the OER potential window; in ZnFe_2O_4 it dilutes active Fe centers, lowering the density of redox-active sites compared with Ni/Co ferrites.

A major OER advance with ZnFe_2O_4 uses it only as a precatalyst; under anodic cycling it reconstructs to an active $\text{Zn}(\text{Fe})\text{OOH}$ shell, overcoming the inactivity of lattice Zn^{2+} .

3. Stability and surface reconstruction:

Pristine ZnFe_2O_4 has been "largely ignored" for OER because of low stability and conductivity, and the need for in-situ transformation to oxyhydroxides for high activity.

Multiple groups show best performance when ZnFe_2O_4 is combined with conductive scaffolds (N-doped graphene) or coated with $\text{NiFeO}_x/\text{Al}_2\text{O}_3$

1.5 $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ BINARY NANOCOMPOSITE ELECTROCATALYST

Binary ZnFe_2O_4 architectures demonstrate that combining multiple functional components significantly enhances OER performance. For instance, $\text{ZnFe}_2\text{O}_4/\text{NiAl-LDH}/\text{MWCNTs}$ show a low overpotential of 217 mV at 10 mA cm^{-2} with a Tafel slope of 66.6 mV dec^{-1} , retaining activity after 2000 cycles, indicating good durability[13]. Similarly, Cu-doped $\text{ZnFe}_2\text{O}_4 + \text{CuO}$ nanocomposites achieve 280 mV at 10 mA cm^{-2} due to increased electrochemically active surface area and reduced charge-transfer resistance[14].

Hence, $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ is expected to exhibit synergistic enhancement in conductivity, active sites, and overall OER efficiency.

1.5.1 ROLE, BENEFITS AND LIMITATIONS OF AgCl

AgCl is usually not the main conductive phase in $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ systems; instead, it acts as a halide semiconductor that works synergistically with ZnFe_2O_4 .

1. Electronic & active-site tuning:

AgCl modifies the electronic structure of Ag, improving adsorption of oxygen intermediates (O^* , OH^* , OOH^*). Ag-Cl environments often show better catalytic behavior than metallic Ag alone due to optimized intermediate binding.

2. Interfacial synergy:

AgCl forms strong heterointerfaces with metal oxides (e.g., ZnFe_2O_4), creating new active sites and enhancing charge transfer, which improves catalytic kinetics.

3. Stability via $\text{AgCl} \rightleftharpoons \text{Ag}$ transformation:

AgCl can partially convert to Ag under reaction conditions and regenerate back to AgCl, helping maintain catalytic activity and surface stability over long-term operation.

Representative OER Performance with Ag Modification

1. Ag/C in alkaline medium:

Ag acts as the main active phase for OER; however, it suffers from significant Ag dissolution at high potentials, resulting in poor long-term catalytic stability. [22]

2. Ag-impregnated perovskite (LBCF-A):

Ag functions as a surface modifier at low loading, which reduces overpotential ($\sim 317 \text{ mV}$ at 10 mA cm^{-2}) and improves charge transfer, enhancing overall OER efficiency.[23]

Limitations of AgCl for OER

1. Thermodynamic and kinetic instability:

Under anodic OER potentials, AgCl is unstable and tends to transform into Ag or Ag₂O or undergo dissolution. Similar to Ag/C systems, this instability leads to loss of active material and reduced durability during operation.

2. Lower intrinsic activity:

Compared with state-of-the-art OER catalysts such as IrO₂, RuO₂, and transition-metal oxides/perovskites, AgCl shows inferior catalytic activity and stability. Modern catalyst design principles (eg occupancy, scaling relations, O-O coupling pathways) rarely identify silver halides as efficient OER hosts.

3. Competition with chlorine evolution reaction (CER):

In Cl⁻-containing electrolytes, OER competes with chlorine evolution (CER). Ag-modified systems are often designed to favor CER rather than OER, making AgCl less suitable as a primary OER catalyst.

1.5.2 RELEVANT STUDY INTERPRETATIONS OF ZnFe₂O₄/AgCl IN OER

Relevant ZnFe₂O₄ and Zn-Fe OER behavior

OER activity:

Bare or modified ZnFe₂O₄ spinel shows good alkaline OER performance ($\eta_{10} \approx 240$ –320 mV, Tafel ≈ 50 –80 mV dec⁻¹). Activity improves with oxygen vacancies, Al/Cr substitution, or graphene supports, which enhance conductivity and increase active sites.

Reaction mechanism:

ZnFe₂O₄ catalysts follow Adsorbate Evolution Mechanism (AEM) and/or Lattice Oxygen Mechanism (LOM/LOPM) depending on cation substitution and oxygen vacancy concentration, which influence oxygen intermediate formation and charge transfer.

Silver- and ZnO-based systems relevant to AgCl

1. Silver Oxide–Carbon Composites:

AgO@rGO and ZnO@rGO nanocomposites are OER-active, with AgO@rGO slightly outperforming ZnO@rGO ($\eta \approx 440$ vs 470 mV at 10 mA cm⁻²; Tafel 184 vs 212 mV dec⁻¹). Differences are linked to surface area and double-layer capacitance, showing that noble-metal silver oxides can contribute active OER sites while carbon improves conductivity and ECSA. [33]

2. Transition-Metal-Doped ZnO:

Limitations of AgCl for OER

1. Thermodynamic and kinetic instability:

Under anodic OER potentials, AgCl is unstable and tends to transform into Ag or Ag_2O or undergo dissolution. Similar to Ag/C systems, this instability leads to loss of active material and reduced durability during operation.

2. Lower intrinsic activity:

Compared with state-of-the-art OER catalysts such as IrO_2 , RuO_2 , and transition-metal oxides/perovskites, AgCl shows inferior catalytic activity and stability. Modern catalyst design principles (eg occupancy, scaling relations, O-O coupling pathways) rarely identify silver halides as efficient OER hosts.

3. Competition with chlorine evolution reaction (CER):

In Cl^- -containing electrolytes, OER competes with chlorine evolution (CER). Ag-modified systems are often designed to favor CER rather than OER, making AgCl less suitable as a primary OER catalyst.

1.5.2 RELEVANT STUDY INTERPRETATIONS OF $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ IN OER

Relevant ZnFe_2O_4 and Zn-Fe OER behavior

OER activity:

Bare or modified ZnFe_2O_4 spinel shows good alkaline OER performance ($\eta_{10} \approx 240$ – 320 mV, Tafel ≈ 50 – 80 mV dec^{-1}). Activity improves with oxygen vacancies, Al/Cr substitution, or graphene supports, which enhance conductivity and increase active sites.

Reaction mechanism:

ZnFe_2O_4 catalysts follow Adsorbate Evolution Mechanism (AEM) and/or Lattice Oxygen Mechanism (LOM/LOPM) depending on cation substitution and oxygen vacancy concentration, which influence oxygen intermediate formation and charge transfer.

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2. Transition-Metal-Doped ZnO:

Fe/Cr-doped ZnO nanoparticles reach $\eta \approx 305$ mV and an unusually low Tafel slope (46 mV dec^{-1}), emphasizing that transition-metal doping into Zn-based oxides greatly improves OER kinetics compared with pure ZnO. [34]

3. ZnO Composite Heterostructures:

Multiple ZnO-containing composites ($\text{Co}_3\text{O}_4/\text{ZnO}$, $\text{Co}_3\text{O}_4/\text{ZnO}$) exploit p-n junctions and interfacial charge transfer to lower overpotentials ($\approx 260\text{--}290$ mV at 10 mA cm^{-2}) and Tafel slopes ($59\text{--}80 \text{ mV dec}^{-1}$). [35] [36]

Key Design Implications for $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ OER System

1. ZnFe_2O_4 core:

Acts as the main OER active phase, providing Fe-based active sites that follow AEM and/or LOM pathways. Oxygen vacancies are crucial for improving conductivity and facilitating oxygen intermediate formation. [10] [24] [26]

2. AgCl phase:

Primarily functions as an electronic or structural modifier, helping improve interfacial charge transfer. Current evidence mainly supports its role in ORR or photocatalysis, rather than as a direct OER active site. [28] [29]

Defects and vacancies at the $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ interface that could promote a LOM-type pathway, as oxygen-deficient ZnFe_2O_4 shows superior OER via lattice oxygen participation.

1.5.3 IMPORTANCE OF HETEROSTRUCTURE

Across photocatalysis and electrocatalysis, heterostructures are important because interfacial electronic reconstruction, charge separation, and synergistic active sites systematically improve activity, selectivity, and durability beyond what single-phase catalysts can offer.

1. Improved charge separation & transport

Heterojunctions create built-in electric fields that separate electrons and holes, reducing recombination and enhancing charge transfer. Large interfacial contact (e.g., 2D/2D structures) enables faster electron movement and higher current density.

2. Tunable electronic structure

Heterostructure formation modifies band edges, work function, and d-band center, optimizing adsorption strength of reaction intermediates and lowering reaction barriers, resulting in improved catalytic kinetics.

3. More active sites via synergy

Interfaces provide defect-rich, strained, or mixed-composition sites that act as highly active catalytic centers. Combining materials with complementary roles

produces strong synergistic enhancement in reactions such as HER, OER, and CO₂ reduction

1.6 IMPORTANCE OF ALKALINE MEDIUM IN OER

Alkaline electrolytes are crucial because they enable cheap, earth-abundant catalysts, change the reaction mechanism and kinetics, and shape interfacial structure and stability, all of which strongly affect OER performance.

1. Mechanistic and kinetic effects of alkaline pH:

- In alkaline media the OER proceeds via OH⁻ adsorption rather than water deprotonation, changing the elementary steps and energetics of *OH, *O and *OOH intermediates.
- At medium-high pH, microkinetic modeling and experiments show alkaline conditions dominate OER rates compared with acidic/near-neutral systems, especially at technologically relevant current densities (>20 mA cm⁻²).
- High pH favours formation of active transition-metal oxyhydroxides (e.g. ZnFeOOH) that are the real catalytic phase in alkaline media.
- Lattice-oxygen-mediated mechanisms, which can bypass thermodynamic limits of the classical adsorbate evolution pathway, are most readily activated in alkaline oxyhydroxides with flexible layered structures.

2. Materials choice, stability, and interfacial engineering:

- Strongly alkaline media allow replacement of scarce Ir/Ru with non-precious Ni, Fe, Co oxides/(oxy)hydroxides, carbon composites, and reconstructed phases that are unstable in acid but active in base. Benchmark acidic OER catalysts typically include Ir- and Ru-based oxides such as IrO₂, RuO₂, and mixed oxides (e.g., IrRuO_x), which are highly active but limited by cost and scarcity..
- Alkaline operation still faces degradation (e.g., Fe leaching, phase reconstruction), but mechanisms and mitigation strategies (defect engineering, supports, ionomers) are now well mapped.
- The alkaline double-layer environment (hydrated cations, OH⁻, water structure) stabilizes oxygenated intermediates and can tune lateral interactions, sometimes yielding similar intrinsic activity to acid for IrO_x but with different interfacial physics.

1.7 OBJECTIVE OF THE PROJECT

Based on the urgent need for sustainable energy technologies, electrochemical water splitting has emerged as a promising approach for hydrogen production. However, the Oxygen Evolution Reaction (OER), which occurs at the anode, suffers from sluggish reaction kinetics due to the complex four-electron transfer mechanism, resulting in high overpotential and reduced overall efficiency. Although transition metal oxides such as ZnFe_2O_4 possess good chemical stability, low cost, and environmental compatibility, their practical application as electrocatalysts is limited by poor electrical conductivity, slow charge transfer kinetics, and insufficient active catalytic sites.

To overcome these limitations, heterostructure engineering through the incorporation of conductive components has been widely explored as an effective strategy to enhance electrocatalytic performance. In this context, the formation of a $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite is expected to improve interfacial charge transfer, electrical conductivity, and catalytic activity through synergistic interactions between the metal oxide and AgCl phases. The presence of AgCl can facilitate faster electron transport and improve the adsorption-desorption behavior of oxygen intermediates, thereby enhancing OER efficiency in alkaline medium.

Specific Objectives

- To synthesize $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite using an appropriate chemical synthesis method that enables controlled formation of heterostructure interfaces.
- To characterize the crystalline structure and phase composition of the synthesized material using X-ray diffraction (XRD) analysis.
- To investigate the formation of heterojunction interfaces between ZnFe_2O_4 and AgCl and evaluate their influence on charge transfer behavior.
- To examine the effect of AgCl incorporation on the electrical conductivity, surface properties, and catalytic active sites of ZnFe_2O_4 .
- To evaluate the electrocatalytic activity of the $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite toward the Oxygen Evolution Reaction in alkaline medium using electrochemical techniques.
- To analyze the stability and potential applicability of the synthesized nanocomposite as an efficient OER electrocatalyst.
- To contribute to the development of cost-effective, non-precious metal-based catalyst materials for clean energy conversion and sustainable hydrogen production.

Overall, this study aims to demonstrate that heterostructure engineering of ZnFe_2O_4 with AgCl can effectively enhance OER performance, thereby supporting the advancement of efficient and economically viable electrocatalysts for renewable energy technologies.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 PREPARATION OF ZINC FERRITE

Zinc ferrite (ZnFe_2O_4) is a cubic spinel ferrite widely used in catalysis, photocatalysis, and electrochemical applications. In this work, ZnFe_2O_4 was synthesized via a controlled co-precipitation method, followed by stabilization using trisodium citrate (TSC) and in-situ incorporation of Ag species through silver nitrate (AgNO_3). The method ensures controlled nucleation, uniform particle formation, and high phase purity.

MATERIALS REQUIRED

Chemical	Molecular weight	Concentration	Volume	Calculated mass
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	270.3	0.1M	200ml	5.406g
ZnCl_2	136.28	0.05M	200ml	1.3628 g
NaOH	40	0.4M	400ml	6.4g
AgNO_3	169.87	0.01M	400ml	0.6794g
TSC (Trisodium citrate)	294.1	0.1M	400ml	11.764g

The required masses were calculated using

$$\text{Mass} = \frac{\text{Molecular weight} \times \text{Molarity} \times \text{Volume}}{1000}$$

2.2 SYNTHESIS METHOD OF ZINC FERRITE / SILVER CHLORIDE



Fig 1.1

Step 1: Preparation of metal precursor solution:

Prepare aqueous solutions of ferric chloride (FeCl_3) and zinc chloride (ZnCl_2) (200 ml each). Mix the two solutions and stir continuously for 15 minutes to obtain a homogeneous distribution of Fe^{3+} and Zn^{2+} ions (Fig 1.1).



Fig 1.2

Step 2: Preparation of alkaline solution:

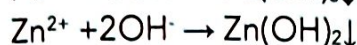
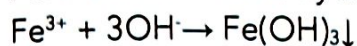
Prepare 400 ml sodium hydroxide (NaOH) solution in water. Transfer this solution to a burette for controlled addition.

Step 3: Formation of Zn-Fe hydroxide precursor:

Heat the mixed FeCl_3 - ZnCl_2 solution to 80°C under constant stirring. Add the NaOH solution dropwise from the burette (Fig 1.3). Continue addition until about 300 ml of NaOH has been added and the pH reaches ~ 12 . A brownish / greenish precipitate forms, indicating formation of mixed Zn-Fe hydroxide precursor, which is the precursor for spinel ZnFe_2O_4 (Fig 1.4).

Chemical reaction:

- Formation of metal hydroxides:



($\downarrow$ indicates the formation of a solid precipitate)

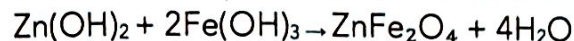


Fig 1.3



Fig 1.4

- Formation of spinel zinc ferrite on heating:



ZnFe_2O_4 forms through dehydration and rearrangement of hydroxide intermediates at elevated temperature.

Step 4: Preparation of Ag precursor solution:

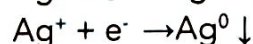
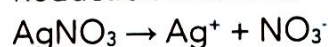
Prepare 200 ml trisodium citrate (TSC) solution and 200 ml silver nitrate (AgNO_3) solution separately in water.

Step 5: Reduction of AgNO_3 using TSC:

Heat the AgNO_3 solution to 80°C under continuous stirring. Add the TSC solution slowly to the AgNO_3 solution.

Here, TSC acts as a reducing agent, converting Ag^+ ions to metallic Ag nanoparticles and assisting in controlled formation of silver species.

- Reduction reaction:



TSC provides electrons for reduction of $\text{Ag}^+ \rightarrow \text{Ag}^0$ nanoparticles

Step 6: Formation of $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ composite

Transfer the Zn-Fe precursor solution to a burette and add it dropwise into the hot AgNO_3 -TSC solution under continuous stirring at 80°C .

During this process:

- Reduced Ag nanoparticles (Ag^0) are formed
- Ag^+ reacts with Cl^- ions (from $\text{FeCl}_3/\text{ZnCl}_2$) forming AgCl precipitate
- Zn-Fe hydroxide converts into ZnFe_2O_4 spinel phase
- AgCl formation reaction: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$



Fig 1.5



Fig 1.6

Step 7: Final product:

The obtained precipitate was separated from the reaction mixture by centrifugation (Fig 1.5). The solid product was washed several times with distilled water (and ethanol if used) to remove impurities and unreacted ions. The collected material was then dried at 100 C at 2 hours. The dried sample was ground into powder and calcined at 700°C for continuous 6 hours and sample was named as CS700.

The same dried sample, after grounded to powder was calcinated at 800°C for continuous 6 hours and named as CS800.

Thus two samples CS700 and CS800 was obtained (Fig 1.6).

2.3 CHARACTERIZATION TECHNIQUES

2.3.1 X-RAY DIFFRACTION

X-ray diffraction is a nondestructive method to probe the atomic structure of crystalline materials, using the interference of X-rays scattered by periodic arrays of atoms. It underpins modern materials science, geology, metallurgy, pharmaceuticals, and increasingly fields like food technology and battery research.

Fundamental Theory of XRD

X-ray diffraction (XRD) is based on the constructive interference of X-rays scattered by atoms arranged in a periodic crystal lattice. When monochromatic X-rays interact with a crystalline material, they are diffracted by atomic planes. The condition for diffraction is described by Bragg's law, which relates the wavelength of X-rays and the spacing between crystal planes.

$$n\lambda = 2d\sin\theta \quad (3)$$

Where

- λ = wavelength of X-ray (Cu K α = 1.5406 Å)
- θ = diffraction angle (half of 2θ from XRD peak)
- d = interplanar spacing
- $n=1$ (usually)

Since the interatomic spacing (≈ 0.15 – 0.4 nm) is comparable to the wavelength of X-rays (3–8 keV), crystals behave like natural diffraction gratings. Each crystalline material produces a unique XRD pattern (fingerprint) based on peak positions and intensities.

XRD analysis provides important structural information such as:

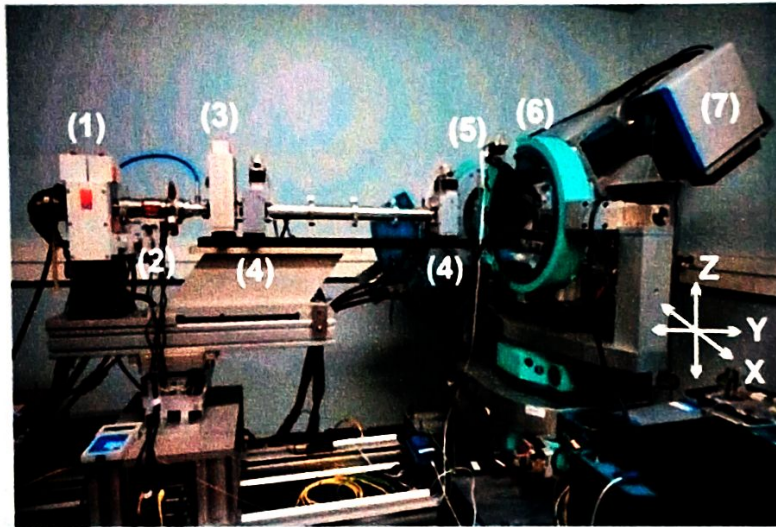


Figure 1: XRD Apparatus with labelled components.

The X-ray diffractometer is used to analyze the crystal structure, phase composition, and crystalline size of materials by measuring the diffraction of X-rays from atomic planes.

Main Components and Functions

1. X-ray source (Mo anode):

Generates monochromatic X-rays using a rotating molybdenum (Mo) anode. The emitted X-rays interact with the crystal lattice of the sample.

2. Multilayer optics (VariMax):

Focuses and directs the X-ray beam into a parallel and intense beam, improving diffraction accuracy and signal intensity.

3. Monochromator (Ge(111) crystal):

Filters the X-rays to obtain a single wavelength, removing unwanted radiation and improving peak resolution.

4. Motorized slit system and flight tube:

Controls the beam size and divergence. The evacuated tube minimizes air scattering and absorption of X-rays.

5. Video microscope camera:

Helps in accurate alignment and positioning of the sample before measurement.

6. Six-circle goniometer with XYZ stage:

Holds the sample and allows precise angular movement (θ , 2θ) and positioning along X, Y, Z axes, ensuring correct orientation for diffraction.

7. Area detector (PILATUS 300K-W):

Detects diffracted X-rays and converts them into digital signals to produce the XRD pattern (intensity vs angle).

Working Principle

The X-ray beam strikes the crystalline sample mounted on the goniometer. When the Bragg condition is satisfied, constructive interference occurs, producing diffraction peaks that are recorded by the detector. The obtained pattern is used to determine crystal structure, phase purity, lattice parameters, and crystallite size.

2.4 STUDY OF OER

OER is usually studied as an electrochemical reaction at an anode in water-splitting cells. Researchers measure catalyst performance (how fast O_2 forms at a given voltage) and, at the same time, monitor the catalyst surface and intermediates with advanced "in situ" and "operando" techniques.

Basic Electrochemical Measurement

1. Setup: Catalyst coated on a conductive substrate in an electrochemical cell with aqueous electrolyte; potential is applied vs. a reference electrode.

2. Key measurements:

- Polarization curves and Tafel plots to get activity and reaction kinetics.
- Overpotential at a target current density (e.g., 10 mA/cm^2) as a performance metric.
- Control of substrates, gas bubbles, impurities, and cell design to ensure reliable data.

Electrochemical Performance Parameters for OER Evaluation

The electrocatalytic performance of the synthesized $ZnFe_2O_4/AgCl$ nanocomposite toward the Oxygen Evolution Reaction (OER) is evaluated using several important electrochemical parameters. These parameters provide insight into the catalytic activity, reaction kinetics, surface properties, and long-term stability of the material in alkaline medium.

Overpotential and Tafel Slope

Overpotential is one of the most important parameters used to evaluate OER activity. It represents the extra potential required beyond the thermodynamic potential (1.23 V vs RHE) to drive the oxygen evolution reaction at a desired current density. A lower overpotential indicates better catalytic efficiency and faster reaction kinetics. The Tafel slope provides information about the reaction mechanism and rate-determining step of the OER process. A smaller Tafel slope suggests faster electron transfer and improved catalytic performance of the electrocatalyst.

Electrochemically Active Surface Area (ECSA)

Electrochemically active surface area (ECSA) is used to estimate the number of active catalytic sites available for the OER process. A higher ECSA indicates greater exposure of active sites, which enhances the interaction between electrolyte and catalyst surface. This helps distinguish between intrinsic catalytic activity and activity due to increased surface area.

Stability Analysis

The stability of the electrocatalyst is evaluated using chronoamperometry or chronopotentiometry techniques. These methods measure the ability of the catalyst to maintain consistent current density or potential over an extended period of time. High stability indicates strong structural integrity and resistance to degradation under alkaline OER operating conditions, which is essential for practical energy applications.

Gas Evolution and Faradaic Efficiency

Gas evolution measurements and Faradaic efficiency analysis confirm that the measured current is effectively used for oxygen production. High Faradaic efficiency indicates that most of the electrical energy supplied during electrolysis contributes to the generation of oxygen gas, demonstrating the effectiveness and selectivity of the catalyst toward OER.

In Situ / Operando Characterization

To see what happens during OER, measurements are done while the reaction runs:

- Spectroscopies: Raman, X-ray absorption, X-ray photoelectron, Mössbauer, UV-vis, IR, differential electrochemical mass spectrometry

These help to determine :

- Oxidation states and structure changes (e.g., $\text{CoOOH} \rightarrow \text{Co(IV)}$ superoxide, NiFe oxyhydroxides).
- Chemical oxygen species like M-OH^* , M-O^* , M-OOH^* , superoxides.
- Surface reconstruction and oxygen defects that create the real active sites.

Mechanistic and Data-Driven Approaches

- Combine electrokinetics with spectroscopy and isotope labeling ($^{16}\text{O}/^{18}\text{O}$) to identify mechanisms such as adsorbate evolution, lattice oxygen redox, and oxide path mechanisms.
- Use simulation and machine learning to fit current-voltage data and extract hidden energy profiles and rate-limiting steps.

CHAPTER 3

RESULTS AND OBSERVATIONS

3.1 X-RAY DIFFRACTION ANALYSIS OF ZINC FERRITE / SILVER CHLORIDE

The X-Ray Diffraction XRD pattern confirms the formation of crystalline phases present in the synthesized $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite by comparing diffraction peaks with standard JCPDS reference data.

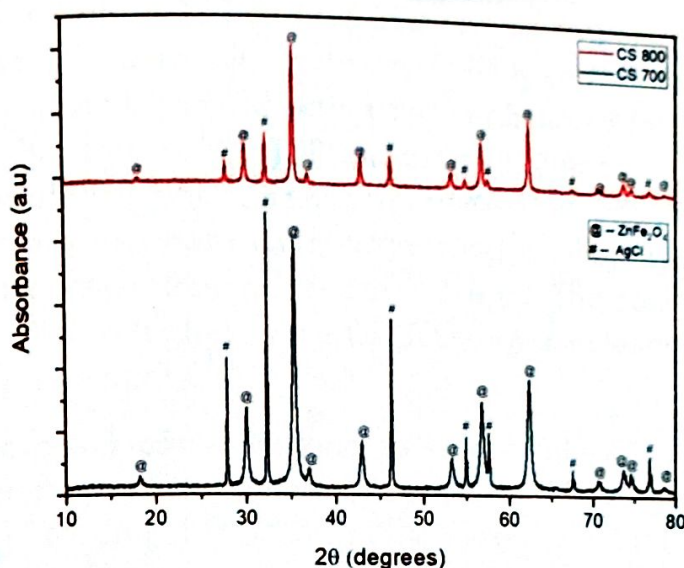


Fig 3.1 XRD graph of CS700 and CS800

Based on the given diffraction patterns and JCPDS references for ZnFe_2O_4 (00-022-1012) and AgCl (01-071-5209), both samples show formation of a spinel ferrite-halide heterostructure. The main difference arises from the calcination temperature (700 °C vs 800 °C), which affects crystallinity, peak sharpness, and phase purity.

1. Spinel ZnFe_2O_4 phase (Common for both)

The diffraction peaks observed at:
18.28°, 30.01°, 35.36°, 42.93°, and 62.27°

Correspond to the crystal planes:
(111), (220), (311), (400), (440)

Which match well with the standard data for spinel ZnFe_2O_4 (JCPDS No. 00-022-1012).

The most intense peak appears at 35.36°, corresponding to the (311) plane, confirming the formation of a cubic spinel crystal structure of ZnFe_2O_4 . The sharp peaks indicate good crystallinity of the ferrite phase.

2. AgCl phase identification (Common for both)

Additional peaks observed at:
27.90°, 32.32°, 46.28°, 54.85°, and 67.48°

Are indexed to the planes:
(111), (200), (220), (311), (400)

The most intense peak appears at 32.30° , corresponding to the (200) plane. These correspond to AgCl (JCPDS No. 01-071-5209). The presence of these peaks confirms successful formation of the silver chloride phase in the composite.

3. Crystallinity and composite formation

The XRD comparison of CS-700 and CS-800 reveals that calcination temperature plays a significant role in determining the crystallinity and structural ordering of the $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ composite. The diffraction peaks observed for CS-800 are sharper and more intense than those of CS-700, indicating higher crystallinity and improved structural ordering at the higher calcination temperature of 800°C . In contrast, CS-700 exhibits relatively broader peaks, suggesting smaller crystallite size and the presence of greater lattice strain or structural defects. The background noise in the CS-700 pattern is slightly higher, while CS-800 shows a cleaner diffraction profile, indicating better phase purity.

The characteristic peaks corresponding to spinel ZnFe_2O_4 are present in both samples; however, they appear more pronounced in CS-800, confirming enhanced formation of the cubic spinel structure at higher temperature. Similarly, the AgCl peaks are observed in both patterns, but they are clearer and better defined in CS-800, indicating improved composite formation and stronger phase integration. Secondary phases are minimal in CS-700 and nearly negligible in CS-800, suggesting that higher calcination temperature improves phase stability. Overall, the increase in calcination temperature from 700°C to 800°C promotes crystallite growth, resulting in larger grain size, improved structural stability, and better crystallinity, which are beneficial for enhanced electrochemical performance.

5. Relevance to OER performance

The formation of $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ heterointerfaces is expected to enhance electrocatalytic performance due to:

- modified electronic structure via AgCl
- stable spinel framework of ZnF
- e_2O_4 providing active catalytic sites

Thus, the XRD pattern verifies the successful synthesis of a crystalline binary nanocomposite suitable for oxygen evolution reaction (OER) applications.

3.1.1 CRYSTALLITE SIZE AND LATTICE PARAMETER

1. Crystallite Size:

The average crystallite size of the synthesized $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite was estimated from the X-ray diffraction (XRD) peak broadening using the Debye-Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4)$$

Where:

D = crystallite size (nm)

K = shape factor (0.89)

λ = wavelength of Cu K α radiation (1.5406 Å = 0.15406 nm)

β = full width at half maximum (FWHM) in radians

θ = Bragg angle ($\theta = \frac{1}{2}$ of 2θ)

Calculation from XRD peaks

The most intense diffraction peak of ZnFe₂O₄ and AgCl corresponding to the planes (311) and (200) respectively was selected for size estimation because it represents the dominant phases.

	Sample	2 θ	θ	B (degrees)	D
ZnFe₂O₄	CS700	35.359°	17.679°	0.369°	22.616 nm
	CS800	35.359°	17.679°	0.392°	21.29 nm
AgCl	CS700	32.325°	16.162°	0.146°	56.718 nm
	CS800	32.325°	16.162°	0.162°	51.200 nm

Interpretation

The calculated crystallite sizes confirm that both ZnFe₂O₄ and AgCl exist in the nanocrystalline range. The relatively small crystallite size increases the surface-to-volume ratio, exposing more active catalytic sites and facilitating faster electron transfer during the oxygen evolution reaction (OER).

The smaller crystallite size of ZnFe₂O₄ (~32.5 nm) suggests a high density of surface-active sites, while the larger AgCl crystallites (~51.5 nm) contribute to stable heterointerface formation with ZnFe₂O₄. Such nanoscale structural features are beneficial for improving electrocatalytic efficiency, charge transport, and durability of the ZnFe₂O₄/AgCl binary nanocomposite.

2. LATTICE PARAMETER

The lattice parameter of the synthesized ZnFe₂O₄/AgCl nanocomposite was determined from the X-ray diffraction (XRD) peak positions using Bragg's law and the geometric relation for cubic crystal systems. The obtained lattice parameter values were compared with standard JCPDS data to confirm the phase formation and structural integrity of the nanocomposite.

From equation (3)

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

For cubic structures such as ZnFe_2O_4 and AgCl , the lattice parameter is calculated using:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (5)$$

Where

a = lattice parameter (Å)

h, k, l = Miller indices of the plane (from JCPDS card)

d = interplanar spacing calculated from Bragg law

	Sampl e	2 θ	θ	(hkl)	Calculated lattice parameter a	Standard lattice parameters a
ZnFe₂O₄	CS700	35.36°	17.68°	(311)	8.44 Å	8.44 Å
	CS800	35.36°	17.68°	(311)	8.44 Å	8.44 Å
AgCl	CS700	32.30°	16.15°	(200)	5.54 Å	5.54 Å
	CS800	32.30°	16.15°	(200)	5.54 Å	5.54 Å

This matches the standard lattice parameters, confirming Correct phase formation, Good crystallinity, No major lattice distortion after composite formation in $\text{ZnFe}_2\text{O}_4/\text{AgCl}$ nanocomposite.

3.2 ELECTROCHEMICAL PERFORMANCE OF OER

Electrochemical measurements for the oxygen evolution reaction (OER) were carried out using a standard three-electrode configuration in 0.2 M KOH aqueous electrolyte. The working electrode was prepared by coating the catalyst ink of the synthesized samples onto a graphite sheet substrate having a geometric area of $0.5 \times 0.5 \text{ cm}^2$. The catalyst ink was prepared using DMF (Dimethylformamide) and PVDF (Polyvinylidene fluoride) as solvent and binder, respectively.

A platinum (Pt) wire served as the counter electrode, while a Saturated Calomel Electrode (SCE) was used as the reference electrode. All electrochemical potentials were initially recorded with respect to SCE.

Linear Sweep Voltammetry (LSV) measurements were performed at a scan rate of 5 mV s^{-1} in the anodic potential region to evaluate OER catalytic activity.

Since the measured potentials were referenced to SCE, conversion to the Reversible Hydrogen Electrode (RHE) scale was carried out using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059 \times \text{pH} \quad (6)$$

For 0.2 M KOH electrolyte, the pH was estimated to be approximately 13.3, which resulted in a correction factor of approximately +1.02 V. Thus yielding,

$$\begin{aligned} E_{\text{RHE}} &= E_{\text{SCE}} + 0.241 + (0.059 \times 13.3) \\ E_{\text{RHE}} &\approx E_{\text{SCE}} + 1.02 \text{ V} \end{aligned} \quad (6.1)$$

Therefore, all reported potentials were converted to the RHE scale by adding 1.02 V to the experimentally measured potentials versus SCE.

3.2.1 RESULTS AND OBSERVATIONS

3.2.1a LINEAR SWEEP VOLTAMMETRY (LSV) ANALYSIS

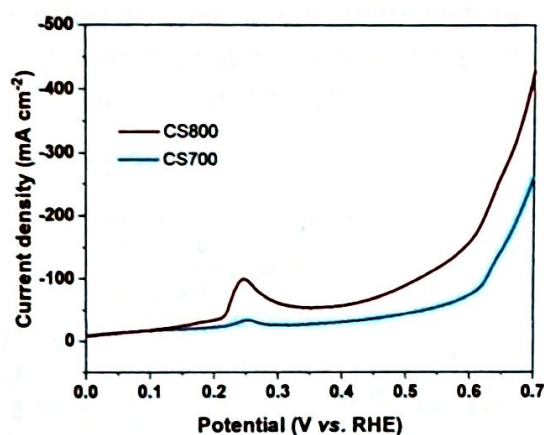


Fig 3.1 Linear Sweep Voltammetry (LSV) curves for oxygen evolution reactions by CS700 and CS800 samples.

The electrocatalytic activity of CS700 and CS800 (Fig 3.1) towards the oxygen evolution reaction was evaluated using Linear Sweep Voltammetry (LSV) in 0.2 M KOH electrolyte under a three-electrode configuration. The catalyst-coated graphite sheet acted as the working electrode, with Pt wire as the counter electrode and SCE as the reference electrode.

The polarization curves exhibit the typical anodic behavior associated with oxygen evolution. At lower potentials, both samples show negligible current density corresponding to the non-faradaic region. As the applied potential increases, the onset of oxygen evolution becomes evident, followed by a rapid increase in current density, indicating activation of catalytic sites and progression of the OER process.

Among the two samples, CS800 exhibits a lower onset potential and higher current density compared to CS700, indicating superior electrocatalytic performance

The improved performance of CS800 can be attributed to the effect of higher thermal treatment temperature, which enhances:

- Crystallinity of the material
- Electrical conductivity
- Charge transfer efficiency
- Exposure of catalytically active sites

Higher crystallinity reduces grain boundary resistance and facilitates faster electron transport from active sites to the current collector.

Furthermore, catalytic activity is strongly influenced by cation distribution and oxidation states of iron. The presence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, observed as a peak near 0.25 V, plays an important role in facilitating adsorption and transformation of OER intermediates such as OH^* , O^* , OOH^* .

These intermediates are essential for oxygen evolution, and their optimized adsorption lowers the activation energy barrier for OER.

In contrast, CS700, synthesized at lower temperature, likely contains higher structural disorder and fewer accessible active sites, resulting in comparatively slower reaction kinetics and lower catalytic efficiency.

3.2.1b TAFEL SLOPE ANALYSIS

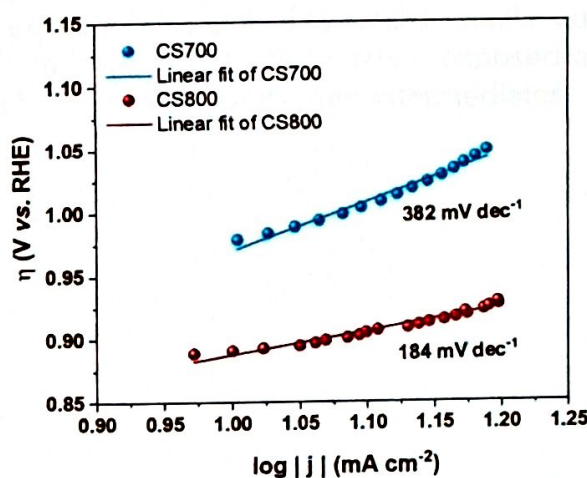


Fig 3.2. Tafel slopes for OER by CS700 and CS800 samples

The kinetics of the OER process were further analyzed using Tafel slope calculations, derived from the LSV polarization curves.

The Tafel equation, derived from the Butler-Volmer relationship, from equation (1),

$$\eta = a + b \log j$$

where:

- η = overpotential
- j = current density
- b = Tafel slope

The Tafel slope (expressed in mV dec^{-1}) provides insight into the reaction kinetics and helps identify the rate-determining step of the OER mechanism.

Tafel plots were obtained by plotting overpotential (η) against the logarithm of current density ($\log j$) within the linear region of the polarization curve.

The results indicate that CS800 exhibits a lower Tafel slope compared to CS700, demonstrating:

- Faster reaction kinetics
- More efficient charge transfer
- Reduced energy barrier for the rate-determining step

The improved kinetics of CS800 may be attributed to:

- Improved electronic structure
- Optimized adsorption energies of OER intermediates
- Enhanced conductivity due to higher crystallinity
- Favorable $\text{Fe}^{3+}/\text{Fe}^{2+}$ cation distribution

On the other hand, CS700 shows a relatively higher Tafel slope, indicating slower kinetics and higher overpotential required to achieve similar current densities. This behavior may result from lower conductivity, fewer exposed active sites, and less favorable adsorption characteristics for oxygen intermediates.

CHAPTER 4

FUTURE SCOPE

4.1 FUTURE DIRECTIONS IN (OER RESEARCH

OER limits the efficiency of water splitting and many energy devices. Recent work highlights that fully understanding charge transfer, recombination, and dynamic catalyst restructuring under realistic (often illuminated) conditions is central to future progress.

4.1.1 CHARGE TRANSFER, RECOMBINATION AND IMPEDANCE SPECTROSCOPY

Photoelectrochemical impedance spectroscopy (PEIS) is used to analyse charge transfer kinetics, recombination behaviour, and interfacial resistance in semiconductor photoanodes during the photo-oxygen evolution reaction (photo-OER). In hematite ($\alpha\text{-Fe}_2\text{O}_3$), PEIS helps distinguish between rate constants for electron transfer and electron-hole recombination, enabling identification of key efficiency limitations.

Charge Transfer and Recombination Behaviour

PEIS studies show that bulk electron-hole recombination is the major factor limiting $\alpha\text{-Fe}_2\text{O}_3$ performance. Many photogenerated carriers recombine before reaching the surface, reducing the number of holes available for OER and lowering photocurrent efficiency.

Fermi-level pinning caused by surface states also affects band bending at the semiconductor-electrolyte interface, shifting the photocurrent onset potential and increasing the required applied bias.

Role of Impedance Spectroscopy

Impedance analysis provides quantitative information on charge transfer resistance, carrier lifetime, and recombination rates through equivalent circuit modelling. These parameters help identify rate-limiting steps and guide material modifications such as surface passivation, heterojunction formation, and catalyst integration.

4.1.2 PHOTO-INDUCED OER AND INTERFACIAL ELECTRIC FIELDS

Interface-specific sum frequency generation (SFG) spectroscopy is used to study surface processes occurring during the photo-oxygen evolution reaction (photo-OER) on hematite ($\alpha\text{-Fe}_2\text{O}_3$). SFG can directly detect the formation of highly oxidized surface species such as Fe(IV)=O , which represent accumulated photogenerated holes involved in the OER mechanism.

Role of Interfacial Electric Fields

Under illumination, a space-charge electric field develops at the semiconductor-electrolyte interface. This field drives separation of photogenerated electrons and holes and influences the population of reactive Fe(IV)=O intermediates. The observations support multi-hole OER mechanisms, where multiple holes accumulate at surface sites before oxygen evolution occurs.

4.1.3 OPERANDO AND COMPUTATIONAL PROBES OF OER MECHANISM

Recent studies emphasize the importance of combining operando spectroscopy with computational modelling to understand the oxygen evolution reaction (OER) under realistic working conditions (applied potential, current density, and electrolyte environment). These approaches help identify true active sites, metastable phases, and reaction intermediates that may not be detectable under ex-situ conditions.

Role of Operando Spectroscopy

Techniques such as operando X-ray spectroscopy and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) allow direct observation of surface chemical states during OER. These methods provide evidence for key reactive species such as:

- Electron-deficient oxygen species
- Lattice oxygen participation
- O-O bond formation via oxide pathway coupling

Such observations improve understanding of catalytic behaviour in both noble-metal oxides (e.g., RuO_2 , IrO_2) and 3d transition-metal oxides (e.g., Fe, Co, Ni based catalysts).

4.1.4 BROADER RESEARCH OPPORTUNITIES IN OER MECHANISM STUDIES

1. Advanced Reaction Mechanisms

Future research should move beyond the conventional adsorbate evolution mechanism (AEM) and explore alternative pathways such as lattice oxygen mechanism (LOM), oxide-path mechanisms, and direct O-O radical coupling. These mechanisms can be systematically verified using isotope-labeled mass spectrometry and operando spectroscopic techniques, enabling direct identification of oxygen sources and reaction intermediates.

2. Multi-Scale Theoretical Modelling

There is a need to develop realistic multi-scale models that incorporate electric fields, electrolyte effects, and explicit reaction kinetics. Such models, when benchmarked with operando experimental data, can more accurately predict catalytic behaviour under practical operating conditions.

3. Stability, Defects and Structural Evolution

Operando tools can also be used to investigate defects, catalyst restructuring, and degradation processes, such as the formation of oxygen vacancies and changes in oxidation states (e.g., Ir redox evolution). Understanding these factors is essential to achieve an optimal balance between high catalytic activity and long-term stability.

Overall, integrating advanced experimental and theoretical approaches will enable deeper mechanistic understanding and support the rational design of highly efficient and durable OER electrocatalysts.

References

1. Taffa, D., Dillert, R., Ulpe, A., Bauerfeind, K., Bredow, T., Bahnemann, D., & Wark, M. (2016). Photoelectrochemical and theoretical investigations of spinel type ferrites ($MxFe_{3-x}O_4$) for water splitting: a mini-review. *Journal of Photonics for Energy*, 7. <https://doi.org/10.1117/1.jpe.7.012009>.
2. Dymerska, A., Kukułka, W., Biegun, M., & Mijowska, E. (2020). Spinel of Nickel-Cobalt Oxide with Rod-Like Architecture as Electrocatalyst for Oxygen Evolution Reaction. *Materials*, 13. <https://doi.org/10.3390/ma13183918>.
3. Gong, M., & Dai, H. (2014). A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts. *Nano Research*, 8, 23-39. <https://doi.org/10.1007/s12274-014-0591-z>.
4. Thakur, M., Kothari, D., & Sarawade, P. (2025). Nickel Cobalt Oxide as an Efficient Electrocatalyst for Overall Water Splitting in Alkaline Media. *Physica status solidi (a)*, 222. <https://doi.org/10.1002/pssa.202500447>.
5. Sahnoune, D., Makhloufi, S., & Omari, M. (2022). Structural and Electrochemical Properties of $NiFe_{2-x}Cu_xO_4$ Spinel for Oxygen Evolution Reaction. *Biointerface Research in Applied Chemistry*. <https://doi.org/10.33263/briac131.008>.
6. Zou, X., Lu, Q., Tang, M., Wu, J., Zhang, K., Li, W., Hu, Y., Xu, X., Zhang, X., Shao, Z., & An, L. (2024). Catalyst-Support Interaction in Polyaniline-Supported Ni_3Fe Oxide to Boost Oxygen Evolution Activities for Rechargeable Zn-Air Batteries. *Nano-Micro Letters*, 17. <https://doi.org/10.1007/s40820-024-01511-4>.
7. Appiah-Ntiamoah, R., Baye, A., & Kim, H. (2020). In Situ Electrochemical Formation of a Core-Shell $ZnFe_2O_4@Zn(Fe)OOH$ Heterostructural Catalyst for Efficient Water Oxidation in Alkaline Medium., 7, 3478-3486. <https://doi.org/10.1002/celc.202000834>.
8. Soni, A., Maurya, S., Malviya, M., Lal, B., & Tiwary, D. (2024). Evaluating Zn ferrite ($Zn_xFe_{3-x}O_4$; $0 \leq x \leq 1$) for alkaline water oxidation: electrochemical and spectro-electrochemical study. *Journal of Applied Electrochemistry*, 55, 147 - 161. <https://doi.org/10.1007/s10800-024-02164-2>.

9. Attarzadeh, N., Haritha, K., Nalam, P., Sanchez, F., Saini, K., Sreenivasan, S., Tan, S., Shutthanandan, V., Das, D., & Ramana, C. (2025). Enhanced Electrocatalytic Activity of Ecofriendly and Earth-Abundant (Zn,Cu)Fe₂O₄ + CuO Nanocomposites for Water Splitting.. ACS applied materials & interfaces. <https://doi.org/10.1021/acsami.4c03062>.
10. Singh, A., Kumar, S., Yadav, B., Vishwakarma, A., & Kumar, N. (2023). Evidence of oxygen evolution over sputtered zinc ferrite (ZnFe₂O₄) thin film by enhanced lattice oxygen participation. Applied Physics Letters. <https://doi.org/10.1063/5.0154955>.
11. Tan, R., Jeong, Y., Li, Q., Kang, M., & Cho, I. (2023). Defect-rich spinel ferrites with improved charge collection properties for efficient solar water splitting. Journal of Advanced Ceramics. <https://doi.org/10.26599/jac.2023.9220709>.
12. Taffa, D., Dillert, R., Ulpe, A., Bauerfeind, K., Bredow, T., Bahnemann, D., & Wark, M. (2016). Photoelectrochemical and theoretical investigations of spinel type ferrites (M_xFe_{3-x}O₄) for water splitting: a mini-review. Journal of Photonics for Energy, 7. <https://doi.org/10.1117/1.jpe.7.012009>.
13. Lee, D., Ahmad, H., Khan, A., Danish, M., & Jo, W. (2024). Versatile platform of 3D/2D/1D:ZnFe₂O₄/NiAl-LDH/MWCNTs nanocomposite for photocatalytic purification of dinoseb and electrocatalytic O₂ evolution reaction.. Environmental research, 120367 . <https://doi.org/10.1016/j.envres.2024.120367>.
14. Attarzadeh, N., Haritha, K., Nalam, P., Sanchez, F., Saini, K., Sreenivasan, S., Tan, S., Shutthanandan, V., Das, D., & Ramana, C. (2025). Enhanced Electrocatalytic Activity of Ecofriendly and Earth-Abundant (Zn,Cu)Fe₂O₄ + CuO Nanocomposites for Water Splitting.. ACS applied materials & interfaces. <https://doi.org/10.1021/acsami.4c03062>.
15. He, W., Zhang, R., Liu, H., Hao, Q., Li, Y., Zheng, X., Liu, C., Zhang, J., & Xin, H. (2023). Atomically Dispersed Silver Atoms Embedded in NiCo Layer Double Hydroxide Boost Oxygen Evolution Reaction.. Small, e2301610 . <https://doi.org/10.1002/smll.202301610>.
16. Göl, E., Aytekin, A., Özkahraman, E., & Karabudak, E. (2020). Investigation of oxygen evolution reaction performance of silver

- doped Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} perovskite structure. *Journal of Applied Electrochemistry*, 50, 1037 - 1043. <https://doi.org/10.1007/s10800-020-01457-6>.
17. Wu, L., Zhang, J., Wang, S., Jiang, Q., Feng, R., Ju, S., Zhang, W., & Song, F. (2022). Silver Decorated Hydroxides Electrocatalysts for Efficient Oxygen Evolution Reaction. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2022.136168>.
 18. Liu, J., Sang, X., Zhao, P., Li, J., Li, S., Dong, H., Zhou, X., Liu, M., & You, W. (2024). Constructing AgO/Ag₂O Electrocatalysts with Highly Exposed and Tightly Contacted Active Facets for Efficient Oxygen Evolution.. *Chemistry*, e202402951 . <https://doi.org/10.1002/chem.202402951>.
 19. Simondson, D., Chatti, M., Gardiner, J., Kerr, B., Hoogeveen, D., Cherepanov, P., Kuschnerus, I., Nguyen, T., Johannessen, B., Chang, S., Macfarlane, D., Hocking, R., & Simonov, A. (2022). Mixed Silver-Bismuth Oxides: A Robust Oxygen Evolution Catalyst Operating at Low pH and Elevated Temperatures. *ACS Catalysis*. <https://doi.org/10.1021/acscatal.2c03065>.
 20. Huo, Z., Wang, P., Zhang, Y., Hu, Y., Dong, G., Cheng, J., Geng, D., & Zhang, Y. (2024). Enhanced oxygen evolution reaction activity of oxygen-deficient perovskite catalysts with A-site defects boosted by self-assembled silver nanoparticles. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2024.09.246>.
 21. Mahmoudi, E., Fattahi, E., Bakranova, D., Delibaş, N., Asghari, E., Çoruh, A., & Niaei, A. (2025). Perovskite engineering for efficient oxygen evolution reaction through iron and silver doping. *Scientific Reports*, 15. <https://doi.org/10.1038/s41598-025-17479-z>.
 22. Căta, A., Taranu, B., Ienascu, I., & Sfirloagă, P. (2024). New PVP-Ag or Pd-Doped Perovskite Oxide Hybrid Structures for Water Splitting Electrocatalysis. *Applied Sciences*. <https://doi.org/10.3390/app14031186>.
 23. Mahmoudi, E., Fattahi, E., Bakranova, D., Delibaş, N., Asghari, E., Çoruh, A., & Niaei, A. (2025). Perovskite engineering for efficient oxygen evolution reaction through iron and silver doping. *Scientific Reports*, 15. <https://doi.org/10.1038/s41598-025-17479-z>.

24. Olowoyo, J., & Kriek, R. (2022). Recent Progress on Bimetallic-Based Spinel as Electrocatalysts for the Oxygen Evolution Reaction.. Small, e2203125 .
<https://doi.org/10.1002/sml.202203125>.
25. Luo, S., Liu, Z., Yin, X., Zhang, S., & Guo, M. (2025). CoFe₂O₄/Ag Heterocatalysts Grown on Carbonized Wood for Light-Promoted Oxygen Evolution Reaction.. Small, e2410968 .
<https://doi.org/10.1002/sml.202410968>.
26. Yang, X., Yi, G., Lv, P., Wen, S., Zhao, Y., Jing, Z., Wang, Q., Li, B., & Tang, P. (2025). Oxygen Vacancy Engineering of Metal Oxide Materials for Photoelectrochemical Water Splitting. Electron, 3. <https://doi.org/10.1002/elt2.70011>.
27. Liu, X., Zhang, G., Wang, L., & Fu, H. (2021). Structural Design Strategy and Active Site Regulation of High-Efficient Bifunctional Oxygen Reaction Electrocatalysts for Zn-Air Battery.. Small, e2006766 .
<https://doi.org/10.1002/sml.202006766>.
28. Wang, K., Zhan, S., Zhang, D., Sun, H., Jin, X., & Wang, J. (2021). Three-dimensional graphene encapsulated Ag-ZnFe₂O₄ flower-like nanocomposites with enhanced photocatalytic degradation of enrofloxacin. RSC Advances, 11, 4723 - 4739.
<https://doi.org/10.1039/d0ra09582f>.
29. Das, K., Sahoo, D., Mansingh, S., & Parida, K. (2021). ZnFe₂O₄@WO₃-X/Polypyrrole: An Efficient Ternary Photocatalytic System for Energy and Environmental Application. ACS Omega, 6, 30401 - 30418.
<https://doi.org/10.1021/acsomega.1c03705>.
30. Abdulwahab, K., Khan, M., & Jennings, J. (2023). Ferrites and ferrite-based composites for energy conversion and storage applications. Critical Reviews in Solid State and Materials Sciences, 49, 807 - 855.
<https://doi.org/10.1080/10408436.2023.2272963>.
31. Ali, A., Yi, C., & Santos, R. (2021). X-Ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. Minerals.
<https://doi.org/10.20944/preprints202112.0438.v1>.

32. Geßwein, H., Stüble, P., Weber, D., Binder, J., & Mönig, R. (2022). A multipurpose laboratory diffractometer for operando powder X-ray diffraction investigations of energy materials. *Journal of Applied Crystallography*, 55, 503 – 514. <https://doi.org/10.1107/s1600576722003089>.
33. Ali, F., Ali, A., Din, G., Younas, U., Nazir, A., Akyürekli, S., Iqbal, M., Mnif, W., & Algarni, Z. (2024). Silver and zinc oxide decorated rGO nanocomposites as efficient electrocatalysts towards oxygen evolution reactions under alkaline conditions. *Diamond and Related Materials*. <https://doi.org/10.1016/j.diamond.2024.111378>.
34. Bodicherla, N., T.V.M, S., Kumcham, P., Kisoo, Y., & Jonghoon, K. (2024). Role of Fe and Cr doped ZnO nanoparticles for electrocatalytic oxygen evolution reaction. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2024.07.437>.
35. Hanan, A., Lakhan, M., Walvekar, R., Ubaidullah, M., Al-Kahtani, A., & Khalid, M. (2024). Co₃O₄ derived ZnO: An effective electrocatalyst for oxygen evolution reaction in alkaline media. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2024.05.087>.
36. Mallikarjuna, K., Ganta, K., Kumar, T., Kumar, N., Asif, M., Vattikuti, S., & Shim, J. (2024). Enhancing Electrochemical Performance of Co₃O₄/ZnO Composite Nanostructures through Interface Engineering for Oxygen Evolution Reaction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. <https://doi.org/10.1016/j.colsurfa.2024.135858>.