Extended Abstract

$\mathrm{Fe^{III}Mo^{IV}}$-based Bifunctional Electrocatalysts for Industrial Water Splitting and Wastewater Remediation

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Scope of the Thesis

Sustainable development goals (SDGs) drive the transition from hydrocarbon-based energy systems to clean and sustainable energy systems owing to the collective threats of geopolitical instability, depleting fossil fuel reserves, and the escalating climate crisis. Among the sustainable energy alternatives, Hydrogen, with the highest gravimetric energy density of 142 MJ kg^{-1}, is the cleanest fuel alternative. Electrocatalytic water splitting using renewable energy sources represents a sustainable approach to hydrogen production. The theoretical thermodynamic cell potential required to split water into hydrogen and oxygen at room temperature is 1.23 V, corresponding to a Gibbs free energy change (ΔG) of + 237 kJ mol^{-1}. In practice, however, a higher cell voltage, ~ 1.48 V is required to achieve efficient water splitting owing to sluggish kinetics of the oxygen evolution reaction (OER), parasitic side reactions, and ohmic losses within the system. Furthermore, an additional heat input of approximately 48.6 kJ mol^{-1} is necessary for the adiabatic dissociation of water into gaseous products. To surmount this issue, transition metal-based electrocatalysts such as mono- and mixed-metal oxides, nitrides, phosphides, and sulfides have been explored due to their natural abundance. However, such catalysts are synthesized by energy-intensive processes– calcination (300–800°C), pyrolytic reduction, and use of expensive polymeric binders such as nafion 117. All of which substantially increase production costs of hydrogen. Moreover, these catalysts suffer from long-term stability during electrochemical operation, especially at high cell voltages needed for industrial scale. Hence, there is a scope of designing of durable, active electrocatalysts based on non-precious and highly abundant metal ions for reducing the Levelized Cost of Hydrogen Production (LCOH). Moreover, integration of light as an external stimulus to accelerate sluggish OER kinetics remains a hitherto unexplored area of research.

Questions that have been addressed in this thesis are:

- Scalable and energy-efficient methodology development for the synthesis of FeMo-based bifunctional electrodes.
- What sustainable binder can replace commercial Nafion^{TM} 117 for immobilizing electrocatalysts onto industrial-grade Ni foam?
- Can the synthesized electrocatalysts be benchmarked for their performances at industrial current densities?
- How can synergistic interactions among metal ions be established to achieve superior catalytic activity of electrocatalysts?
- Can light be integrated as an external stimulus to accelerate sluggish OER kinetics during water electrolysis?

Chapter 1: ***Introduction*****:** This chapter provides a comprehensive overview of the current state of green hydrogen production technologies– electrochemical, thermochemical, photochemical, photo(electro)chemical, microbial, and paired-electrochemical systems. A systematic classification of electrocatalysts is presented, encompassing noble metals as well as earth-abundant transition metal-based oxides, hydroxides, sulfides, phosphides, nitrides, and heterostructures. Various electrocatalyst fabrication methodologies are discussed. The chapter further elaborates on the fundamental electrochemical principles governing water splitting, with emphasis on the Volmer, Heyrovsky, and Tafel mechanisms. Detailed descriptions of electrochemical techniques such as cyclic voltammetry, linear sweep voltammetry, and bulk electrolysis are included. This chapter discusses geometrical activity parameters for electrocatalytic water splitting, including overpotential, Tafel slope, mass loading, substrate dependency, scan rate, iR compensation, charge-transfer resistance, and electrochemically active surface area (ECSA), and their influence on catalytic performance. The importance of intrinsic activity descriptors such as turnover frequency (TOF) and Faradaic efficiency (FE) is also emphasized. The principles of light-assisted electrocatalysis and their role in enhancing catalytic efficiency are also introduced.

Chapter 2: ***Materials and Methodology***: This chapter includes the list of all chemicals and reagents used. It presents various electrochemical characterization techniques–Chronoamperometry (CA), Chronopotentiometry (CP) including two-electrode and three-electrode configurations. It also includes charge-transfer and kinetics studies using Electrochemical Impedance Spectroscopy (EIS), including Nyquist and Bode plot analyses, along with long-term stability tests at industrial current densities. Interface characterization through Mott–Schottky analysis, intrinsic activity evaluation using TOF, exchange current density, ECSA, and double-layer capacitance (Cdl) measurements are also presented. Faradaic efficiency and hydrogen/oxygen quantification through water displacement and gas chromatography (GC) analyses are discussed. In addition to electrochemical methodologies, this chapter covers major physicochemical and structural characterization techniques such as gas chromatography for product quantification, X-ray photoelectron spectroscopy (XPS) for surface chemical state analysis, Raman spectroscopy for structural and defect investigation, electron microscopy – TEM and SEM for morphology and elemental mapping, powder X-ray diffraction (PXRD) for crystallographic characterization. These techniques provide comprehensive insight into the structure–property–performance relationships of synthesized catalysts.

Chapter 3: *Binder-Free $Fe^{III}Cu^{I}Mo^{IV}$ Electrocatalysts for Durable Water Splitting at Industrial Current Density.*

The development of highly active and durable electrocatalysts based on earth-abundant Fe, Cu, and Mo via an energy-efficient one-pot synthesis marks a decisive advancement in alkaline water electrolysis. In this chapter, a ligand-assisted one-pot strategy is adopted for the synthesis of an $Fe^{III}Cu^{I}Mo^{IV}$ electrocatalyst. Compositional tuning between Cu-rich and Mo-rich variants induces pronounced morphological evolution, including cubic and spherical structures. Among them, Fe_3CuMo_{11}, with an average particle size of 28 ± 6 nm, exhibits exceptional bifunctional activity in 1 M KOH, evidenced by overpotentials of only 85 mV for hydrogen evolution reaction (HER) at 10 mA cm^{-2} and 90 mV for the oxygen evolution reaction (OER) at 10 mA cm^{-2} along with a low Tafel slope of 70.2 mV dec^{-1}. Remarkably, a two-electrode electrolyzer assembled using Fe_3CuMo_{11}/NF as both the anode and cathode achieves a cell voltage of merely 2.082 V at 200 mA cm^{-2}, maintaining exceptional operational stability for over 500 hours under alkaline water electrolysis. The superior catalytic performance has been attributed to synergistic coupling among FeOOH, Cu_2S, and MoS_2 phases, which offer optimal adsorption energetics and accelerates charge-transfer kinetics. Our study offers a robust platform for industrially relevant alkaline water electrolysis.

Chapter 4: ***$MoO_3/Fe_2O_3/MoS_2$ Nanoflakes for Light-Assisted Water Electrolysis***

Hydrogen production via alkaline water electrolysis is limited by sluggish oxygen evolution reaction (OER) kinetics, poor durability of non-precious, earth-abundant electrocatalysts, and the energy-intensive synthesis of these catalysts. In this chapter, temporal decoupling strategy has been adopted in solvothermal synthesis of $MoO_3/Fe_2O_3/MoS_2$ heterojunction. Dimethyl formamide-extract of lemon grass serves as the effective binder to Industrial grade Ni-Foam (NF) substrate. Synthesized electrocatalyst $FeMo_{5.6}$ with a nanoflake morphology and Fe_2O_3 enrichment, exhibits OER activity with η_{10} = 76 mV and a Tafel slope of 57.96 mV dec^{-1} in 1 M KOH. Whereas $FeMo_{8.5}$ having globular shape with MoS_2-rich constituent, achieves a Hydrogen Evolution Reaction (HER) activity with η_{10} = 89 mV. Moreover, a two-electrode configuration comprising FeMo5.6/NF || FeMo8.5/NF requires only 2.4 V to reach current density of 450 mA cm^{-2} with near-unity Faradaic efficiency (~100%) and stable operation for over 500 h, meeting industrial benchmarks. Moreover, visible light harvesting capability of $MoO_3/Fe_2O_3/MoS_2$ heterojunction has been harnessed to demonstrate light integration as an impactful strategy to overcome intrinsic limitations. Under visible light illumination Fe_2O_3 facilitates hole accumulation for OER, while MoO_3 and MoS_2 support light harvesting and charge transport. This synergy lowers kinetic barriers, delivering ~85% enhanced OER activity in light-assisted water electrolysis.

Chapter 5: ***Switchable activity of FeMo heterostructure from Electrocatalytic Oxidation to Adsorptive Removal of Methylene Blue.***

In this chapter we report on FeMo-based catalysts for methylene blue (MB) dye degradation. The study examined dye concentrations ranging from 30 to 60 ppm, achieving removal efficiencies between 95% and 74% within 90 minutes. This process follows pseudo-second-order kinetics, indicating that surface-controlled interactions were the rate-limiting factor. Additionally, fitting the data to the Langmuir isotherm has confirmed that monolayer adsorption occurred on homogeneous active sites. Structural characterization of catalyst confirms the co-existence of $Fe_2(MoO_4)_3$ and MoO_3 phases - a heterostructure that provides rich Lewis's acid sites and redox-active Mo^{6+}/Mo^{5+} centres critical for dye adsorption and oxidative degradation. BET analysis reveals a surface area of 7.35 m^2/g with a mesoporous architecture (pore diameter 41.73 nm), which enhances the accessibility of dye molecules to the active sites. Recyclability tests demonstrate the stable activity of catalyst. FeMo deposited on carbon cloth also exhibit electrocatalytic oxidation of dye. MB concentration is reduced from 20 ppm to 1.4 ppm (~93% removal) within 1 hour at 0.1 V in 1 M Na_2SO_4. Catalyst durability has been confirmed over 6 hours of continuous operation, establishing FeMo as a promising dual-functional material for wastewater remediation.

Chapter 6: ***Summary and Future Scope:***

In this chapter, results have been summarized, and the future scope of the work has been outlined.

References:

Patent:

Panda, D., Kumar, M; S. Arvind; Md. Aash. "*Bifunctional Electrocatalyst for Hydrogen Production at Industrial Current Density and Process for Preparing the Same*" **Published 2025 (Application No.: 202511017168) .** *Status: Response after* 1^{st} *hearing Submitted.*

Publications:

Arvind, Md. Aash, M. Kumar, D. Panda, "*Binder-Free* $Fe^{III}Cu^{I}Mo^{IV}$ *Electrocatalysts for Durable Water Splitting at Industrial Current Density*."

Advanced Sustainable Systems (2026) *In Press***.** DOI: 10.1002/adsu.70480

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Arvind, Md. Aash, M. Kumar, D. Panda, "*Switchable activity of FeMo heterostructure from Electrocatalytic Oxidation to Adsorptive Removal of Methylene Blue*."

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