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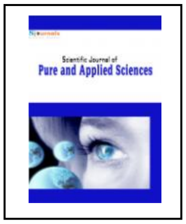

**Original article**

# Electrocatalytic oxidation of ethanol using zeolite modified carbon paste electrode

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ABSTRACT

In this research application of synthesized ZSM-5 zeolite to prepare the modified carbon paste electrodes was studied. To prepare of modified electrode, the nickel ions as mediator for electrochemical oxidation of ethanol were doped to ZSM-5 zeolite framework through ion exchange mechanism and oxidation of ethanol on the surface of proposed electrode in the alkaline solution was investigated using cyclic voltammetry and chronoamperometry methods. Also, the catalytic rate constant for oxidation of ethanol (k) was reported.

## 1. Introduction

Using direct alcohol fuel cells (DAFCs), identified as an important power source in ranging from portable electronic devices to fuel cell vehicles. Recently, researchers largely focused on the methanol based fuel cells, e.g. direct methanol fuel cells (DMFCs), because of the easy availability, handleability and transportation of the methanol fuel. On the other hand, some disadvantages, such as its toxicity, low boiling point and unrenewability, provoke researchers to use other small organic molecules specially alcohols. Among various alcohols, ethanol is considered most attractive, because it has less toxicity, higher energy density and boiling point relative to other alcohols, and can be produced with great quantities by the fermentation of sugar containing raw materials (Chen et al., 2009; He et al., 2011; Raoof et al.,2011; Abrishamkar et al., 2012). Zeolite-modified electrodes (ZMEs) from a sub-category of the so-called chemically modified electrodes (CME), were largely studied and promoted by several researchers (Murray , 1980; Ojani et al., 2012). The use of zeolites as supported electrodes represents one of the solutions overcome the problem of catalytic oxidation of ethanol. Zeolites are crystalline microporous solids that provide molecular-sized cage and passage ways for excellent strict control of reaction paths (Abrishamkar and Bagherfard, 2013; Abrishamkar and Izadi, 2012; Abrishamkar et al., 2011 and 2010). In the present study, the preparation of the Ni-modified zeolite electrode and its application to catalysis oxidation of ethanol in alkaline media was reported.

## 2. Materials and methods

### 2.1. Apparatus and chemicals

The ZSM-5 zeolite was synthesized by a literature method [3]. Graphite powder and nickel chloride were from Fluka. Ethanol and sodium hydroxide used in this work were also purchased from Merck. Electrochemical experiments were carried out using a potentiostat/galvanostat (sama 500-c Electrochemical Analysis system, sama, Iran). An $Hg|Hg_2Cl_2|KCl$ (4.6M) electrode as reference electrode, a platinum wire as the auxiliary electrode and carbon paste electrode modified with zeolite as the working electrode were used.

### 2.2. Electrode preparation

0.5 g of ZSM-5 zeolite was lightly ground and immersed to 10 ml 1 M $NiCl_2$ solution for 5 h. Then the solide was dried in oven at 373 k for 8 h. The zeolite exchanged washed with deionized water to remove surface-adsorbed species. The 30% (W/W) zeolite loading $Ni^{2+}$ was made by mixing the given quantity of zeolite loading Ni2+ in diethyl ether and hand mixing with 70 times its weight of graphite powder. The solvent was evaporated by stirring a mixture and paraffin was blended by hand mixing and the resulting paste was inserted in the bottom of a glass tube (with internal radius 1.4 mm). At least, modified electrode was immersed in 1 M $Ni^{2+}$ solution for 5 min. Then, this modified electrode (Ni/NiZSM-5/CPE) was washed to remove surface-adsorbed species. The CPE, used for comparison, was prepared in the same was but omitting the zeolite addition step.

## 3. Results and discussion

### 3.1. Electrochemical behavior of Ni/NiZSM-5/CPE

Successive cyclic voltammograms of Ni/NiZSM-5/CPE in 0.1 M NaOH solution is shown in Fig. 1.

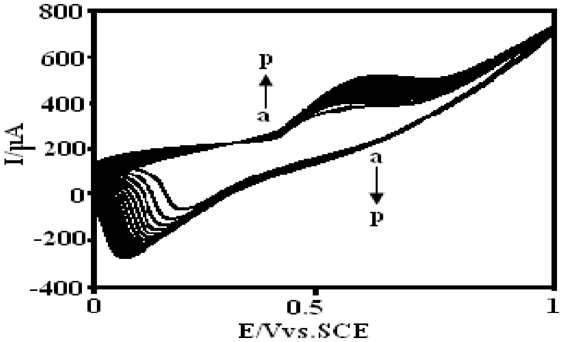

**Fig. 1.** Cyclic voltammograms of Ni/NiZSM-5/CPE in 0.1 M NaOH solution in different cycles (a) first, (c) third, (K) 11th, (p) 20th at the scan rate 100 $mVs^{-1}$.

As can be seen in first scan, the mount of currents due to $Ni(OH)_2/NiOOH$ redox couple is low, but during cycling it increases which can be attributed to diffusion of OH- ion into zeolite framework and more conversion of $Ni^{2+}$ to $Ni(OH)_2$ species according to the following reaction [1]:

$$Ni^{2+} + 2OH^{-} \rightleftarrows Ni(OH)_2 \qquad (1)$$

### 3.2. Electrocatalytic oxidation of ethanol on the surface of Ni/NiZSM-5/CPE

Figure .2 shows the cyclic voltammograms Ni/NiZSM-5 (A) and CPE (B) in 0.1 M NaOH solution, in the (a) absence and (b) presence of 0.03 M ethanol. As can be seen in Fig.2 (A) two peaks appear in the cyclic voltammogram (CV). These peaks represent the oxidation of $Ni(OH)_2$ to the nickel oxy-hydroxide [NiOOH] in the anodic run and the reduction of the produced oxy-hydroxide to $Ni(OH)_2$ in the cathodic half cycle, respectively in accordance with the following reaction [2]:

$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-$ (2)

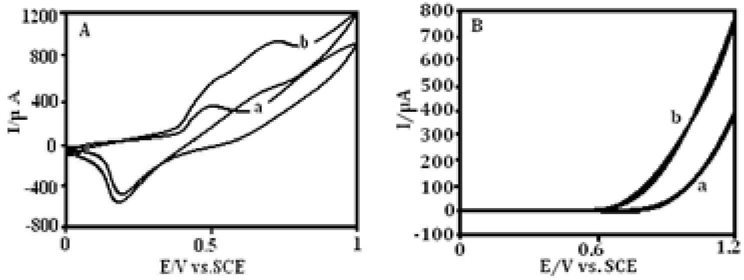

**Fig. 2.** Cyclic voltammograms of (A) Ni/NiZSM-5/CPE and (B) CPE in the (a) absence and (b) presence of 0.03 M ethanol in 0.1 M NaOH solution at the scan rate 20 $mVs^{-1}$.

The comparison of Fig.2 (A) curve (b) with the cyclic voltammogram of the electrode in blank NaOH (curve a), considerable anodic current was observed for the ethanol oxidation. A cathodic peak is also observed here, however, its current value is much smaller than the anodic one as a result of the oxy-hydroxide reduction. The relative decrease of the cathodic peak height in presence of ethanol is attributed to the partial consumption of nickel oxy-hydroxide species for oxidation of ethanol with the formation of nickel hydroxide in accordance with the following equation [3]:

$NiOOH + ethanol \rightleftharpoons Ni(OH)_2 + products$ (3)

Also, under the same experimental condition, the electrochemical oxidation of ethanol was studied at the surface of CPE (Fig.2B). As shown, at potential 1.2 V vs. $Hg|Hg_2Cl_2|KCl$ (4.6M) at the surface of CPE no anodic peak was observed, whereas the oxidation peak of ethanol at the surface of Ni/NiZSM-5 is 0.69 V vs. $Hg|Hg_2Cl_2|KCl$ (4.6M) in the same condition. Thus, this result indicates that the applied modifier in this process participates directly in the electrocatalytic oxidation of ethanol. For optimization of the amount of modifier (Ni-ZSM-5 zeolite), three ratio of 20,30 and 40% (w/w) of zeolite to graphite powder were examined by cyclic voltammetry in the presence of 0.03 M ethanol in 0.1 NaOH solution. The results revealed that the optimum ratio of Ni-zeolite in the modified electrode was 30%. High amounts of the modifier, the resistance of modified electrode was increased and at the low amounts of modifier the amount of Ni ions existed in the zeolite framework became low and produced current became low.

### 3.3. Chronoamperometric study

Double step chronoamperograms were recorded by setting the working electrode potential at desired values. Fig. 3A shows double step chronoamperogram of the modified electrode in the absence (a) and in the presence (b,c,d,e) of ethanol. The applied potential steps were 0.7 and 0.35 V vs. $Hg|Hg_2Cl_2|KCl$ (4.6M) for various concentrations of ethanol. As can be seen, the forward and backward potential step chronoamperometry of the modified electrode in blank solution showed an almost symmetrical chronoamperogram with almost equal charge which is consumed for the oxidation and reduction of surface confined Ni(II)/Ni(III) sites (Fig. 3B, curve á). However, in the presence of ethanol, the charge value associated with the forward chronoamperometry, Q is greater than of that observed for the backward, (Fig. 3B, curve é). These results indicate the electrocatalytic ability of this modified electrode for oxidation of ethanol in alkaline media.

The rate constant for the chemical reaction between the ethanol and redox sites of Ni/NiZSM-5/CPE can be evaluated by chronoamperometry according to the method described using Toefel equation as bellow:

$I_C/I_L = \gamma^{1/2} [\pi^{1/2} \mathrm{erf} (\gamma^{1/2}) + \exp(-\gamma) \gamma^{1/2}]$ (1)

Where $I_C$ is the catalytic current of the Ni/NiZSM-5/CPE in the presence of ethanol, $I_L$ is the limiting current in the absence of ethanol and $\gamma = kC_0t$ (C0 is the bulk concentration of ethanol) is the argument of the error function. In cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduce to: $I_C/IL = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0t)^{1/2}$ (2)

Where k, $C_0$ avd t are the catalytic rate constant ($cm^3\ mol^{-1}$ s-1), etanol concentration (mol $cm^{-3}$) and time elapsed (s), respectively. We can simply calculate the value of k for a given concentration of substrate from the slope of the $I_C/I_L$ vs $t^{1/2}$ plot. The inset (C) of Fig. 3 shows one such plot, constructed from the chronoamperogram of the Ni/NiZSM-5/CPE in the absence and presence of 0.1 M ethanol. The mean value for k was founded to be 1.4 × $10^5$ $cm^3$s-1mol$^{-1}$.

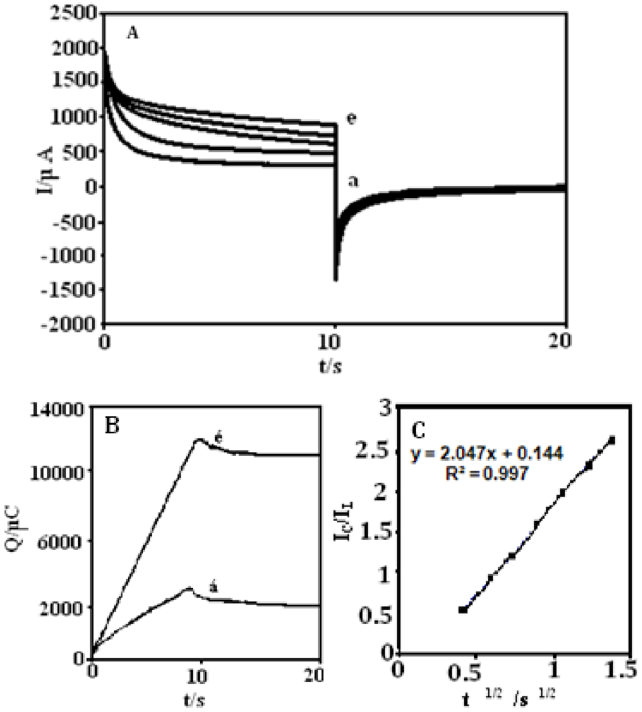

**Fig. 3.** Chronoamperograms obtained at the Ni/NiZSM-5/CPE in the absence (a) and presence of (b) 0.003, (c) 0.008, (d) 0.06, and (e) 0.1 M of ethanol in 0.1 M NaOH solution. (B) Plot of Q vs. t derived from the data of chronoamperogram of a and c of (A) and (C) dependence of $I_C/I_L$ on $t^{1/2}$, derived from the data of chronoamperograms of (a) and (e) of (A).

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