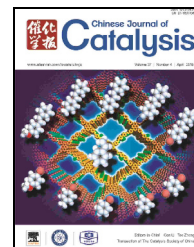


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Article

Electrooxidation of methanol and ethanol on carbon electrodeposited Ni–MgO nanocomposite

H. B. Hassan ^{a,*}, Z. Abdel Hamid ^{b,#}, Rabab M. El-Sherif ^a^a Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt^b Central Metallurgical Research and Development Institute, Cairo, Egypt

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ABSTRACT

Ni–MgO nano-composites were prepared on carbon anodes by electrodeposition from a nickel Watts bath in the presence of fine MgO reinforcement particles. Their performance as electrocatalysts for the oxidation of methanol and ethanol in alkaline medium was investigated and compared with that of carbon coated pure Ni (Ni/C). The chemical composition, phase structure, and surface morphology of the deposited nano-composites were studied by energy dispersive X-ray spectroscopy, X-ray diffractometry, and scanning electron microscopy, respectively. Different electrochemical techniques were used to estimate the catalytic activity of the prepared electrocatalyst anodes, including cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy (EIS). The Ni/C electrocatalyst alone exhibited remarkably low catalytic activity and poor stability toward the electrooxidation process. The inclusion of MgO significantly promoted the catalytic activity of the Ni catalyst for the alcohol electrooxidation and enhanced its poisoning resistance. The EIS results confirmed those of CV and revealed a lower charge transfer resistance and enhanced roughness for the Ni–MgO/C nano-composite electrodes compared with those of Ni/C.

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1. Introduction

Research on direct alcohol fuel cells (DAFCs) has gained momentum because they are considered to be promising power sources for many applications such as portable electronic devices and electric vehicles [1,2]. However, the commercialization of fuel cells is still suffering many problems, particularly for those using acid media, owing to kinetic restriction of the methanol oxidation reaction (MOR) and the high catalyst cost that prevents the use of Pt at a commercial level [3].

However, the efficiency of the methanol or ethanol electrooxidation reaction in alkaline electrolyte is clearly better than that in acidic electrolyte, and there is a wider choice of catalysts that are operable in alkaline electrolytes [4,5]. Taking

these limitations into consideration, it has become necessary to move toward optimization of alternative electroactive catalysts for the oxidation process. The limited choice of efficient, highly active, available, and cheap anode catalysts for DAFCs is still a great challenge for energy conversion systems [6]. Considerable efforts have been devoted to the fabrication of high performance Ni-based catalysts for the electrooxidation of methanol and ethanol in alkaline media [7–13]. Ni is a relatively low cost material and is produced in large amounts; moreover, it displays potential catalytic properties in a wide number of processes such as energy conversion in alkaline fuel cells [14,15]. The electrocatalytic properties of Ni in alkaline media depend on the formation of nickel hydroxide (Ni(OH)₂) and oxyhydroxide (NiOOH) species under anodic polarization [16].

* Corresponding author. Tel: +20-1003871963; E-mail: hanaa20055@hotmail.com# Corresponding author. E-mail: zamiabdelhamid@hotmail.com

Recently, metal oxide composites have attracted significant attention as electrocatalysts owing to their low cost, easy preparation methods, and excellent catalytic activity [17]. Ni–metal oxide composite films have been reported to be much superior to pure Ni films in respect to the electrocatalysis of methanol and ethanol oxidation [6,7,18]. Composite electroplating is one of the various techniques that have been used to prepare efficient Ni composites. This method involves the co-deposition of fine particles such as ZnO, TiO₂, Al₂O₃, or Cr₂O₃ into a plated layer under the effect of an electric field [6,7,19–23]. The rate of fine particle inclusion depends on the size, shape, and charge of the particles. It also depends on the plating conditions, such as current density, temperature, pH, and time. In our previous work [6,23], we have successfully demonstrated the possibility of fabricating Ni–metal oxide nanoparticles on carbon electrodes using electrodeposition or electroless techniques.

The enhancement effect of the incorporation of reinforcement particles such as metal oxides on the catalytic activities of metal catalysts has been demonstrated in the literature. It has been found that incorporating oxide particles results in a low overvoltage for alcohol oxidation, and they act as effective anode materials [23]. TiO₂ or Cr₂O₃ deposited with Ni as a nanocomposite improves the electrocatalytic activity and stability of the Ni in electrooxidation processes [6,7,23]. The use of CeO₂, Co₃O₄, or Mn₃O₄ can remarkably enhance the catalytic activity and reduce the usage of precious metal catalysts [24]. Adding Co₃O₄ nanoparticles to multiwalled carbon nanotubes (MWCNTs) enhances the surface area of the modified electrode and the electron transfer rate for hydrogen peroxide detection [25]. Ni–V₂O₅ exhibits high electrocatalytic activity toward dopamine (DA) oxidation owing to the promotion of the electroactive V⁵⁺/V⁴⁺ redox reaction by Ni²⁺ [26]. Pt–CoO electrode has shown electrocatalytic activity toward the mediated electrooxidation of ascorbic acid, glucose, and methanol [27]. The addition of NiO to Pt/C or Pd/C improved the catalytic activity and poisoning resistance of the electrodes toward methanol electrooxidation [28]. Additionally, Ni-modified MgO is significantly active for the electrooxidation of methanol [29]. Finally, MgO increases the anti-poisoning ability of the catalyst and improves the kinetic processes [30].

Several different strategies have been attempted in the literature to improve the catalytic activities of Ni-based catalysts, including the use of Ni–metal oxide composites. However, the role of such metal oxides in enhancing the catalytic activities of Ni catalysts toward the electrooxidation of methanol or ethanol has not studied yet and needs further investigation. The purpose of the present work was to synthesize and study the performance of Ni–MgO composites supported on carbon as potential electrocatalysts for fuel cells. Ni–MgO composites were prepared using a facile electrodeposition route. The role of MgO in enhancing the catalytic activity, anti-poisoning ability, and stability of the Ni catalyst during the electrocatalytic oxidation of methanol and ethanol in alkaline environment was elucidated through surface investigation and electrochemical techniques.

2. Experimental

2.1. Pretreatment and preparation of the electrode

Carbon substrates were mechanically polished using emery papers of different grades up to 1000, and subsequently degreased with acetone, rinsed with triply distilled water, and dried with soft tissue paper. The apparent surface area of the substrates was calculated from the geometric area and the current density referred to below. A Nickel Watts bath was used to deposit Ni or Ni–MgO composite film on the carbon substrates using a galvanostatic technique. The composition of the deposition bath and the operating conditions are given in Table 1. Pure Ni metal and carbon electrodes were used as the anode and cathode, respectively. Prior to the co-deposition, MgO particles having an average particle size of ~8 μm were stirred in the plating solution for about 2 h using a magnetic stirrer at 150 r/min to obtain a uniform suspension and prevent agglomeration of the MgO. During the co-deposition process, the bath also was stirred with a magnetic stirrer (150 r/min) to keep the particles dispersed and prevent their sedimentation in the electrolyte. Various composite electrodes were prepared at different deposition current densities. After the preparation of the modified carbon electrodes, no further pretreatment of the electrode was carried out to avoid any changes to the electrode surface.

2.2. Electrochemical measurements

A conventional three-electrode glass cell was used for electrochemical studies. The reference electrode was Hg/HgO/1.0 mol/L NaOH (MMO) ($E_0 = 0.140$ V vs NHE), and a Pt sheet was used as a counter electrode. Measurements were carried out at room temperature (30 ± 1 °C) in 1.0 mol/L NaOH solution. Ethanol and methanol were used as received without further purification. All the reagents used in this work were Sigma-Aldrich products of analytical grade and were used without further purifications. Triply distilled water was used throughout for the preparation of solutions.

The electrochemical measurements were performed using cyclic voltammetry (CV) and chronoamperometry techniques using an IviumStat instrument (Ivium Technologies, Eindhoven, the Netherlands). The IviumSoft software was used to control the instrument through a personal computer (PC). The PC was used to specify the parameters of the measurement, display the measured curves, and calculate the results of the measurements. Electrochemical impedance spectroscopy (EIS)

Table 1

Chemical composition of Ni electroplating electrolyte and the operating conditions for electrodeposition of Ni composite coatings on carbon electrode.

Composition	Concentration (g/L)	Operating conditions
NiSO ₄	240	pH 5
NiCl ₂	45	Deposition temperature: 55 °C
H ₃ BO ₃	30	Deposition time: 30 min
MgO	10	Deposition current density: 10–80 mA/cm ²

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