

## SYNTHESIS, CHARACTERISATION AND APPLICATION OF A NOVEL FeO-TiO<sub>2</sub>-GO MIXED OXIDE COMPOSITE CATALYST FOR HYDROGEN EVOLUTION REACTIONS

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### ABSTRACT

The present work deals with the preparation and characterisation of a novel TiO<sub>2</sub>based electrocatalyst for hydrogen evolution reaction. Recently many renewable energy researches are on-going, focus on the electrocatalytic water splitting to generate hydrogen. The most efficient electrocatalysts used for HER are Pt group metals, but they are very expensive and scarce. So modified transition metal catalysts are preferred. TiO<sub>2</sub> is regarded as widely used electrocatalyst in HER due to its high chemical stability, low cost and nontoxic properties. TiO<sub>2</sub> catalysts can be modified using transition metal loading. Modification of electrocatalytic activity of TiO<sub>2</sub> was done by the incorporation of GO and FeO in its frame work. FeO-TiO<sub>2</sub>-GO mixed oxide composite was prepared by thermal decomposition method. The mixed oxide FeO-TiO<sub>2</sub>-GO composite was coated on the mild steel substrate by electroless plating process. The electroless plating process was repeated by varying amounts of prepared catalyst composites. The prepared mixed oxide composite was evaluated by various characterisation techniques such as X- ray diffraction analysis, FT-IR, UV- Visible spectroscopy etc. The improved surface morphology of the prepared mixed oxide composite coated Ni-P/Co-P plate was confirmed by scanning electron microscopy. The electrochemical evaluation of the substrate surface was done by OCP analysis in order to find the long term stability of the FeO-TiO<sub>2</sub>-GO composite incorporated electroless nickel plate. The enhanced electrocatalytic activity and the kinetic behaviour of the prepared composite were studied using Tafel polarisation curves.

**KEYWORDS:** TiO<sub>2</sub> Electrocatalyst, HER, Transition Metal Doping, Graphene Oxide, OCP Analysis, Tafel Polarization Curves.

The global energy demand of modern society will be double within next 30 years. Over consumption of energy, over population, poor distribution system, wastage of energy, all these have a great contribution to future energy crises. Now a days world's energy demand is primarily satisfied by fossil fuels, which is a non-renewable source of energy and leads to environmental issues. So an alternative non-polluting energy source is required. Hydrogen energy is a good alternative to replace conventional carbon based fuels system. Hydrogen can be considered as a green fuel because it combustion generate only water as by product and there will be no carbon dioxide or sulphur dioxide emission. It has a number of advantages like, availability, affordability, efficiency, and eases of conversion and cost effective. Natural hydrogen is always associated with other elements to form water, coal, petroleum. So we have to manufacture hydrogen either from water or from hydrocarbons. Water electrolysis is an important method for extremely pure hydrogen production. Hydrogen Evolution Reaction (HER) takes place through three steps, in the primary step discharged proton get adsorbed to the metal surface (Volmer reaction), in the second step electrochemical desorption of hydrogen from metal surface and which leads to the formation of molecular hydrogen: (Heyrovsky reaction) and in the final step recombination of desorbed hydrogen from metal surface results in H<sub>2</sub> production (Tafel

reaction). But till hydrogen generation from electrochemical water splitting remains a minor contribution 4 %, to overall hydrogen production. In fact this is due to the lack of an efficient catalyst for HER. Generally Pt group metals are using in HER because of its excellent electrochemical activity and minimum over voltage during HER, but due to its expensive and low abundance nature, researchers are rather focused on modified transition metal usage. TiO<sub>2</sub> is widely accepted as an electrocatalyst for HER due to its green, high oxidizing power, high chemical stability, low cost and nontoxic nature (Li et al., 2009). But certain factors like its large intrinsic band gap, fast charge carriers recombination rate inhibit its usage in HER during photochemical pathways. The activity of TiO<sub>2</sub> can be improved by chemical modification of its frame work by metal or non-metal doping process. Several investigations suggest that addition of transition metals or its oxide can improve the electrocatalytic performance of TiO<sub>2</sub>. Catalytic property of Fe/TiO<sub>2</sub> composite has a wide range of application in catalysis, catalytic oxidation (Long et al., 2002) and electrochemical water splitting (Khan et al., 2008). The stability of HER is indirectly related to the support material used. Graphene oxide (GO), a mono layered carbonaceous species has gained more attention in recent years due to its high specific surface area, promising mechanical strength, greatest intrinsic carrier mobility and

high thermal stability (Rong et al., 2009). In large scale hydrogen production modified Hummer's method is used for graphene production (Hailing et al., 2011)

## MATERIALS AND METHODS

### Preparation of Graphene oxide Supported Mixed Oxide Composite

Graphene oxide (GO) used for the preparation of composite was synthesized using modified Hummers method. Briefly, about 2.0 g of graphite powder was put into cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub>. In this mixture about 8.0 g KMnO<sub>4</sub> under stirring condition. The temperature of the mixture was kept between 10 °C by cooling. The reaction mixture was continued for 2 hour, below 10 – 35 °C for 1 hour and further diluted with 100 ml deionized (DI) water under ice cold condition. After the complete addition of 300 ml DI water, approximately 20 ml of 30 % H<sub>2</sub>O<sub>2</sub> was added to the mixture to terminate the reaction. The colour of the mixture changed into black (Hailing et al., 2011).

FeO-TiO<sub>2</sub> mixed oxide composite was prepared by thermal decomposition method. The materials used were ferric chloride (anhydrous), FeCl<sub>3</sub> and titanium isopropoxide, Ti[(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>. The required amount of Ti[(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> and FeCl<sub>3</sub> was dissolved in isopropanol having definite concentration. In order to homogenize, the mixture was kept at room temperature for 4-5 hours with constant stirring and then evaporated to dryness in a china dish followed by heating at 120 °C for 1 hour in an oven. The resulting powder was then ground using a mortar and pestle and then treated at 450 °C in a controlled muffle furnace for 1 hour, for the complete conversion of FeCl<sub>3</sub> and Ti[(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> into their corresponding oxides. The graphene oxide - supported mixed oxide composite (Here after it is designated as FeO-TiO<sub>2</sub>-GO) was prepared by thermal decomposition method. 20 mg GO was mixed in 80 ml DI water and 40 ml ethanol by ultra-sonication treatment for 3 hours, 200 mg FeO-TiO<sub>2</sub> composite is added to it and stirred for 2 hours. The suspension was placed in teflon lined autoclave and maintained at 120 °C for 3 hours to simultaneously achieve the reduction of GO and the deposition of TiO<sub>2</sub>. The resulting composite was recovered by filtration, rinses with DI water and dried at 100 °C.

### Preparation of Electrodes Through Electroless Plating Process

The composition of the plating solution and the operating conditions has great influence on the properties of the substrate. Plating is carried out by the immersion of

substrate with a catalytic coating in a solution containing Ni ions, Cu ions and a suitable reductant sodium hypophosphite at temperature 85 ± 2 °C. The factors like pH and temperature will also affect the coating process. More than 70 % bath composition is deposited on the substrate by the reduction of sodium hypophosphite. The main advantage of these solutions includes low costs, greater ease of process control etc. The composition of plating bath and conditions as given in table.1. The substrate used for the present study was mild steel having the dimension of (1 cm × 1 cm × 0.1 cm). The pretreatment of mild steel substrate carried out according to standard method. After physical and chemical treatment of the substrate, it undergoes a 2 step activation process. In the first step cleaned substrate is treated with a solution containing SnCl<sub>2</sub>/HCl and then placed in a nucleation solution having PdCl<sub>2</sub>/HCl. After the surface activation of the substrate the prepared FeO-TiO<sub>2</sub>-GO composite catalyst was coated on the mild steel by electroless plating process. The electroless plating process are repeated by varying different amount of prepared composites. The mixed oxide incorporated Ni-P coatings were developed by adding the composite on electroless Ni-P bath at the deposition process. The entrapment of FeO-TiO<sub>2</sub>-GO composite in Ni-P matrix was carried out at 85 ± 2 °C for 2 hours. The amount of sodium hypophosphite in electroless bath was constant (2 g/L) with varied concentration of FeO-TiO<sub>2</sub>-GO composite as 1 g/L, 2 g/L and 3 g/L. The pH of the bath selected as above 7.0 which was achieved by adding suitable amount of ammonia solution.

**Table 1: Showing electrode bath composition for electroless plating process**

Sl. No.	Chemical Used	Composition (g/L)
1	Nickel sulphate	10
2	Succinic acid	2
3	Sodium hypophosphite	2
4	Cobalt sulphate	10,0
5	Trisodium citrate	1.5
6	Ammonium sulphate	1.5
7	Composite	5,3,1
<b>pH&gt;7, Temperature = 85±2°, plating duration = 2 hours</b>		

## CHARACTERIZATION

The prepared mixed oxide composite of FeO-TiO<sub>2</sub>-GO is evaluated by various characterisation techniques such as X- ray diffraction analysis, FT-IR, UV-Visible spectroscopy etc. Crystalline nature and phase analysis of the composite was studied by recording their X ray diffraction analysis on a Bruker D8 advance X ray

diffractometer equipped with monochromated Cu K<sub>α</sub> radiation at a tube voltage of 40 kV and a tube current of 30 mA, based on standard JCPDS values. It also aids in the finding the chemical composition of the prepared FeO-TiO<sub>2</sub>-GO composite. The particle size of the composite and GO was determined by Scherrer equation. The FT-IR analysis was performed to investigate the structural and functional group present in the prepared composite. The absorption spectra was recorded over the range of 4000-650 nm, it gives an idea about the electronic level interactions and band gap of the composite. The improved surface morphology of the FeO-TiO<sub>2</sub>-GO mixed oxide composite coated Ni-P/Co-P plate is confirmed by scanning electron microscope SEM JEOL JSM-840A at different magnifications.

### Electrochemical Measurements

FeO-TiO<sub>2</sub>-GO incorporated Ni-P/Co-P electrode was prepared by electroless plating process. In present work 1g/L prepared catalyst was dispersed in electrode bath solution containing 1:1 Ni-Co solution, Succinic acid, sodium hypophosphite, trisodium citrate. The electrochemical evaluation of the substrate was done by a three electrode system. The OCP analysis of the plate in 32 % NaOH was measured with reference to Hg/Hg<sub>2</sub>Cl<sub>2</sub> 1M Cl<sup>-</sup> electrode using a multimeter [Aplab, model 1089] in order to find the long term stability of the FeO-TiO<sub>2</sub>-GO composite incorporated electroless nickel plate. The enhanced electro catalytic activity and the kinetic behaviour of the composite were evaluated from Tafel polarisation studies. The tafel analysis is done DIGI-IVY potentiostat and the tafel parameters were calculated by using the equation,  $\eta = k \times \ln \frac{i}{i_0}$ .

## RESULTS AND DISCUSSION

### Surface and Compositional Characterization

The crystalline nature and phase analysis of the samples were studied by X-ray Diffraction analysis. The XRD patterns of graphite, graphene oxide (GO) and mixed oxide composite FeO-TiO<sub>2</sub>-GO catalysts are depicted in Fig.1. Graphene oxide shows a sharp peak at 11.68° which corresponds to (001) plane, which is in good agreement with previous studies (Cao et al., 2004] whereas graphite shows a peak 26.58° which corresponds to the plane (002). Using Scherrer equation it was found that GO has a high interlayer distance as compared to graphite. Graphite is a 2D hexagonally packed carbonaceous species with lack of chemical reactivity. But the presence of surface defects makes it easier for modification. Oxygen

containing functional groups such as epoxy, carbonyl, hydroxyl are incorporated to its surface to synthesis GO. The increase in interlayer distance reveals the attachment of chemical groups and thus indicates the successful synthesis of GO from graphite. The incorporation of Fe was confirmed by the peak broadening at 2θ = 28.26°. The well-defined sharp peak obtained in the spectra reveals the crystalline nature of the composite. The particle size of GO and composite were determined by Scherrer equation as 0.096 nm and 1.215 nm respectively.

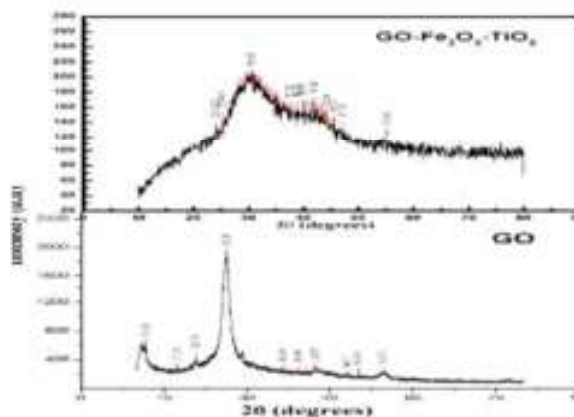
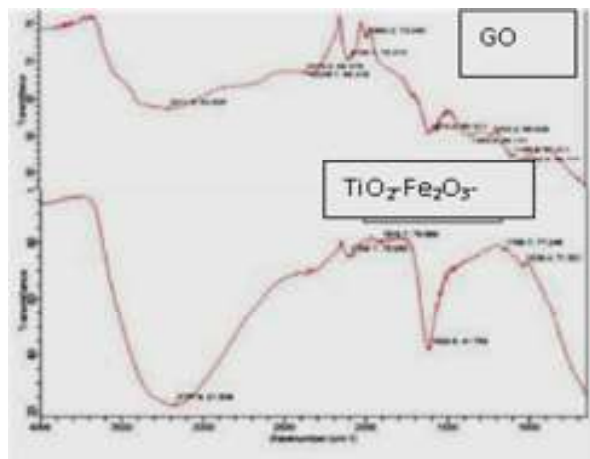


Figure 1: XRD pattern of GO and Mixed oxide

IR spectra analysis was performed to investigate the structure and functional groups of the materials, as shown in Figure 2(b). GO was produced by oxidative treatment of graphite via modified Hummers method. The absorption peak at 1233 cm<sup>-1</sup> and 1363 cm<sup>-1</sup> are assigned to stretching of epoxy and tertiary C-OH group respectively. The band at 1613 cm<sup>-1</sup> is due to aromatic vibration and at 1050 cm<sup>-1</sup> is assigned to C-O stretching vibrations. The presentation of oxygen-containing functional groups, such as C=O and C-O, further confirmed that the graphite indeed was oxidized into GO and was consistent with the literatures (Abiye et al., 2016, Cao et al., 2009, Qui et al., 2012). The presence of C=C groups showed that even graphite had been oxidized into GO. The main structure of layer graphite was still retained. The FeO-TiO<sub>2</sub>-GO composite showed apparent adsorption bands for the O-H (3177.9 cm<sup>-1</sup>), aromatic C=C (1620 cm<sup>-1</sup>), carbonyl, C=O (1918 cm<sup>-1</sup>), Ti-OH (1158 cm<sup>-1</sup>), epoxy C-O (1039 cm<sup>-1</sup>) groups. The results of XRD and FT-IR synthesis both further demonstrated the successful synthesis of FeO-TiO<sub>2</sub>-GO composite.



**Figure 2: Shows the FTIR spectra of GO and prepared composite TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-GO.**

Improved surface morphology of coating was confirmed by Scanning Electron Microscopy (SEM). The SEM images of the plates are shown in figure 3. The difference in the morphology of the pure Ni-P coatings and the plates incorporated with Co is clearly visible from the SEM pictures. The pure Ni-P coating had refined, smooth surface and uniform grains with nodular structure. The appearance of cauliflower like nodules, which is a typical amorphous material, was observed in earlier structure for electroless Ni-P coating (Sankara.Narayanan et al., 2006). The incorporation of cobalt had resulted in the formation of Ni-P-Co coatings with small granules like

structure non uniformly distributed on the surface leading to higher surface area enhancing higher catalytic activity.

### Electrochemical Characterization

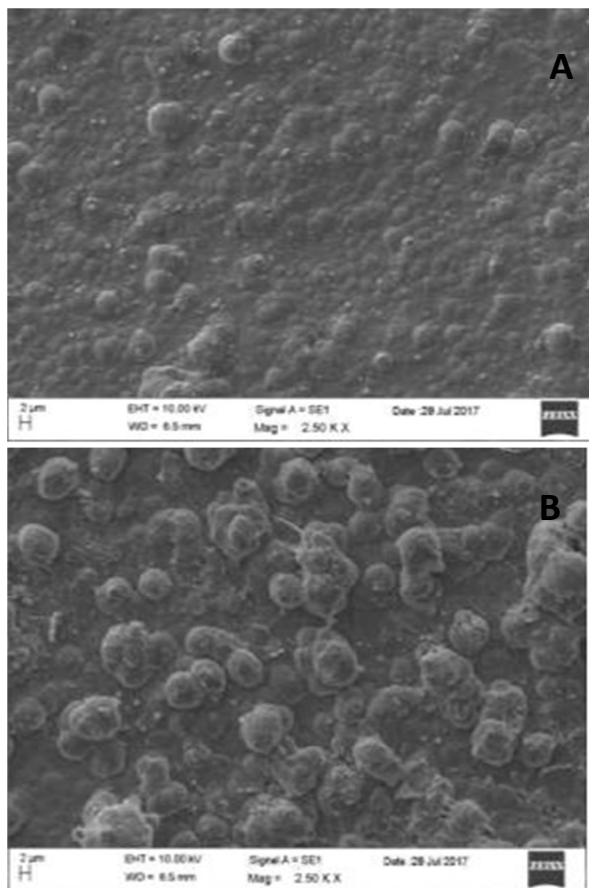
The enhanced catalytic activity and kinetic behaviour of the composite incorporated Ni-P/Co-P plate with 2.0 g phosphorus content was confirmed by the Tafel parameters obtain from Tafel polarization curve. Typical tafel plot of pure Ni-P, 0.1 g composite incorporated Ni-P coating with 2.0 g/L phosphorus contents, pure Ni-P/Co-P and 0.3 g composite incorporated Ni-P/Co-P coating with 2.0 g/L phosphorus contents are compared in Fig.4. The nickel and cobalt incorporated with GO plates exhibit high  $E_{corr}$  value such as 0.278 V and low corrosion current density,  $I_{corr}=1.4555 \mu\text{A}/\text{cm}^2$  than that of other modified electrodes. The  $\beta_c$ ,  $\beta_a$ ,  $E_{corr}$  and  $I_{corr}$  values of the modified electrodes are depicted in Table.2. The Polarisation resistance ( $R_p$ ) is the slope of linear polarization curve, which is inversely proportional to corrosion rate. The  $R_p$  values of the plate with composite content (Ni-P/Co-P + 0.3 g composite) observed as  $8.9018 \times 10^3$  ohm indicate that it has low corrosion rate and is more corrosion resistive than others. Compared to other electrodes, gas evolution kinetics behavior of the composite incorporated (Ni-P/Co-P + 0.3 g composite) was confirmed by tafel plots.

**Table 2: Showing Tafel parameters.**

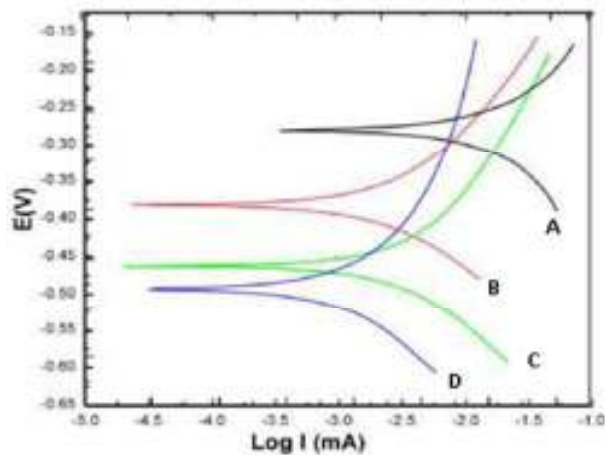
Sample	Composition	$\beta_c$ (mV)	$\beta_a$ (mV)	$E_{corr}$ (mV/dec)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )
A	(Ni-P/CoP+0.3g)	205.3	260.5	-278.502	1.455
B	(Ni-P/Co-P)	153.3	128.8	-381.392	2.722
C	(Ni-P+0.1g)	94.4	84.2	-434.058	10.604
D	(Ni-P)	138.71	108.5	-507.08	12.048

The long term stability of the composite incorporated with 2.0 g/L phosphorous content in 3% NaOH solution was studied by open circuit potential (OCP) analysis. The OCP of FeO-TiO<sub>2</sub>-GO mixed oxide incorporated electroless nickel with varying amounts of composite with fixed amount of sodium hypophosphite was monitored with respect Hg/Hg<sub>2</sub>Cl<sub>2</sub>, Cl<sup>-</sup> reference electrode. The trends in the OCP of composite incorporated Ni-P coating with 2.0 g/L phosphorous content versus time up to a period of 10 days were monitored is shown in figure 3.6. From the OCP values it was clear that 3 g/L FeO-TiO<sub>2</sub>-GO mixed oxide composite incorporated Ni-P-Co plates with phosphorous content (2.0 g/L) has lower shift in the

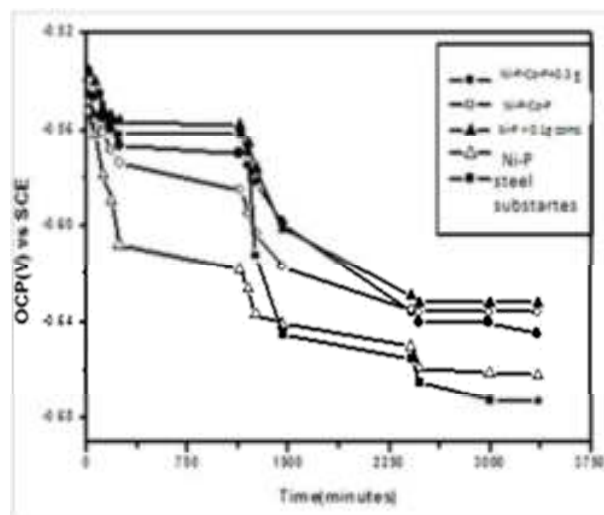
cathodic potential when compared to the plates with low and high composite content and that of pure Ni-P and pure Ni-P-Co coatings. It revealed the higher stability of 0.3 g composite incorporated Ni-P-Co plates in 32 % NaOH solution. In the case of varying composite composition, the shift in cathodic potential was more prominent in 0.3 g composite incorporated Ni-P-Co plate with 2.0 g/L phosphorous content.



**Figure 3:** Showing the SEM image of (A) pure Ni-P coated plate and (B) Co incorporated Ni-P coated plate.



**Figure 4:** The Tafel polarization curves for the HER in 32 % NaOH on (A) pure Ni-P and (B) Ni-P + 0.1 Composite (C) Ni-P +Co-P (D) Ni-P +Co-P+ 0.3 Fe<sub>2</sub>O<sub>3</sub> mixed oxide composite incorporated Ni-P plate with 2.0 g/L phosphorous content.



**Figure 5:** Showing Open circuit potential curves of steel incorporated with varying amount of composite for a period of 10 days immersion in 3 % NaCl at temperature 30 ±2 °C [■– steel substrates, ● – Ni-P + Co-P + 0.3 g Composites, ○ – Ni-P + Co-P, ▲ – Ni-P + 0.1 g composites and Δ - pure Ni-P.

### CONCLUSION

In the present work, the mixed oxides FeO-TiO<sub>2</sub>-GO incorporated Ni-P plates were developed and explored as an efficient electrode for hydrogen production from alkaline electrolytes. Morphological development and the catalytic activity of mixed oxide with FeO-TiO<sub>2</sub>-GO studied. Chemical composition of the coating was measured by X-ray diffraction spectrometry. The electrochemical evaluation of the substrate surface was done by polarization and OCP evaluation in order to evaluate the ability of FeO-TiO<sub>2</sub>-GO for the favorable hydrogen evolution reactions. In this work, we designed and fabricated a novel functional of FeO-TiO<sub>2</sub>-GO by thermal decomposition for catalytic hydrogen evolution reaction. The FTIR indicated that existence of strong interfacial interaction between graphene and FeO - TiO<sub>2</sub> surface. The XRD pattern revealed that the graphene effect on the crystalline behaviour of FeO - TiO<sub>2</sub> surfaces. Morphological analysis of the FeO-TiO<sub>2</sub>-GO revealed that nanoparticles were uniformly assembled on the surface of graphene. The mixed oxide composite and the composite incorporated Ni-P were found to be stable and reliable. The tafel parameters reveal the enhanced hydrogen evolution capacity of the FeO-TiO<sub>2</sub>-GO incorporated substrates. From the above results, the FeO-TiO<sub>2</sub>-GO is a suitable and promising material for high tech

applications such as hydrogen evolution catalysts. In the present work highlights the suitability of incorporated substrate as a catalyst for HER<sub>s</sub>. In the future work the FeO-TiO<sub>2</sub>-GO composite can be used as an electro catalyst for the oxygen evolution reactions (OERs). The composite also be used as coating steel for corrosion protection by electro less nickel plate. The mixed oxide catalyst has yielded significantly very low over potential during HER. Low percentage of TiO<sub>2</sub> (10 wt. %) are sufficient to give high catalytic activity for the HER and reduce the cost of catalyst when compared to bulk noble metal usage.

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