

Foam-Like Electroplated Ni-W/Graphene Oxide Composite Coating with High Porous Surface: An Efficient Electrocatalyst for the Hydrogen Evolution Reaction

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Abstract: In this research, the morphology of the Ni-W coating was modified by adding graphene oxide (GO) nanosheets so that a foam-like structure with high porosity and holes in the form of intertwined tunnels was obtained. Different amounts of GO nanosheets were added to the plating bath, and the resulting coating was examined. To estimate the electrochemically active surface area, the cyclic voltammetry (CV) test was used. Moreover, the linear polarization test (LSV) and chronoamperometry in 1 M NaOH were conducted to investigate the electrocatalytic activity for the hydrogen evolution reaction (HER). It was found that by adding 0.4 g/L GO to the electroplating bath, the electrocatalytic properties are doubled, and the active surface of the electrode is significantly increased.

Keywords: Electrocatalyst, Ni-W/graphene oxide composite coating, Porous surface, Hydrogen evolution reaction (HER), Electrodeposition, Cyclic voltammetry.

1. INTRODUCTION

Pollution of hydrocarbon fuels threatens human life by causing climate changes and health problems. For this reason, the development and use of clean and renewable energy are part of the plans of many governments. On the other hand, developing renewable energy can meet the ever-increasing energy demand in the world. Hydrogen is a crucial and readily available renewable energy, which is also referred to as the energy source of the 21st century [1-4].

Hydrogen is the most abundant element in the world and can be used by humans as a clean, stable, and efficient fuel. Water is the most available source of hydrogen on earth, which can be extracted and stored through electrolysis. Hydrogen is converted into electricity by a fuel cell, and its output is water. Another characteristic of hydrogen is its high specific energy density, producing up to three times more energy per unit volume than gasoline [5-7].

Currently, one of the main goals for the economicization of this clean energy is finding an electrode with high electrocatalytic properties to replace platinum, and many researchers are conducting investigations to address this issue [8-14]. Nickel is one of the elements that has shown good catalytic properties, and various studies have been conducted to modify its

structure and increase its active surface area. Moreover, different alloy elements have been used to improve the properties of the nickel electrode [15-18]. Nickel alloys enriched with elements such as tungsten, cobalt, and molybdenum have promising electrocatalytic properties. This finding underscores the rationale for focusing efforts on improving these electrodes [19-23].

One of the effective ways to increase the catalytic properties of the electrode is to increase the active sites on the surface and acquire a nanostructure. Creating a porous and hollow surface structure is the main approach to achieving this goal. Currently, many materials that have this feature exist in the form of powder. However, by adding polymer adhesives to connect the powder to the surface of the electrode, new challenges, such as the blocking of active sites and the instability of the electrode over extended periods, have been introduced [24-28].

This research has observed a unique morphology change with many foam-like pores by adding graphene oxide (GO) nanosheets to nickel tungsten coating. This morphology contains hollow cavities and interconnected channels that dramatically increase the active surface area of the electrode.

2. EXPERIMENTAL PROCEDURES

A simple carbon steel substrate with dimensions

of 3×6 cm (The exposed surface was 3×3 cm) was sanded with the SiC sheet number 1000. To degrease the surface of the substrate, ethanol and acetone were used for 5 and 15 min in an ultrasonic bath. Then, the samples were washed with distilled water, placed in 10% HCl solution for 20 s for surface activation, immediately washed with distilled water, and placed in the electroplating bath with the combination in Table 1. The GO nanosheet was homogenized by ultrasonication for 30 min and put in the electroplating bath. The amounts of GO added to the tub and the names of the samples are listed in Table 2. The pH of the solution was 4.8, and pure nickel with dimensions of 4×8 cm (The exposed surface was 4×6 cm) was used as the anode. Plating was conducted with an average current of 400 mA/cm^2 , 70% duty cycle, and a frequency of 100 Hz. The bath temperature was kept constant at 60°C , and the distance between the anode and cathode was 30 mm. $\text{Na}_3\text{C}_6\text{H}_5\cdot 2\text{H}_2\text{O}$ and NH_4Cl were used as complexing agents.

Table 1. Composition of electroplating bath

$\text{NiSO}_4\cdot 7\text{H}_2\text{O}$	15.8 g/L
$\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$	46.2 g/L
$\text{Na}_3\text{C}_6\text{H}_5\cdot 2\text{H}_2\text{O}$	147.1 g/L
NH_4Cl	26.7 g/L
NaBr	15.4 g/L

Table 2. Amounts of graphene oxide and names of samples

GO1	GO= 0.1 g/L
GO2	GO= 0.2 g/L
GO3	GO= 0.3 g/L
GO4	GO= 0.4 g/L

To examine and compare the surface morphology of the samples, field emission scanning electron microscopy (FESEM) and X-ray energy diffraction spectroscopy (EDS) were used to determine the chemical composition of the coatings. Electrocatalytic properties were investigated using the linear polarization test (LSV) and chronoamperometry. Moreover, the active surface area of the coating was estimated by cyclic voltammetric (CV) analysis at a potential of +50 to -50 compared to the open circuit potential (OCP) at different scanning speeds from 10 to 100 mV/s. The three-electrode test was performed with a platinum electrode as the counter electrode, the coated sample as the working electrode, and

calomel as the reference electrode in a 1 M NaOH solution. Additionally, the chronoamperometric test was performed at a negative cathode voltage of -1.2 V. Fourier transform infrared spectrometry (FTIR) analysis was used to investigate GO nanosheets.

3. RESULTS AND DISCUSSION

3.1. Morphology and Microstructure of the Coating

As shown in Figure 1, with an increase in GO nanosheets in the electroplating bath, the coating morphology is wholly changed, and a foam-like structure with high porosity is obtained. When GO nanosheets are incorporated into the coating during electroplating, the surface of the sheets becomes a new site for the germination and growth of the nickel-tungsten alloy. In addition, the dispersion of GO nanosheets with random directions creates a porous structure containing holes in the form of intertwined tunnels. The presence of GO nanosheets and the germination of alloy grains on them can be observed in Figure 2. The morphological changes significantly increase the active surface of the catalyst. It has also been observed that an increase in the amount of GO nanosheets in the electroplating bath corresponds to an increased number of GO sheets on which Ni-W alloy germination did not occur or was minimal. The reason for this phenomenon, which is generally observed in the surface layer and the last stage of layering, is the presence of more nanosheets and a sharp increase in suitable places for germination. The results of the EDS analysis and the dispersion of Ni, W, and C elements are displayed in Figure 3.

3.2. Investigation of Electrochemical Properties

A CV test is used in the range of ± 50 mV compared to the OCP when there is no Faraday current to estimate the electrochemically active surface area. In this interval, Equation 1 applies [29]:

$$|j_{dl}| = C_{dl} \cdot v \quad (1)$$

C_{dl} is the electric double-layer capacitance, $|j_{dl}|$ is the capacitive current density, and v is the potential sweep rate. At a given scan rate, the current density is calculated in the direction of movement from the OCP to positive values of the potential (j_{anodic}) and the reverse direction ($j_{cathodic}$). Half of the obtained current density difference is the capacitive current density.

$$2 \times |j_{dl}| = |j_{anodic} - j_{cathodic}| \quad (2)$$

Figure 4 shows the results of the CV analysis. By performing the CV analysis at different scanning speeds and drawing the corresponding graphs, it can be seen that by increasing the potential

scanning speed, the CV rings become larger. At the OCP, the capacitive current density is plotted as a graph in terms of the scan rate, and the slope of this graph is calculated.

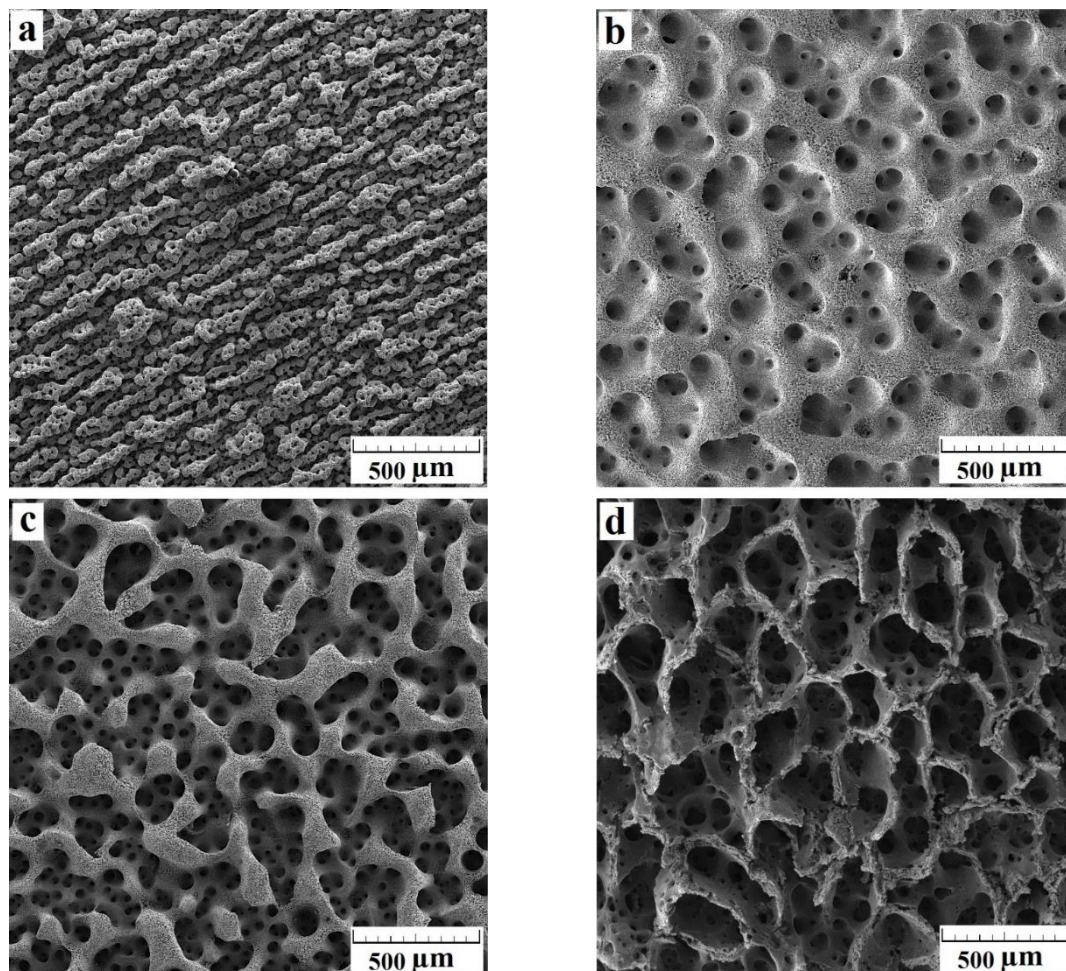


Fig. 1. SEM images related to surface morphology of Ni-W/Go coating a) GO1, b) GO2, c) GO3, d) GO4

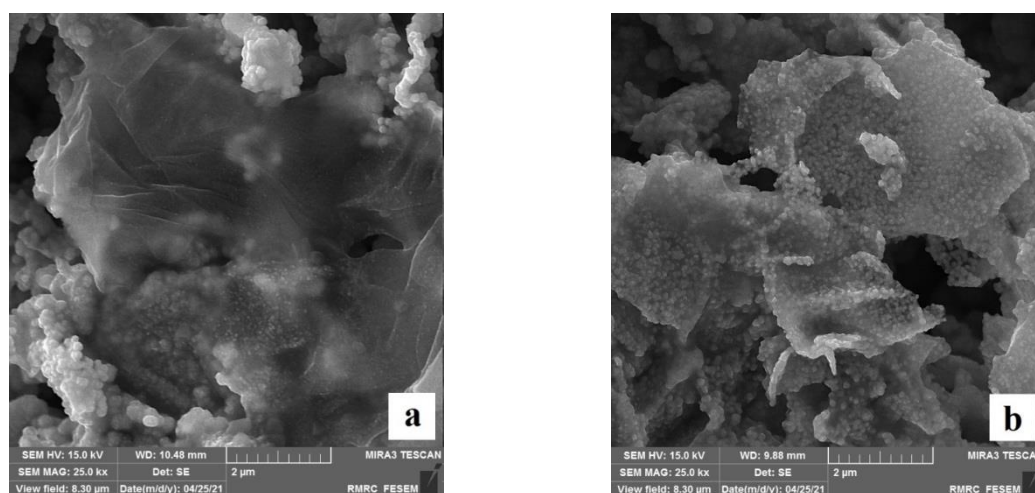


Fig. 2. a) Graphene oxide nano sheet in sample GO4, b) Graphene oxide nano sheet in sample GO2 and alloy germination on it

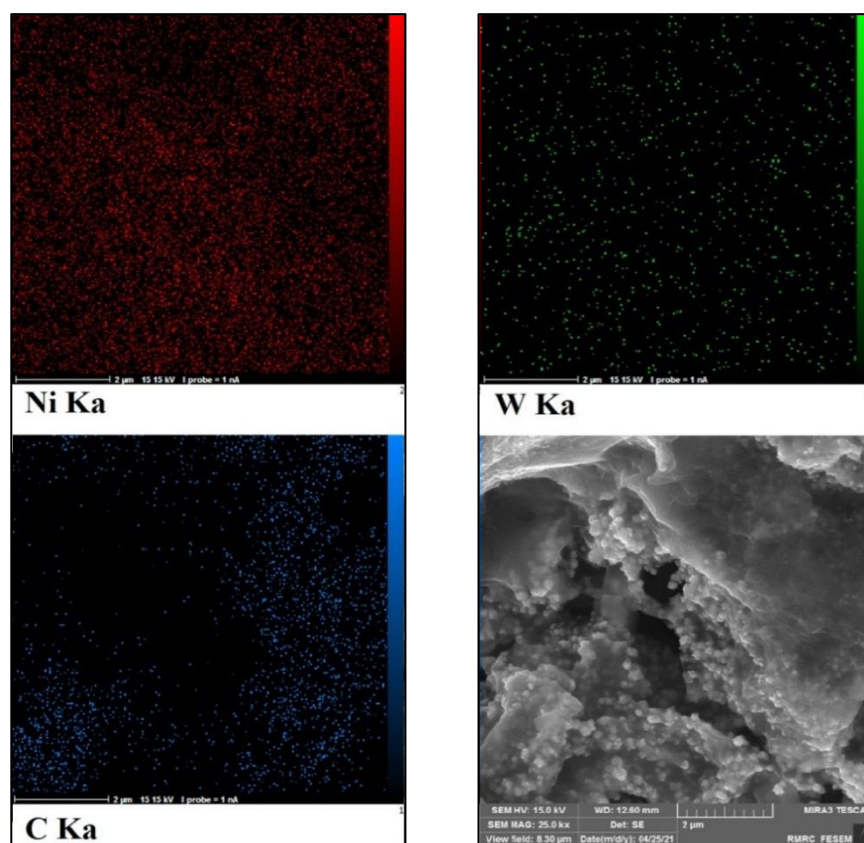


Fig. 3. The results of EDS analysis and dispersion of Ni, W and C elements

A higher slope of this graph indicates an increase in the capacity of the electric double layer and, consequently, a more active surface area of the electrode. In Table 3, the calculated values of the double-layer capacity are presented. By increasing the amount of GO nanosheets in the coating and enhancing the porosity, the electrochemically active surface area increased more than 10 times, which signifies a significant improvement in the catalytic properties of the electrodes.

Table 3. Estimated capacitance for different coatings

Electrode	C_{dl} ($\mu\text{F}/\text{cm}^2$)
GO4	126800
GO3	89500
GO2	56600
GO1	9600

The LSV test results are shown in Figure 5-a. As observed, with an increase in the amount of GO nanosheets at the same cathode potentials of the electrodes, the current values rise, and as a result, the amount of water decomposition and hydrogen

production increases. These results are consistent with the CV analysis results. In fact, by increasing the amount of GO nanosheets in the coating and enhancing the active surface of the electrodes, the number of sites capable of electron transfer for hydrogen reduction and water splitting reaction increases, resulting in an elevation in the hydrogen evolution reaction (HER).

Figure 5-b shows that the Tafel slope in the GO4 coating is 38 mA/decade, which is lower than those obtained from GO3, GO2, and GO1 coatings (51, 58, and 109 mA/decade, respectively) and indicates the faster HER rate. The Tafel slope in GO1, GO2, and GO3 coatings is 40-120 mA/decade, which is categorized as the Volmer-Hydrovsky mechanism, and the Volmer reaction is the rate controller (Equation 3). Moreover, in the GO4 coating, the Tafel slope is 30-40 mA/decade, and the Hydrovsky reaction is the rate controller (Equation 4). In the general case, there is another reaction called the Tafel reaction, in which two atomic hydrogens absorbed on the surface immediately combine, and molecular hydrogen is formed (Equation 5). In this case, the Tafel slope is 30 mA/decade.

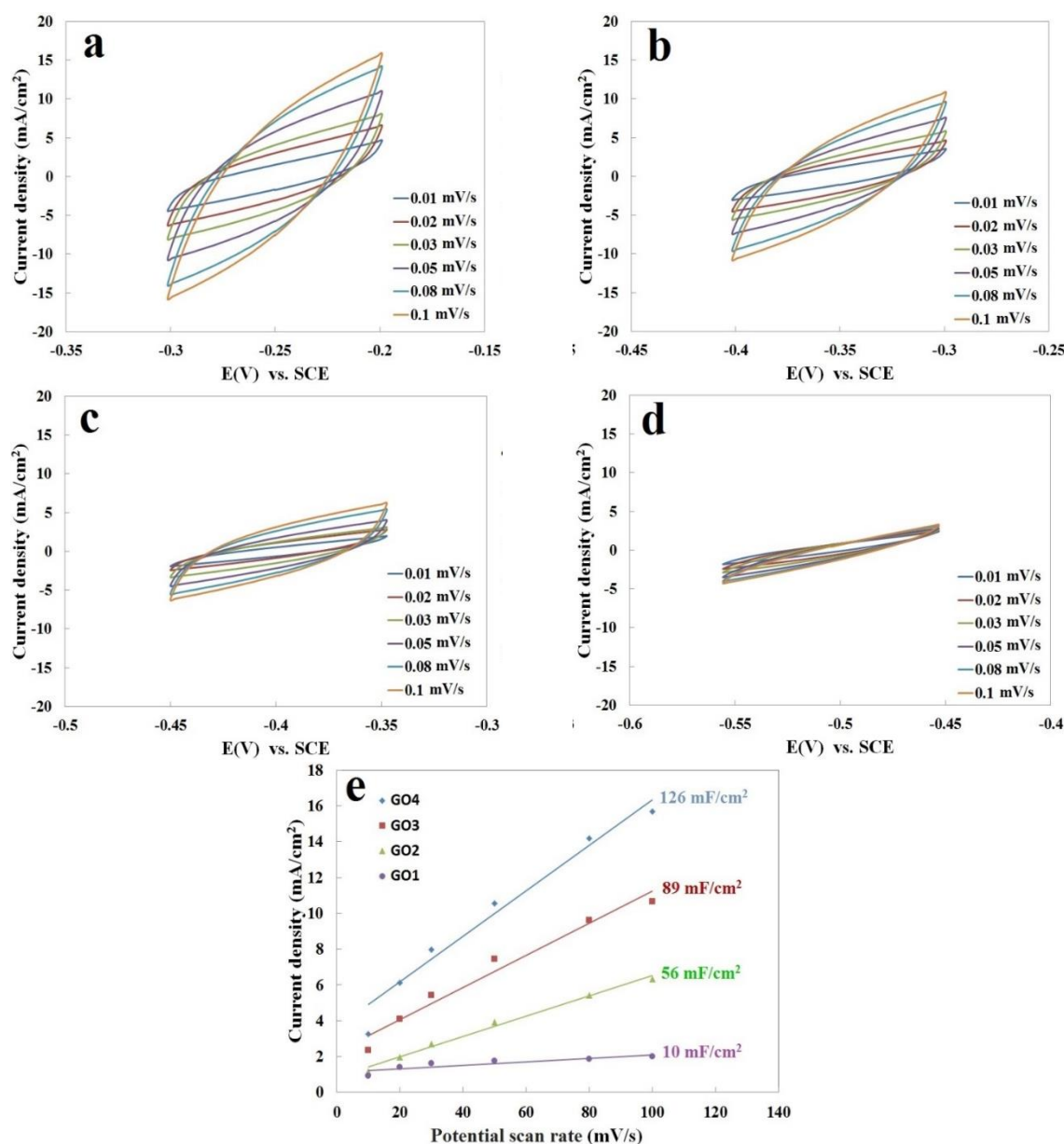
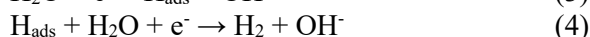


Fig. 4. Results of CV analysis of Ni-W/GO coating: a) GO4, b) GO3, c) GO2, d) GO1, e) capacitive currents vs. scan rates of 10, 20, 30, 50, 80 and 100 mV/s in 1M NaOH



One method to assess the electrocatalytic activity of the samples is to measure the overpotential required to perform HER with a specific current density. In this case, the electrode has better electrocatalytic activity and requires less overpotential energy to carry out the reaction. In Figure 5-c, overpotential levels needed to reach the current of 10, 20, and 100 mA/cm² are extracted from the LSV curves. As can be seen, with an increase in the amount of GO,

the overpotential to reach a current density of 10 mA/cm² decreases, and it is lower for the GO4 coating (64 mV) than the other coatings.

The chronoamperometric test was used to investigate the stability of the electrodes, the results of which are depicted in Figure 5-d. As can be seen, the electrocatalytic properties of the samples have good stability over time, and the current recorded at a constant potential of -1.2 V vs. SCE has not shown a noticeable decrease over time. This test demonstrates that these electrodes can be used in hydrogen production for an extended period without any significant change in efficiency.

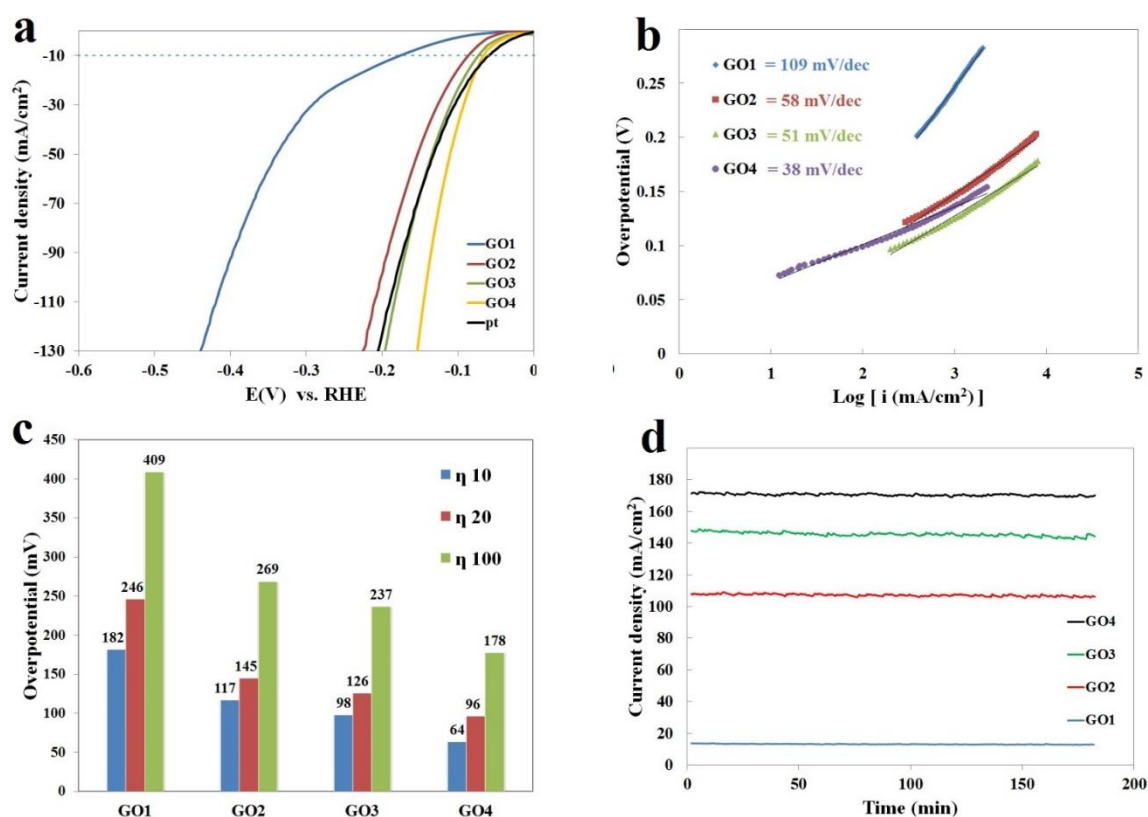


Fig. 5. Electrochemical properties of Ni-W/GO: a- LSV curves, b- Tafel plots, c- The overpotential required to perform the HER with a specific current density, d- Stability test results

3.3. Structural Characterization

The results of the FTIR analysis of GO before and after the addition to the coating were compared, as seen in Figure 6.

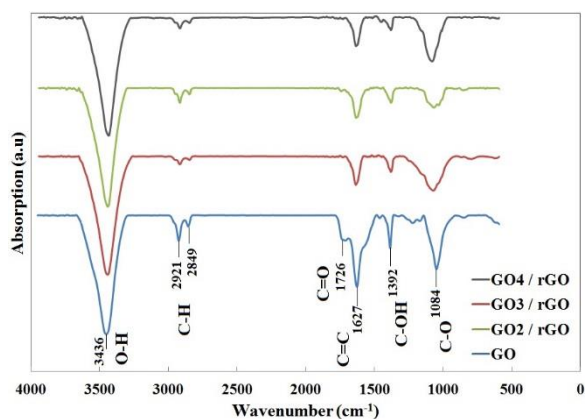
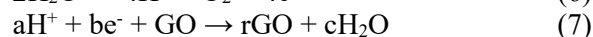
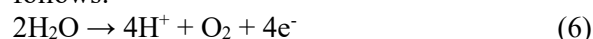


Fig. 6. The results of FTIR analysis with notable peak wavenumbers related to functional groups

The findings show that GO has functional groups containing oxygen. Hydroxyl (-OH) and epoxide are along the basal plane, and carbonyl (C=O) and carboxyl (HO-C=O) are along the edges of the sheet [30]. The FTIR analysis of GO2, GO3, and

GO4 coatings reveals that GO is reduced during plating; the peak at 1726 cm^{-1} corresponding to C=O (in carbonyl or carboxyl) has been completely removed, and the intensity of the peak related to the other functional groups of oxygen is reduced. The general reaction can be expressed as follows:



4. CONCLUSIONS

The Ni-W/GO porous electrocatalyst was successfully coated on a carbon steel substrate. It was observed that by increasing the amount of GO in the electroplating bath up to 0.4 g/L, the active surface of the coating increased significantly, and a porous and foam-like structure was obtained. By analyzing LSV and CA, it was found that this new coating exhibits unique electrocatalytic properties for hydrogen production, and the HER speed increases up to two times. Furthermore, the active surface of the coating has risen dramatically in this case. Therefore, the Ni-W/GO coating can be a suitable alternative for hydrogen production.

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