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A low cost and highly active non-noble alloy electrocatalyst for hydrazine oxidation based on nickel ternary alloy at the surface of graphite electrode



M. Jafarian ^{a,*}, T. Rostami ^a, M.G. Mahjani ^a, F. Gobal ^b

^a Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran
^b Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran

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ABSTRACT

The electrocatalytic oxidation of hydrazine was studied over Ni, Cu, Co and Ni-based ternary alloy on graphite electrodes in alkaline solution. The catalysts were prepared by cycling the graphite electrode in solutions containing Ni, Cu and Co ions at cathodic potentials. The synergistic effects and the catalytic activity of the modified electrodes were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). It was found that, in the presence of hydrazine, the modified Ni-based ternary alloy electrode (G/NiCuCo) exhibited a good catalytic activity for the oxidation of hydrazine at a reduced overpotential and it has a significant high response for hydrazine oxidation. During CA regime the reaction follows a Cottrellin behavior and the diffusion coefficient of hydrazine is found to be 6.28×10^{-6} cm² s⁻¹. EIS studies were used to investigate the catalytic oxidation of hydrazine on the surface of the modified electrode.

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1. Introduction

Hydrazine is employed in areas such as fuel cells, catalysts, rocket propellants and is used as pesticides, plant-growth regulators, pharmaceutical intermediates, photographic chemical, corrosion inhibitor, textile dyes and so on [1–3]. In industrial applications, hydrazine is added to boilers which act as an oxygen scavenger and removes dissolved oxygen reducing corrosion time and extending the life of the boilers [4]. However, hydrazine is toxic by oral, skin and inhalation absorption and quickly spreads throughout the body and produces carcinogens and mutagenic effects [5]. Therefore, the electro-oxidation of hydrazines is a reaction of practical importance. Hydrazine is an ideal fuel for direct liquid-feed fuel cells for a direct fuel cell system from the viewpoint that the fuel electro-oxidation process does not suffer from any poisoning effects [6]. A Fuel cell which hydrazine plays the role of fuel is called direct hydrazine fuel cell (DHFC). Compared with other conventional fuel cells, the DHFC has several advantages [7]: (1) only generation environmental-friendly nitrogen and water (Eq. (1)) without producing species which can poison the electrocatalysts [8–9]. The electrode reactions are as follows [10]:

Anode :
$$N_2H_4 + 40H^- \rightarrow N_2 + 4H_2O + 4e$$
 (1)

Cathode : $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Cell reaction :
$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$
, (3)

(2) higher theoretical electromotive force of hydrazine cell (1.61 V) than conventional hydrazine-air fuel cells (1.21 V), (3) higher energy density of hydrazine fuel cell (5400 Wh L^{-1}) than that of hydrazine fuel cell (4820 Wh L⁻¹), (4) near ambient working temperature and (5) high reactivity. Also, the fuel cells with liquid fuels such as hydrazine, methanol, and ethanol are good examples for electronic applications. Since the kinetic of hydrazine oxidation is slow and incomplete, a catalyst is required to improve the oxidation efficiency. The electrocatalytic oxidation of hydrazine has been of great interest to electrochemists and studied at several electrodes including silver [11], gold [12], nickel [13-14], palladium and palladium-based compounds [15-16], platinum [17], cobalt [18-20] and carbon materials [21-23]. The overpotential for electrooxidation of hydrazine depends on the electrode material [24]. Although metals such as Pt, Au and Ag are very active in the anodic oxidation of hydrazine, they are too expensive for practical applications. Therefore, many attempts have been directed toward the examination of the catalytic activity of cheap metals such as nickel-based electrodes. Transitional metals have been utilized, owing to their extraordinarily catalytic activities for oxidation reactions. The choice of Co and Cu to modify electrocatalyst to improve the hydrazine oxidation is due to the alloys of them present an improved activity for the hydrazine oxidation. The current direction is to enhance the electrocatalytic activity for hydrazine oxidation in the presence of Ni based ternary alloy. The low cost modified electrode prepared so easily and exhibited a significant high response for hydrazine

^{*} Corresponding author. *E-mail address:* mjafarian@kntu.ac.ir (M. Jafarian).

oxidation compared to previous studies [25–28]. In the present study, we have investigated the activity of modified Ni based ternary alloy graphite electrode (G/NiCuCo) and the synergistic effect on the electrocatalytic oxidation of hydrazine in alkaline solution. We have also reported the electrocatalytic properties of the modified electrode for the electro-oxidation of hydrazine.

2. Experimental

2.1. Material and equipment

Sodium hydroxide, nickel sulfate, copper sulfate, cobalt chloride and hydrazine used in this work were Merck products of analytical grade and were used without further purification. All solvents were distilled prior to use.

2.2. Electrode preparation

Prior to each experiment, the graphite rods were polished with emery papers in different grades till a mirror surface obtained. In a typical experiment, the deposition of the ternary alloy on the graphite electrode was performed by repetitive scanning (40 cycles) of the electrode in a solution of soluble salts (0.02 M) over the cathodic potential range of 0 to -1 V vs. Ag/AgCl followed by repetitive scanning (60 cycles) over the anodic potential range of 0 to 1 V vs. Ag/AgCl in NaOH solution. A scan rate of 100 mV·s⁻¹ was applied in both processes.

2.3. Electrochemical methods

Electrochemical studies were carried out in a conventional threeelectrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. The system was run by a PC through M270 and M398 commercial software via a GPIB interface. For impedance measurements, a frequency range of 100 kHz to 10 mHz was employed. The AC voltage amplitude used was 5 mV. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of ZView software. An Ag/AgCl–Sat'dKCl, a graphite rod and a modified graphite rod with a geometric area of 0.11 cm² were used as the reference, counter and working electrodes, respectively. All





2 Theta / degree

Fig. 1. SEM images showing the surface morphology of (A) unmodified graphite and (B) G/NiCuCo modified electrodes. (C) X-ray diffractogram (XRD) of electrodeposited G/NiCuCo, in the range $10^{\circ} < 2\theta < 100^{\circ}$.

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