



Poly(N-methylaniline)/nickel modified carbon paste electrode as an efficient and cheap electrode for electrocatalytic oxidation of formaldehyde in alkaline medium

Jahan-Bakhsh Raouf*, Abdollah Omrani, Reza Ojani, Fatemeh Monfared

Electroanalytical Chemistry Research Laboratory, Department of Analytical Chemistry, Faculty of Chemistry, Mazandaran University, Babolsar, Iran

ARTICLE INFO

Article history:

Received 3 January 2009
Received in revised form 12 April 2009
Accepted 6 May 2009
Available online 6 June 2009

Keywords:

N-methylaniline
Modified carbon paste electrode
Cyclic voltammetry
Nickel oxyhydroxide
Formaldehyde

ABSTRACT

This research in finding a cheap and efficient catalyst for electrooxidation of formaldehyde give us an attempt to make and examine the behavior of poly(N-methylaniline)/nickel modified carbon paste electrode (Ni/P(NMA)/MCPE) in absence and presence of formaldehyde. This involves in situ electropolymerization of N-methylaniline at carbon paste electrode, which is following to the incorporation of Ni(II) to polymeric layer by immersion of modified electrode in 1.0 M nickel sulphate solution. The electrocatalytic oxidation of formaldehyde was studied by cyclic voltammetry and chronoamperometry methods. The effects of scan rate and formaldehyde concentration on the electrocatalytic oxidation of formaldehyde were also investigated at the surface of Ni/P(NMA)/MCPE. The diffusion coefficient ($D = 14.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and some kinetic parameters such as the transfer coefficient ($\alpha = 0.45$) and also second-order rate constant ($k = 8.96 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of formaldehyde were calculated.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The electrochemical oxidation of small organic molecules has been studied due to their potential utilization as fuels in energy conversion systems. The reasons for that are related to their facility of storage and handling and mainly their high energy density. Moreover, due to their simple molecular structure, they should undergo a more straightforward reaction mechanism than other possible organic fuels [1].

Although using formaldehyde (CH_2O) is a risk to human health. But recent data show that formaldehyde fuel cells are attractive alternatives for proton exchange membrane (PEM) fuel cells [2,3] and researches show that there has been significant interest in the electrochemical oxidation of formaldehyde for many years [4–7].

Mechanism and kinetic of formaldehyde oxidation have been studied under a wide ranges of conditions and on various electrodes including Pt [8,9], binary and ternary alloys [10–11] and nano-composites [12,13]. But the great importance of nickel electrochemistry in alkaline medium has attracted the attention of many researchers either to study the behavior of nickel-based electrode itself or its electrochemical activity toward many other molecules. In addition to the pure nickel electrode, other different nickel-based electrode such as nickel hydroxide modified glassy

carbon electrode (GCE), nickel complexes/glassy carbon electrode or nickel-based alloys have been tested for amperometric detection of carbohydrates, amines and amino acids [14–20], electrocatalytic oxidation of alcohols [21–26] and hydrogen peroxide [27] related to fuel cell technology development. Electrochemical studies using nickel-based modified electrodes have established that various electroreactant species can be determined with a high rate of heterogeneous electron transfer, good sensitivity and reproducibility [28].

Moreover, electrochemical polymerization offers the advantage of reproducible deposition in terms of film thickness and loading, making the immobilization procedure of a nickel-based electrocatalyst very simple and reliable [29,30]. Therefore in the present work, we dispersed a cheap catalyst, nickel ions, to an organic polymer which was electropolymerized on carbon paste electrode. Then, this modified electrode was used for electrooxidation of formaldehyde.

2. Experimental details

2.1. Chemical reagents

N-methylaniline (NMA) was purchased from Merck. Sulfuric acid from Fluka was used as the supporting electrolyte. Sodium hydroxide and formaldehyde obtained in analytical grade from Merck and used without further purification. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was utilized as the pasting

* Corresponding author. Tel.: +98 112 5342392; fax: +98 112 5342350.
E-mail address: j.raouf@umz.ac.ir (J.-B. Raouf).

liquid for carbon paste electrode. Graphite powder (particle diameter = 0.1 mm) from Merck was employed as the working electrode (WE) substrate.

2.2. Preparation of working electrode

A mixture (70:30% w/w) of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius = 3.4 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube.

2.3. Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (Sama 500-C Electrochemical Analysis System, Sama, Iran) coupled with a Pentium IV personal computer to acquire gain the data. A platinum plate was used as the auxiliary electrode. The poly(*N*-methylaniline)/nickel modified carbon paste electrode (Ni/P(NMA)/MCPE) and double junction Ag|AgCl|KCl (3 M) electrode were used as working and reference electrodes, respectively.

3. Results and discussion

3.1. Preparation of poly(*N*-methylaniline) modified carbon paste electrode (P(NMA)/MCPE)

As it is well documented in the literature, poly(*N*-methylaniline) (P(NMA)) films were prepared at the surface of glassy carbon, tin oxide and Pt electrodes [31–33]. In this work, galvanostat technique was employed as the reliable method for electropolymerization of NMA on the surface of CPE. The polymer was formed in 0.5 M sulfuric acid solution containing 0.05 M *N*-methylaniline as a monomer by holding the current at 2.55 mA for 16 s.

The electrochemical behavior of the obtained polymer was strongly dependent on the pH of the electrolyte solution. As can be seen in Fig. 1a, a well defined redox behavior was observed in acidic media (0.5 M H₂SO₄), while the response obtained in an alkaline solution (0.1 M NaOH) showed an electroinactive behavior in the potential ranges from 0.2 to 0.7 V vs. Ag|AgCl|KCl (3 M) (Fig. 1b).

3.2. Incorporation of Ni(II) ions into P(NMA)/MCPE and the electrochemical behavior of Ni/P(NMA)/MCPE

In order to incorporate Ni(II) ions into polymeric film, the freshly P(NMA)/MCPE was placed in a well stirred 1.0 M NiSO₄

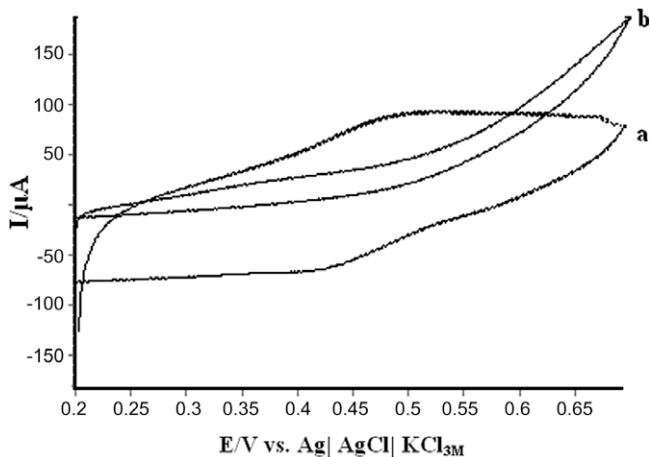


Fig. 1. Cyclic voltammograms of P(NMA)/MCPE in (a) 0.5 M H₂SO₄ and in (b) 0.1 M NaOH solutions at $\nu = 20 \text{ mV s}^{-1}$.

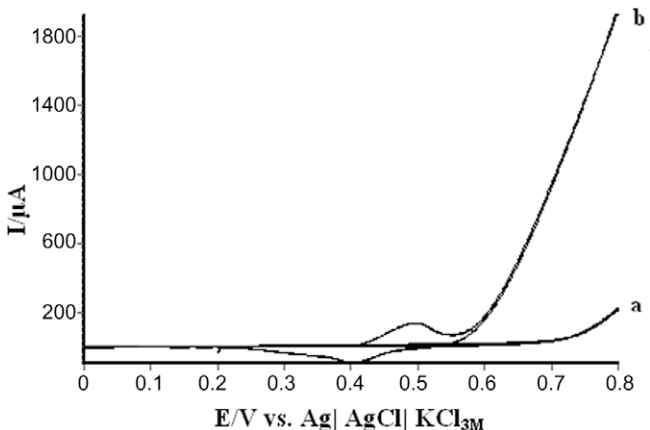


Fig. 2. Cyclic voltammograms of (a) P(NMA)/MCPE and (b) Ni/P(NMA)/MCPE in 0.1 M NaOH solution at potential scan rate of 20 mV s^{-1} .

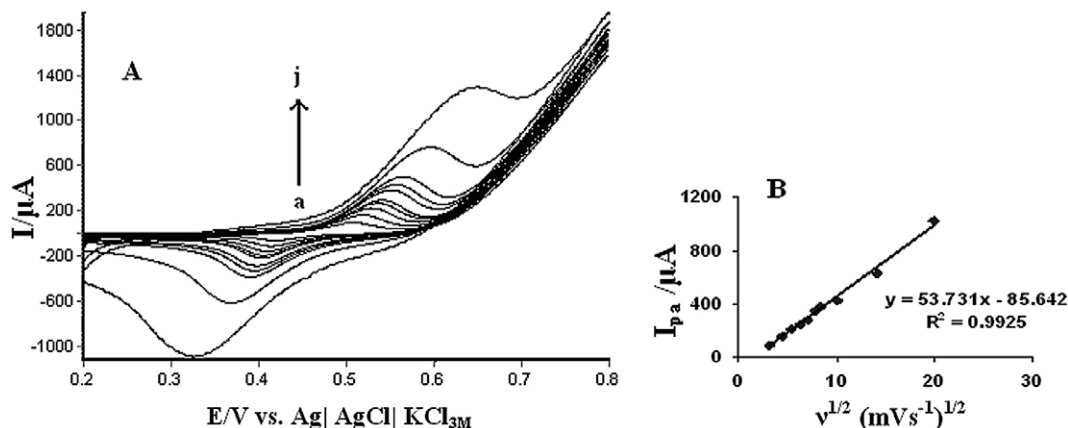


Fig. 3. (A) Cyclic voltammograms of Ni/P(NMA)/MCPE, at various scan rates: (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 100, (i) 200 and (j) 400 mV s^{-1} . (B) Plot of I_{pa} vs. $\nu^{1/2}$.

Download English Version:

<https://daneshyari.com/en/article/220197>

Download Persian Version:

<https://daneshyari.com/article/220197>

[Daneshyari.com](https://daneshyari.com)