

Development of Nickel based Chalcogenides (NiIn₂S₄) Nano Electrocatalysts for Hydrogen Production

Sujay K M¹, Shivaraj B W¹, Manjunatha C^{2*}, Ashok S³, Nishchith B S⁴

¹Dept. of Mechanical Engineering, RV College of Engineering, Bengaluru -59

²Dept. of Chemistry, RV College of Engineering, Bengaluru -59

³Dept of Chemistry, School of Engineering, DSU, Bengaluru-68

⁴Dept of Physics, School of Engineering, DSU, Bengaluru-68

Abstract

Developing the efficient Oxygen Evolution Reaction (OER) electrocatalysts such as nickel-based chalcogenides (NiIn₂S₄) is of great importance to advance renewable hydrogen fuel toward further practical applications. Transition-metal sulphides have appeared to be promising non-noble metal electrocatalysts in the OER to meet future energy demands. Meanwhile, many studies focus on the fabrication of transition metal dichalcogenide because of their remarkably superior catalytic activity. XRD patterns of NiIn₂S₄ showed cubic phase with the crystallite size of 13.24 nm. Scanning Electron Microscopy (SEM) showed the average particle size of 200 nm. EDAX results showed that NiIn₂S₄ compound is composed of 61.95 weight % of Indium, 21.25 weight % of Sulphur and 16.79 weight % of Nickel. Electrochemical results showed NiIn₂S₄ has overpotential of 340 mV at current density of 50 mA/cm² solution resistance of 1.6 ohm and Reversible Hydrogen Electrode potential (RHE) onset potential from the polarization curve was 1.57 V.

Keywords: Nickel Indium Sulfide; Hydrogen Evolution Reaction; Oxygen Evolution Reaction; Transition metal dichalcogenide; Water Splitting.

1.0 Introduction

The increasing energy crisis and environmental threat produced by the excessive use of fossil fuels demand the commercialization of sustainable energy conversion and storage technologies like fuel cells, batteries, and supercapacitors to reduce the dependency on fossil fuels [1,2]. Among them, the fuel cell is reliable energy conversion technology due to its high energy density, rapid start-up, zero emissions, environmental

*Mail address: Manjunatha C, Assistant Professor, Chemistry, RV College of Engineering, Bengaluru – 59, Email: manjunathac@rvce.edu.in Ph: 9036651277

friendliness, and low operating temperature Hydrogen is considered as an ideal alternative to fossil fuels in the future [3]. Electrochemical water splitting plays a key role in the future sustainable hydrogen production and can be divided into two half reactions, cathodic Hydrogen Evolution Reaction (HER) and anodic oxygen evolution reaction (OER). OER involves multi-proton-couple electron transfer steps and suffers from intrinsically very sluggish reaction kinetics, imposing serious overpotential requirement and decreasing overall efficiency [4]. An efficient electrocatalyst is thus needed to prompt the reaction rate [5]. Currently, precious metal oxides such as RuO₂ and IrO₂ shows the highest OER [6, 7], but the scarcity and high cost of noble metals have greatly hampered their practical widespread applications.

Aiming to lower the operating overpotential, great efforts have been devoted to OER catalyst design [8]. Due to the oxygen involved reaction mechanism, oxide/hydroxide is the first choice as OER catalysts. Among various progresses, Ni, Co, Fe based catalysts show much improved activity, but a significant overpotential is still required for the state-of-the-art catalysts. Very recently, theoretical simulation indicated that there existed a ~200 mV overpotential limit for first-row (3d) transition metal oxide based OER catalyst due to a constant energy barrier between the 2nd step intermediates and the final state of the catalyst [9]. To breaking such scaling law, non-3d high-valency metals (such as W) doped Co, Fe based catalysts show further improved OER activity through near-optimal *OH energetics for OER, but a ~190 mV overpotential is still required.

Review of open literature [1-9] it was observed that many OER and HER catalysts have been reported, nickel-based chalcogenides are active in alkaline environments and also exhibit good stability with high current densities up to 100–500 mA cm⁻². Although nickel sulphides and selenides on Nickel Foams (NFs) have been prepared as OER and HER catalysts, they require high overpotentials to afford high current densities and exhibit very poor long-term durability. To the best of our knowledge, Nickel Indium Sulphide grown directly on NF for both OER and HER with long-term durability in alkaline media have not been reported previously.

2.0 Experimental Details

2.1 Materials

Nickel Nitrate [Ni(NO₃)₂.6H₂O], Indium Acetate In(OOCCH₃)₃ and Sodium Sulfide (Na₂S) was purchased from Lakumi Scientific,

Bengaluru, India. All chemicals were used as received without any further purification.

2.2 Synthesis of NiIn₂S₄ electrocatalyst

For synthesise of NiIn₂S₄ by the simple hydrothermal method using 1.396g of Nickel Nitrate, 2.805g of Indium Acetate and 1.5g of Sodium Sulfide was transferred into 100 ml Teflon tube then mixed, stirred with 80ml pure distilled water and then teflon tube is secured into 100ml autoclave sterilizer. The mixture is heated for 170 °C for 2 hours. After heating, the autoclave was taken out and cooled at room temperature, the hydrothermal treated mixture will be then transferred into a glass beaker, further it is centrifuged for 6500 RPM for three minutes so that the residues settled at the bottom of the centrifuge tube. Final residue was then transferred to a petri dish using an organic solvent and it is placed in a vacuum oven at 80 °C for one hour to evaporate the moisture, resulting in a pure NiIn₂S₄ formation. Finally, 3 mg of NiIn₂S₄ was weighed and dissolved in 0.5 ml of pure distilled water with the help of micro litre pipette for drop casting on Nickel foam Electrode (NFE). Further NFE is dried for 1 hour for proper deposition of the mixture on the electrode in a hot air oven at 70°C. After drying the NFE (Working Electrode) is dipped in the buffer solution of KOH with 13.6pH which contain the Platinum electrode (Counter Electrode) and Ag/AgCl electrode (Reference Electrode) dipped in it.

2.3 Characterization

X-ray powder diffraction (XRD, Rigaku D/max 2500) with scanning range of 10- 80° using Cu K α as radiation source with a wavelength of 1.5406Å. Scanning Electron Microscopy (SEM, TESCAN-VEGA3 LMU) were utilized to monitor the morphology and structure of nano materials.

2.4 Electrode preparation and Electrochemical Studies

The working electrodes was prepared by using drop casting method. Briefly 3mg of sample was dispersed in 300 μ L of pure distilled water with the assistance of ultrasonication for at least 1 h to form a homogeneous catalyst ink. Subsequently, the working electrode substrate, nickel foam of required area 1cm² was sonicated for 10 minutes and dried for 15 minutes in an oven in order to remove the impurities. Then, 300 μ L of the catalyst ink was dropped onto the Ni foam (1 cm \times 1 cm) at 70°C for 3 hours. The active material coated Ni foam electrode, Pt strip and Ag/AgCl in saturated KCl were used as the working, counter, and reference electrodes, respectively. The linear

sweep voltammetry (LSV) of the electrodes were recorded. Similarly, the impedance behaviour of the electrodes were recorded over the frequency interval of 0.01–100 kHz. All electrochemical measurements were carried out in a freshly prepared 1.0 mol L^{-1} KOH aqueous solution and it was used as the electrolyte under ambient temperatures and pressures.

3.0 Results and Discussion

3.1 X-Ray Diffraction

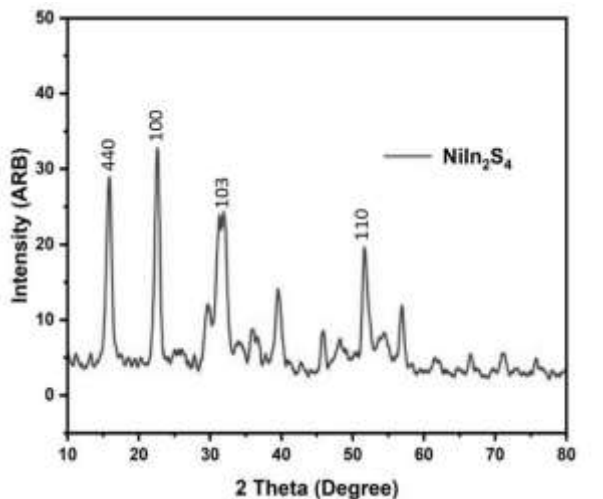


Fig 1. XRD of NiIn_2S_4 nanoparticles

Fig.1 shows the crystal structure revealed of the NiIn_2S_4 with the scanning range is from 10 - 80° . The diffraction peaks at 2θ values 16° , 23° and 33° corresponds to the (440), (100) and (103) planes respectively of the cubic system of the NiIn_2S_4 which confirms formation of NiIn_2S_4 . This XRD pattern matches well with the reported data of cubic NiIn_2S_4 with JCPDS card file No.65-6502. The crystallite size obtained for the NiIn_2S_4 (100) is 13.42 nm. Similarly, for the peaks 16° and 33° crystallite size obtained for the NiIn_2S_4 (440) and (103) is 14.19nm and 25.38nm respectively [10-12].

3.2 Scanning Electron Microscopy

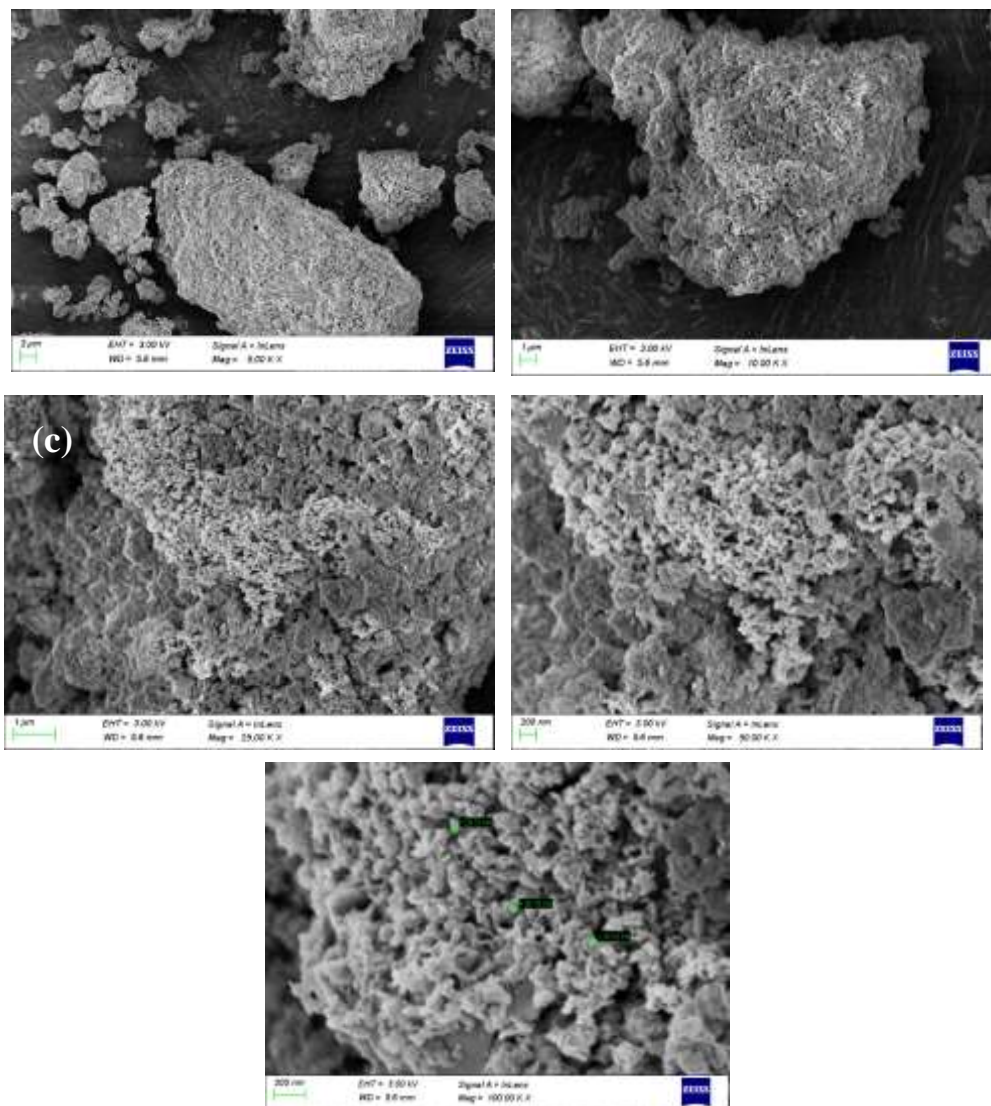


Fig. 2 SEM micrographs of NiIn_2S_4 at magnification (a) 5kx (b)10kx (c) 25 kx (d) 50 kx (e)100 kx

Fig 2 (a, b, c, d and e) shows SEM micrographs at the magnification scale of 5kx, 10kx, 25kx, 50kx and 100kx. SEM was used to study the surface morphology and information on microstructure of synthesized NiIn_2S_4 nanoparticles (13-16). It was observed that average diameter of nanoparticle was 34.9 nm and surface of nanoparticles indicating proper growth of particle and nucleation process.

3.3 Energy Dispersive X-ray Analysis (EDAX)

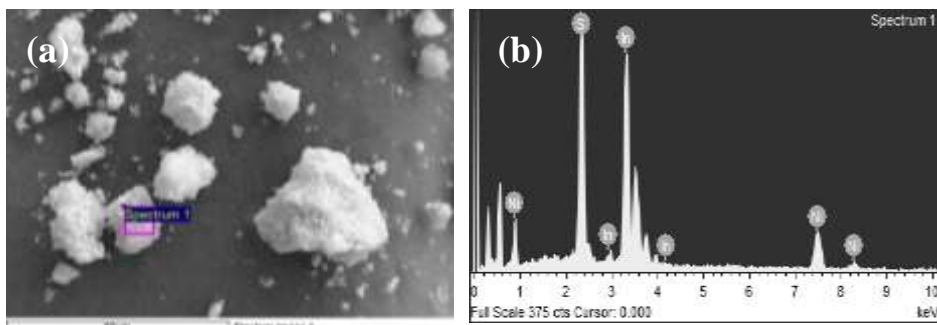


Fig. 3 (a) EDAX Spectrum of NiIn_2S_4 Fig 3.3(b)EDAX graph of NiIn_2S_4

Fig 3(a) shows the EDAX spectrum processing of NiIn_2S_4 nanoparticles. Fig 3(b) it can be observed that 61.95 % of Indium, 21.25 % of Sulphur and 16.79 % of Nickel is present [17-20].

3.3 Electrochemical Studies

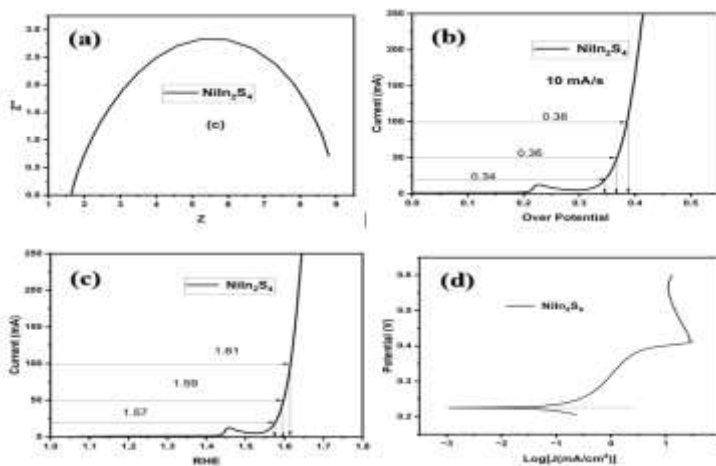


Fig.4 Electrochemical Studies (a) Nyquist plot (b) over potential (c) RHE (d) polarization Curve

Impedance and Linear Sweep Voltammetry (LSV) in 1.0 M KOH solution at a scan rate of 10 mV/s have been used in electrochemical investigations to assess the water electrocatalytic oxidation performance of NiIn_2S_4 nanoparticles made on Ni foam. NiIn_2S_4 was not coated on Ni foam with any binder materials in order to prevent any potential harm to the catalyst ability of NiIn_2S_4 . [21-23]

Electrochemical Impedance Potenti Solution resistance has been calculated using spectroscopy (PEIS). Figure 3.4(a) shows the PEIS results as Nyquist plots obtained in 1.0 M KOH at open circuit

potential. The solution resistance of Nickel Indium Sulfide (NiIn₂S₄) has been found to be 1.6 ohm [24-26].

NiIn₂S₄ shows the better water splitting ability towards OER. The overpotential (η) reported for NiIn₂S₄ electrocatalyst at current density of 20, 50 and 100 mA cm⁻² is found to be 340, 360 and 380 mV respectively which is as shown in fig 3.4 (b). Figure 3.4 (c) illustrates the redox peaks against the reversible hydrogen electrode (RHE), which is attributed to the redox process [27-30]. The values of RHE of NiIn₂S₄ electrocatalyst at current density of 20, 50 and 100 mA cm⁻² are found to be 1.57, 1.59 and 1.617 V respectively [31-34]. Fig 3.4 (d) shows the polarization curve for the NiIn₂S₄. From the plot different parameters are obtained, which includes $E_{corr} = 0.225$ V, $I_{corr} = 0.8485$ mA/cm², $\beta_a = 0.02884$ V and $\beta_c = 0.08787$ V [35-37].

4.0 Conclusion

The developed Nickel indium Sulphide as electrocatalyst by simple hydrothermal method for OER which has been found to be a highly efficient, stable, cost-effective, and low overpotential oxygen evolution electrocatalyst. NiIn₂S₄ as electrocatalyst showed OER at low overpotential of 340 mV at 20 mA cm⁻² in 1.0 M KOH. The oxygen evolution onset happened at a low potential of 1.577V (vs RHE), and this oxygen evolution potential is the lowest for Ni-based chalcogenides electrocatalyst reported so far. The synthesis of NiIn₂S₄ electrocatalysts is very simple, making it a very appealing and competitive nonprecious catalyst for OER. These results are very inspiring for non-noble metal electrocatalyst for water oxidation, and it is foreseen that this exploration will further promote the methods and knowledge to develop highly stable, efficient and robust electrocatalysts for water oxidation.

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