AEMR
Advances in Energy and Materials Research
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Electro-Oxidation of Glycerol on a Nickel-Based Metal-Organic Framework/Multiwall Carbon Nanotubes Composite Electrode

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Article Info

Article type:
Research Article

Article history:
Received 19 Mar 2024
Received in revised form 24 Jun 2024
Accepted 2 Aug 2024
Published online 28 Sep 2024

Keywords:
metal-organic framework, carbon nanotube, fuel cell, glycerol, electrocatalytic oxidation.

ABSTRACT

In this study, the electrochemical oxidation of glycerol was investigated using a nickel-based metal-organic framework (Ni-MOF)/multiwall carbon nanotube (CNT) composite electrode. The surface morphology of the composite electrode was characterized by scanning electron microscopy (SEM). Cyclic voltammetry was employed to assess the electrocatalytic performance for glycerol oxidation, while chronoamperometry was used to evaluate electrode stability via current-time curves. The electrochemical performance of the Ni-MOF was compared before and after compositing with CNTs. The results demonstrate that the Ni-MOF/CNT composite electrode exhibits enhanced electrocatalytic activity for glycerol oxidation, attributed to the synergistic effects of the CNTs' high electrical conductivity and large surface area and the Ni-MOF's high electrocatalytic activity and porous structure. These properties make the composite a promising material for glycerol fuel cell applications.

Cite this article: Hadi, M. (2025). Electro-oxidation of glycerol on a nickel-based metal-organic framework/multiwall carbon nanotubes composite electrode, *Advances in Energy and Materials Research*, 2 (1), 34-39. https://doi.org/10.22091/jaem.2024.10622.1010

DOI: 10.22091/jaem.2024.10622.1010
Publisher: University of Qom.

1. Introduction

Direct alkaline fuel cells (DAFCs) have garnered significant interest due to their ability to utilize cost-effective metal catalysts [1]. A critical factor in developing high-efficiency DAFCs is the design of anodic materials with superior electrocatalytic activity [2]. In recent years, nickel and nickel-containing compounds have been extensively studied for their promising catalytic activity, cost-effectiveness, and stability in alkaline media for DAFC applications [3]. Nickel in forms such as oxides, hydroxides [4], layered double hydroxides [5], sulfides [6], and phosphides [7] has been investigated as catalysts for alcohol oxidation. Alloying or doping nickel with elements such as Pd [8], Ag [9], Co, Fe [10], or Pt [11] has been proposed to enhance catalytic performance.

Recently, nickel-based metal-organic frameworks (Ni-MOFs) have emerged as promising catalysts for DAFCs due to their large surface area, high porosity, and abundant accessible active metal sites, which facilitate extensive catalyst-electrolyte contact [12, 13]. Notable examples include bimetallic NiCo-MOFs [14], Ni-based trinuclear-cluster MOFs [15], ionic liquid-supported Ni-MOFs [16], and MoS_2@CoNi-zeolitic imidazolate MOFs [17], all of which have been successfully applied for methanol electrooxidation. In this study, a Ni-MOF (Ni-BTC, where BTC = 1,3,5-benzenetricarboxylate) was synthesized, and its electrocatalytic performance for glycerol oxidation was evaluated. Glycerol is a promising fuel for DAFCs due to its low toxicity, non-flammability, and high theoretical energy density. Limited studies have explored glycerol electrooxidation using Ni-based electrocatalysts [18, 19].

Despite their advantages, the low electrical conductivity of MOFs often limits their electrochemical applications. This challenge can be addressed by combining MOFs with conductive carbon-based materials, such as carbon nanotubes (CNTs) [20] or graphene-based structures [21]. Several research groups have developed MOF/carbon-based composites for electrochemical applications [22, 23]. Here, Ni-BTC was combined with multiwall CNTs (Ni-BTC/CNTs) to form a composite electrode. The electrocatalytic performance of the Ni-BTC/CNT composite for glycerol electrooxidation was investigated, revealing improved activity compared to Ni-BTC alone.

2. Experimental Section

2.1. Materials

All chemicals were of analytical reagent grade, and solutions were prepared with distilled water. Multiwall carbon nanotube (CNT) powder (50 µm length, 5–15 nm outer diameter) was obtained from US Research Nanomaterials, Inc. Nickel-based metal-organic framework (Ni-BTC, formulated as $Ni_3(btc)_2\cdot 12H_2O$) was synthesized via a hydrothermal method, as described elsewhere [24]. N,N-dimethylformamide (DMF) was used for preparing dispersions.

2.2. Electrode Preparation

Electrochemical experiments were conducted using a PalmSens EmStat potentiostat with a three-electrode system, comprising a platinum plate as the counter electrode, an Ag/AgCl (3 M KCl) reference electrode, and a modified glassy carbon (GC) electrode as the working electrode. The GC electrode was modified with thin films of Ni-BTC (GC/Ni-BTC) or Ni-BTC/CNTs (GC/Ni-BTC/CNTs) using a dry-casting method [24]. Dispersions of CNTs (1 mg/mL) and Ni-BTC (1 mg/mL) were prepared in DMF using an ultrasonic bath. The Ni-BTC/CNT composite was formed by mixing CNTs and Ni-BTC dispersions in a 1:10 ratio, followed by 10 min of ultrasonication to ensure homogeneity. The GC electrode surface was mechanically polished and rinsed with distilled water. Modified electrodes were prepared by depositing 2 µL of Ni-BTC or Ni-BTC/CNT dispersions onto the GC surface, followed by drying under an infrared lamp to form uniform thin films.

3. Results and Discussion

3.1. Surface Morphology of GC/Ni-BTC and GC/Ni-BTC/CNT Electrodes

Scanning electron microscopy (SEM) images of the GC/Ni-BTC (Figure 1A) and GC/Ni-BTC/CNT

(Figure 1B) electrode surfaces are shown in Figure 1. The images reveal a homogeneous distribution of CNTs across the Ni-BTC particles in the composite electrode. The Ni-BTC particles are uniformly coated with CNTs, indicating strong interactions between the two materials, which likely contribute to the enhanced electrocatalytic performance of the composite.

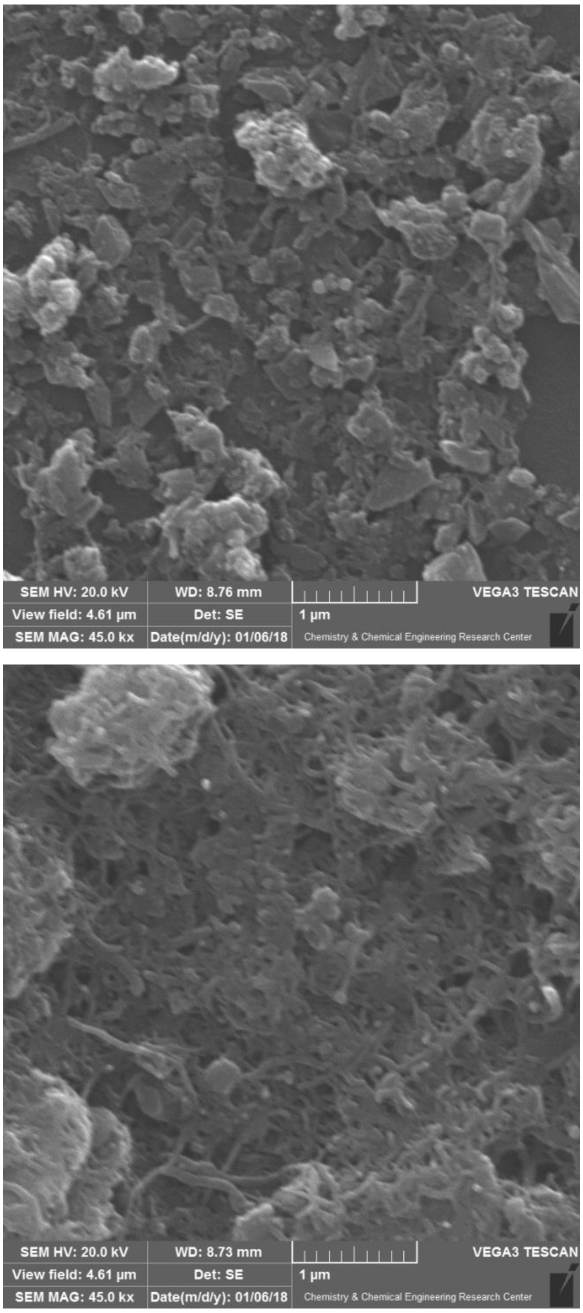

Figure 1. SEM images from the surface of (A) GC/Ni-BTC and (B) GC/Ni-BTC/CNTs electrodes

3.2. Electrochemical properties of GC/Ni-BTC and GC/Ni-BTC/CNTs electrodes toward glycerol oxidation

Fig. 2 (curve a) shows the cyclic voltammogram recorded at the GC/Ni-BTC/CNTs electrode in 0.1 M NaOH supporting electrolyte solution. Two reversible redox peaks that can be seen from curve a in this figure, could be related to the oxidation of Ni^{2+} to Ni^{3+} in anodic direction and the reduction of Ni^{3+} to Ni^{2+} in cathodic direction.

Curve b in figure 2 shows the voltammogram at the GC/Ni-BTC/CNTs electrode recorded after addition of 0.01 M glycerol into the 0.1 M NaOH electrolyte solution. A remarkable increase in anodic peak current and a decrease in cathodic peak current can be observed in the presence of glycerol. This behavior is indicative of Ni^{2+}/Ni^{3+}-mediated electrocatalytic oxidation of glycerol and can be expressed based on the electrochemical/catalytic chemical (EC′) reaction mechanism. This can be represented by the following reactions:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad E \quad (1)$$

$$NiOOH + \text{glycerol} \rightarrow Ni(OH)_2 + \text{products} \quad C' \quad (2)$$

The voltammograms (curve c and d) recorded at the GC/Ni-BTC electrode in the same conditions are also presented in Fig. 2. Comparing curve b with curve d and curve a with curve c indicate a significant higher electrocatalytic efficiency of GC/Ni-BTC/CNTs than that of the GC/Ni-BTC electrode. This clearly shows that the low electrical conductivity of Ni-BTC can be effectively compensated by CNTs. In addition, the large surface area as well as high electrochemical activity of CNTs can render the Ni-BTC/CNTs composite with improved electron transfer kinetics and electrocatalytic performances.

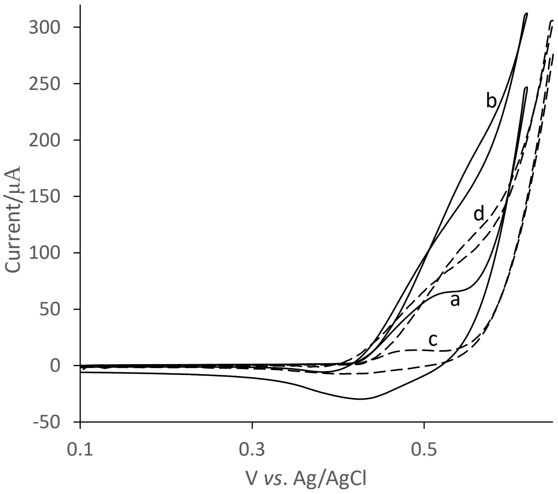

Figure 2. Cyclic voltammograms of GC/Ni-BTC/CNTs in 0.1 M NaOH (a) before and (b) after the addition of glycerol and GC/Ni-BTC in 0.1 M NaOH (a) before and (b) after the addition of glycerol at the scan rate of 100 mV s^{-1}.

3.3. Evaluation of the glycerol concentration

Cyclic voltammograms were recorded at the GC/Ni-BTC/CNTs electrode in the presence of various concentration of glycerol and the plot of the oxidation peak current (I_p) versus the concentration is shown in Fig. 3. As can be seen, the oxidation current of glycerol is increased with the increasing of its concentration upto about 40 mM and at the higher concentrations it almost tends to level off. This is probably due to the surface saturation effect. These results indicate that the Ni-BTC/CNTs can be a promising electrocatalyst with high efficiency for the oxidation of glycerol.

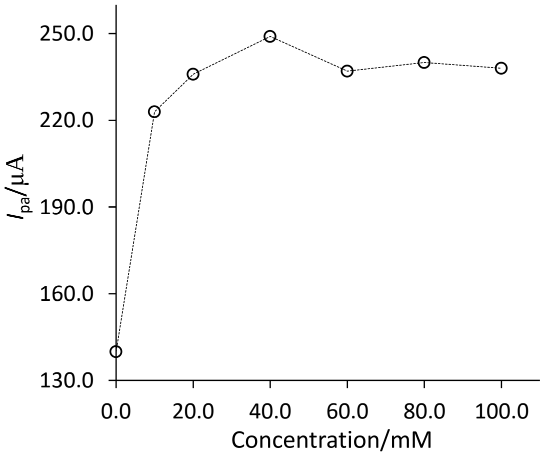

Figure 3. The plot of I_{pa} *vs.* the glycerol concentration.

3.4. Evaluation of the stability of the glycerol oxidation at the GC/Ni-BTC/CNTs electrode

In order to examine the stability of the electrooxidation of glycerol at the GC/Ni-BTC/CNTs electrode, the chronoamperometry experiment was conducted. The current-time curve of the GC/Ni-BTC/CNTs electrode toward 0.01 M glycerol at a constant potential of 0.70 V (*vs*. Ag/AgCl) for 500 s is shown in Fig. 4. During this experiment the solution was agitated at 200 rpm by a magnetic stirrer to retain the homogeneity of the solution near the electrode surface. As can be seen from this figure, the current decreased slightly after 500 s, which indicates high stability of the GC/Ni-BTC/CNTs electrode toward the glycerol oxidation.

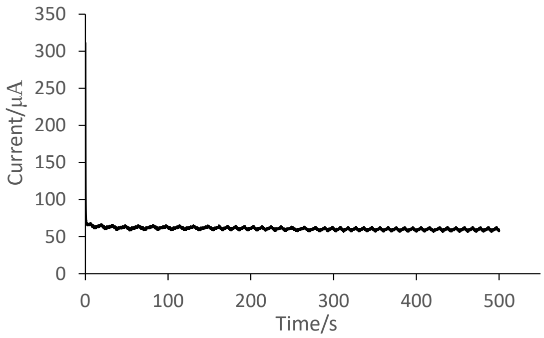

Figure 5. Chronoamperogram recorded at the GC/Ni-BTC/CNTs electrode in 0.1 M NaOH and 0.01 M glycerol solution at potential of 0.7 V (*vs*. Ag/AgCl) for 500 s.

4. Conclusion

The electrocatalytic oxidation of glycerol on the GC/Ni-BTC/CNT composite electrode was investigated using cyclic voltammetry and chronoamperometry. The Ni-BTC metal-organic framework (MOF), when combined with multiwall carbon nanotubes (CNTs), exhibits enhanced electrocatalytic activity for glycerol oxidation. This improved performance is attributed to the synergistic effects of the CNTs' high electrical conductivity and large surface area and the Ni-BTC's highly porous structure and abundant catalytic active sites. Chronoamperometry experiments further confirmed the excellent stability of the GC/Ni-BTC/CNT electrode. These findings demonstrate the potential of the Ni-BTC/CNT composite electrode for applications in glycerol fuel cells.

Conflict of Interest

There are no conflicts to declare.

Acknowledgments

This study has been supported by the University of Qom.

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