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Ethanol oxidation at metal–zeolite-modified electrodes in alkaline medium. Part-1: gold–zeolite-modified graphite electrode

A. M. A. Ouf · Amira M. Abd Elhafeez · A. A. El-Shafei

Abstract Gold–zeolite-modified graphite (AuZG) electrode shows higher catalytic activity for ethanol oxidation in alkaline medium compared with massive gold or gold-modified graphite (Au/G) electrodes. The activity of this electrode depends on the amount of zeolite loaded on the graphite surface and on the soaking time in Au^{3+} solution. The effects of both scan rate and ethanol concentration on the anodic peak height are indicatives of a diffusion-controlled process. Current decay measurements indicate that the activity of studied electrodes towards poisoning tolerance decreases in the following order: AuZG>Au/G>Au.

Keywords Ethanol oxidation · Alkaline media · Gold · Zeolite-modified electrodes

Introduction

In spite of the research effort to find out a cheap anode with high performance for fuel cell application, expensive noble metals are still in use. For this reason, more effort must be devoted to reduce the amount of noble metal loading while the high reactivity is still retained. In order to fulfill this demand, high dispersion of noble metal-containing catalyst on different cheap and conducting substrates has been extensively studied. These substrates include graphite, glassy carbon, polymer matrix, and recently molecular sieve zeolite [1–15]. Zeolites are namely aluminosilicate or aluminophosphate crystals consisting of microporous cages and channels of molecular dimensions of 5–12 Å [16]. Most of zeolite's applications are based on the ability of these open crystalline structures to selectively incorporate and exchange both charged and neutral species within the void spaces and interconnecting channels on a molecular scale. Therefore, the use of zeolite in electrode modification for electrocatalysis has been extensively tested [17–20].

The activity of gold electrode towards the oxidation of alcohols is much greater in alkaline media than in acidic one [21]. In addition, the reactivity of mono and poly alcohols is much higher in alkaline media [22–24]. Among alcohols, ethanol seems to be the best competitive one for its lesser toxicity in comparison to methanol. Moreover, ethanol can be considered as renewable fuel because it can be fabricated by fermentation of agricultural products and biomass. Also, ethanol has lower fuel crossover than methanol through the membrane towards the oxygen electrode [25]. The advantages of ethanol over other alcohols stimulated many studies on the mechanism of its catalytic oxidation [12–15, 26–33].

The present work deals with zeolite-modified electrodes as catalysts for ethanol oxidation. The performance of gold–zeolite-modified graphite electrode towards ethanol oxidation in alkaline media compared with the performance of massive gold or graphite-supported gold towards the same reaction is the principal object of the present investigation. Cyclic voltammetry and chronoamperometry techniques proved to be very helpful in this concern.

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Fig. 1 Graphite electrode

Cu-wire

Teflon Support

Teflon

Cu-Ring

Spring

Cu-Contact

Graphit
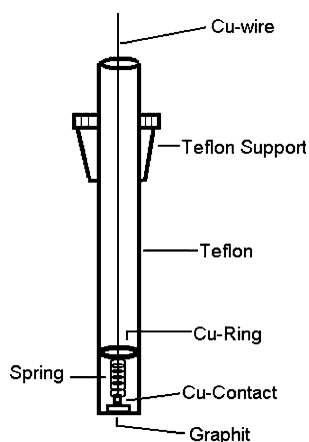
Experimental

The electrolytic solutions were prepared from water obtained with a Megapure system (MP-A6 Corning) and analytical grade chemicals NaOH (Merck) and C_2H_5OH (British Drug House).

Zeolite suspension was made by dispersing a defined weight of NaY–zeolite (0.024, 0.048, or 0.072 g) through ultrasonic vibration in 6-mL distilled water.

A Pt wire was served as a counter electrode. All the potentials are referred to the Ag/AgCl electrode which was used as a reference electrode through this work. Cyclic voltammetric as well as chronoamperometric measurements were obtained using Metrohm 693 VA processor and 694 VA stand.

The working electrode was made from a graphite disc (Union Carbide) with geometric surface area of 0.294 cm^2 bonded to a Teflon tube (Fig. 1). Prior to the modification of the electrode, the graphite surface was polished on a microcloth (Bühler) using aluminum oxide of different diameters (13, 3, 1, 0.3, and 0.05 μm) [32]. The electrode modification was accomplished by transferring one drop of aqueous zeolite suspension to the electrode surface, where it was allowed to dry.

Finally, the electrode was immersed in $5×10^{-3}$-M AuCl$_3$ solution of pH=3 for different soaking times. The electrode was then inserted into the electrochemical cell containing 0.5 M NaOH and finally cycled between −0.85 and 0.65 V versus Ag/AgCl until a steady-state voltammogram was obtained.

Modification of graphite substrate by Au particles has been simply made by cycling the graphite electrode in $4.5×10^{-4}$-M AuCl$_3$ solution (pH=3).

The real surface of Au trapped in the zeolite layer has been determined from the oxygen reduction peak [33].

Scanning electron microscopy (SEM) was performed (using SEM model JEOLSM 5410, Japan) in order to analyze the surface of the samples. Figure 2 shows the

micrographs of NaY–zeolite-modified electrode (Fig. 2a) and of Au-supported electrode (Fig. 2b). Figure 2a shows that the zeolite layer consists of homogenous crystals. After soaking the electrode in $5×10^{-3}$-M AuCl$_3$ solution (Fig. 2b), one can observe that a part of the electrode surface is doped with Au ions.

Results and discussion

Figure 3 shows the cyclic voltammograms of graphite electrode in 0.5 M NaOH before and after modification with NaY–zeolite. The increase in the oxidation current above 0.2 V followed by increase in the reduction current below −0.35 V is observed. This can be attributed to the oxidation–reduction process of oxygen species in zeolite. In addition, the additional resistance obtained from the presence of zeolite particles on the electrode surface cannot be excluded. These two reasons led to the inclination of the baseline of the voltammogram [34]. Upon soaking of the ZG-1 in AuCl$_3$ solution for 20 min, the voltammograms
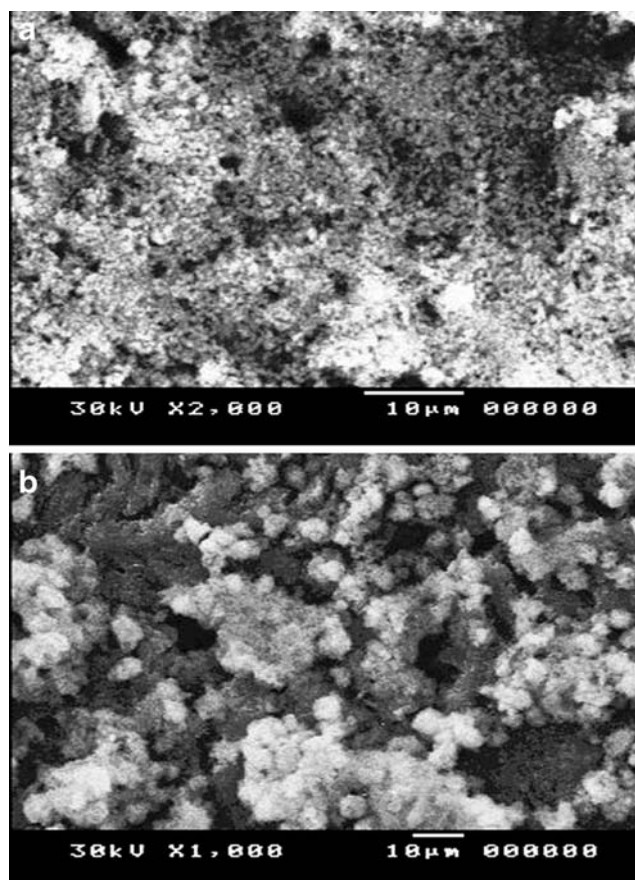
**Fig. 2 a** Scanning electron micrograph for the ZG-1 electrode. **b** Scanning electron micrograph for the AuZG-1 electrode obtained after soaking in AuCl$_3$ solution for 8 min
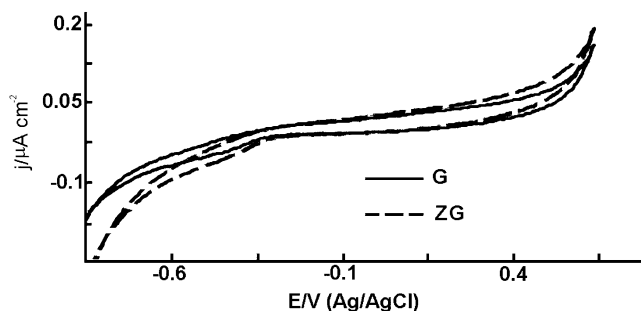
Fig. 3 Cyclic voltammograms of (*solid curve*) G and (*dashed curve*) ZG electrodes in 0.5 M NaOH. Scan rate=50 mV s^{-1}

recorded in 0.5 M NaOH (Fig. 4a) exhibit remarkable differences especially in the potential of Au oxide formation reduction region. However, the onset of the gold oxide formation starts at more negative potential than on massive Au electrode. Another observed feature which has not been observed either on massive gold or Au/G electrodes (Fig. 4, b and c, respectively) is the presence of the reduction wave followed by current rise during the positive sweep direction before the Au oxide formation region. This reduction–oxidation process can be related to the presence of Au^{3+} ions trapped in zeolite cavities because it was not detected
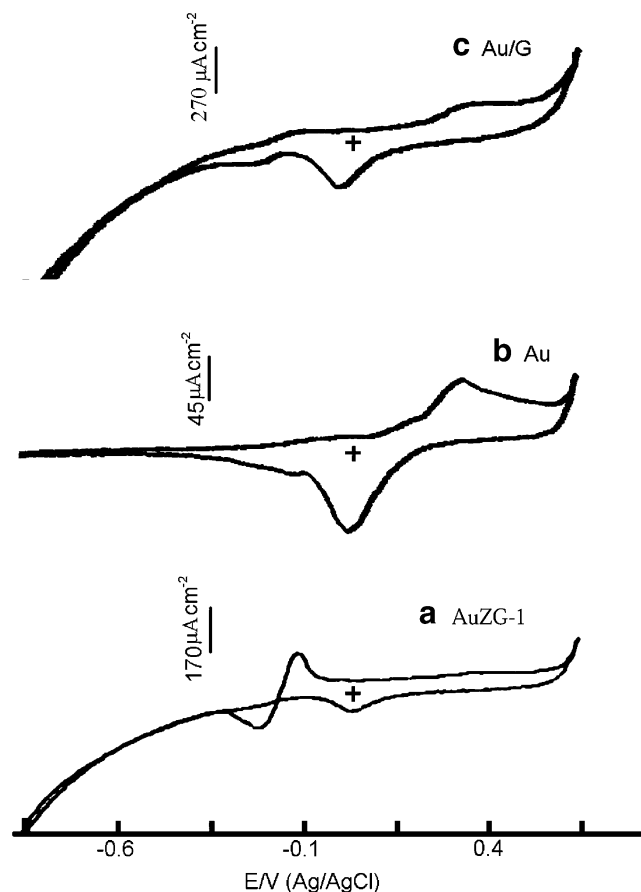
Fig. 4 Cyclic voltammograms of (*a*) AuZG-1, (*b*) Au, and (*c*) Au/G electrodes in 0.5 M NaOH. Scan rate=50 mV s^{-1}
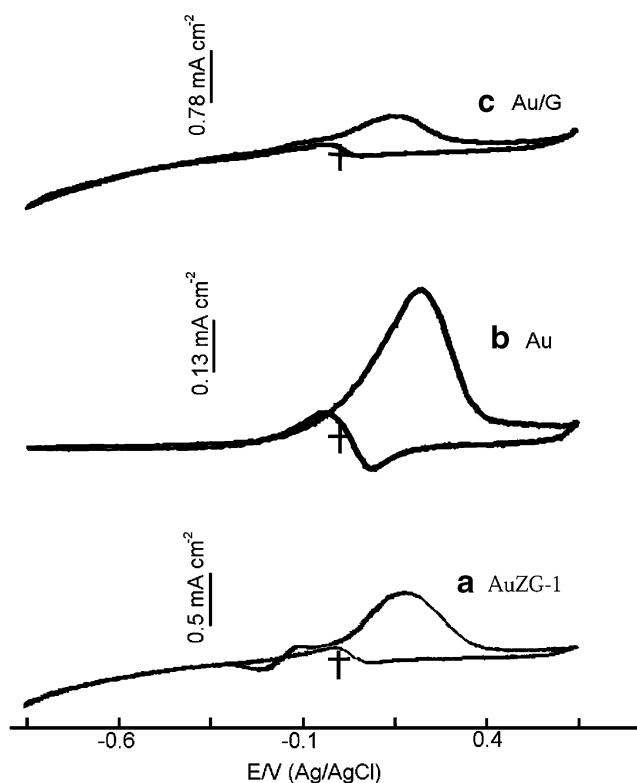

Fig. 5 Cyclic voltammograms of (*a*) AuZG-1, (*b*) Au, and (*c*) Au/G electrodes in 0.5 M C$_2$H$_5$OH+0.5 M NaOH. Scan rate=50 mV s^{-1}

either in absence of Au or in case of Pd-modified ZG electrode (work under study in our laboratory).

The voltammograms recorded for gold–zeolite-modified graphite (AuZG)-1 in 0.5 M NaOH+0.5 M ethanol are shown in Fig. 5a. For the sake of comparison, the voltammograms recorded for both massive Au and Au/G electrodes under the same experimental condition are also included (Fig. 5, b and c). The main differences observed are: (1) the peak position is shifted to a less positive value by approximately 50 mV; (2) the oxidation peak becomes broader in case of AuZG as well as Au/G electrodes than on massive gold; (3) the peak current density decreases in the order: AuZG-1>Au/G>Au. This may be taken as evidence that AuZG electrode exhibits a higher activity towards ethanol oxidation in alkaline media than both Au/G

Fig. 6 Influence of soaking time on the voltammograms of AuZG-3 electrode in 0.5 M C$_2$H$_5$OH+0.5 M NaOH. Scan rate=50 mV s^{-1}
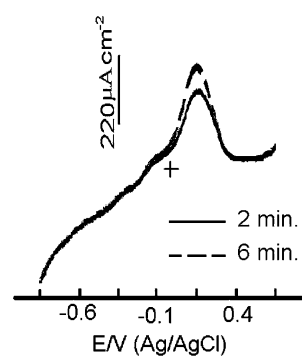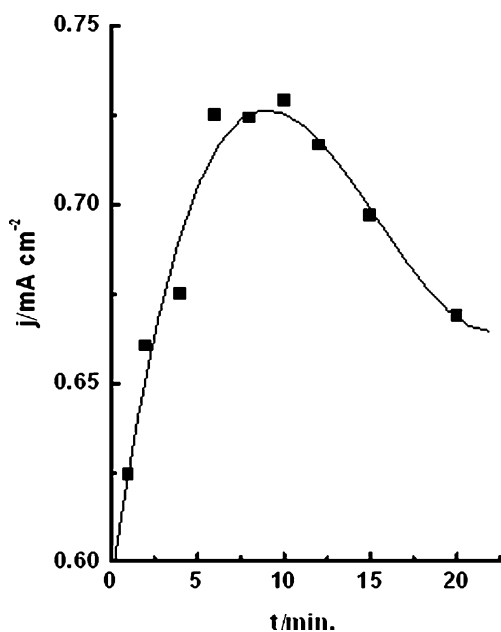
Fig. 7 Current peak density–soaking time relationship for AuZG-3 electrode in 0.5 M C_2H_5OH+0.5 M NaOH

and massive Au electrodes. This activity can be ascribed to the particle size and the crystallographic orientation of the Au deposited on graphite electrodes. Moreover, in case of zeolite-modified electrode, the zeolite–Au interaction is more enhanced. This may be considered as an additional evidence for the electronic interaction.

Examples for the influence of the soaking time of ZG-3 electrode in $AuCl_3$ solutions on the oxidation of ethanol are shown in Fig. 6; for the sake of clarity, the positive sweeps are only drawn. It is shown from Fig. 6 that the main influence is the increase of the current density around the peak position. Figure 7 shows the peak current as a function of soaking time. As the soaking time increases, the activity increases, reaching a maximum at soaking time between 5 and 10 min. Increasing the soaking time beyond this time leads to a decrease in the oxidation current. However, the

Table 1 Variation of catalytic activity, as peak current density of AuZG/peak current density of massive Au, with the soaking time

Time (min)	j_{AuZG}/j_{Au}		
	AuZG-1	AuZG-2	AuZG-3
2	1.64	2.27	1.59
4	1.66	2.32	1.63
6	1.69	2.39	1.76
8	1.78	2.17	1.75
10	1.74	2.09	1.77
12	1.74	1.91	1.74
15	1.73	1.89	1.69
20	1.59	1.87	1.62

Table 2 Variation of catalytic activity, as peak current density of AuZG/peak current density of Au/G, with the soaking time

| Time (min)	$j_{AuZG}/j_{Au/G}$		
	AuZG-1	AuZG-2	AuZG-3
2	1.18	1.64	1.16
4	1.20	1.68	1.18
6	1.21	1.73	1.27
8	1.29	1.56	1.27
10	1.26	1.52	1.28
12	1.25	1.39	1.26
15	1.26	1.38	1.22
20	1.15	1.36	1.17

activity is still higher in comparison with Au/G and massive Au electrodes.

In order to find out the optimum condition for zeolite loading, graphite electrodes with various zeolite loadings were tested. The catalytic activity as represented by the current density obtained at the peak position of AuZG electrode (j_{AuZG}) divided by that of massive Au (j_{Au}) or Au/G ($j_{Au/G}$) electrodes. For all soaking times investigated, the ratios (j_{AuZG}/j_{Au} and $j_{AuZG}/j_{Au/G}$) are listed in Tables 1 and 2, respectively. Increasing zeolite loading from 0.024 to 0.048 g leads to increase of the electrode activity. This may be attributed to the higher uptake of Au^{3+} ions by high zeolite
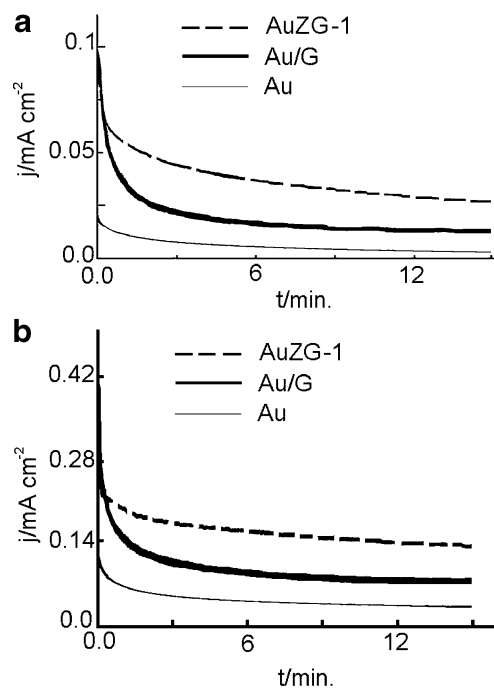
Fig. 8 **a** Current–time curves for (*solid thin curve*) Au, (*solid thick curve*) Au/G and (*dashed curve*) AuZG-1 (soaking time=8 min) electrodes in 0.5 M C_2H_5OH+0.5 M NaOH at $E=-0.1$ V. **b** Current–time curves for (*solid thin curve*) Au, (*solid thick curve*) Au/G and (*dashed curve*) AuZG-1 (soaking time=8 min) electrodes in 0.5 M C_2H_5OH+0.5 M NaOH at $E=0.1$ V

Fig. 9 **a** Current density–soaking time relationship for AuZG electrodes obtained from *i–t* curves recorded at −0.1 V in 0.5 M C₂H₅OH+0.5 M NaOH after 15 min (values obtained for Au and Au/G electrodes are indicated as *dotted* and *dashed lines*, respectively). **b** Current density–soaking time relationship for AuZG electrodes obtained from *i–t* curves recorded at 0.1 V in 0.5 M C₂H₅OH+0.5 M NaOH after 15 min (values obtained for Au and Au/G electrodes are indicated as *dotted* and *dashed lines*)
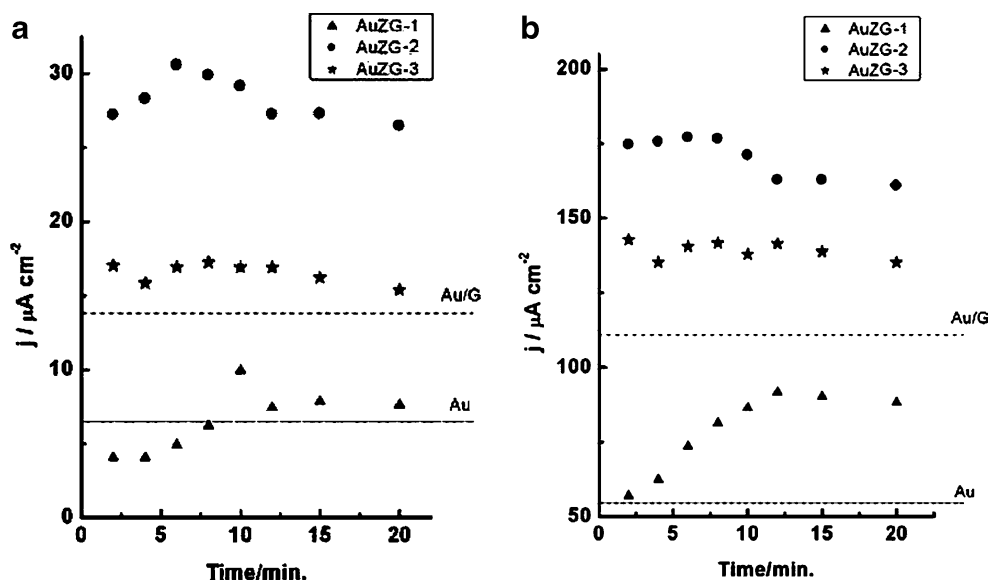
loading. The increase of zeolite loading above this value decreases the electrode activity. This may be due to the increase of the electrode resistivity as zeolite loading increases. The highest catalytic factor which equals 2.4 (against massive gold) or 1.7 (against Au/G) is obtained for AuZG-2 electrode at 5-min soaking time.

Production of high current density at low overvoltage is not the only factor from the practical point of view, but the tolerance against poisoning species is equally important. For this reason, current decay measurements have been performed at a constant potential value (−100 and +100 mV vs. Ag/AgCl) for all electrodes under study. Figure 8 represents selected examples of the current decay measurements for AuZG-2 electrode at 8-min soaking time. For comparison, *i–t* curves are shown for both massive Au and Au/G electrodes. The data collected for all electrodes after

15 min are presented in Fig. 9. It is shown that the activity of electrodes under study decreases in the following order: AuZG-2>AuZG-3>Au/G>AuZG-1>Au. This indicates the high tolerance efficiency of AuZG electrodes against poisoning process, especially at optimum conditions for both Au and zeolite loadings.

Figure 10 shows the effect of ethanol concentration on the cyclic voltammograms of AuZG-1 electrode in 0.5 M NaOH. It is clearly observed that the peak height increases with the increase of ethanol concentration. The data
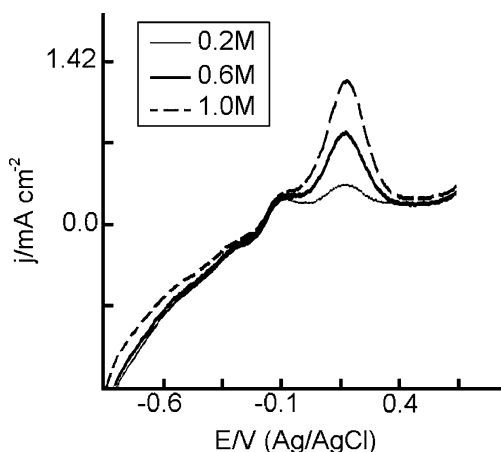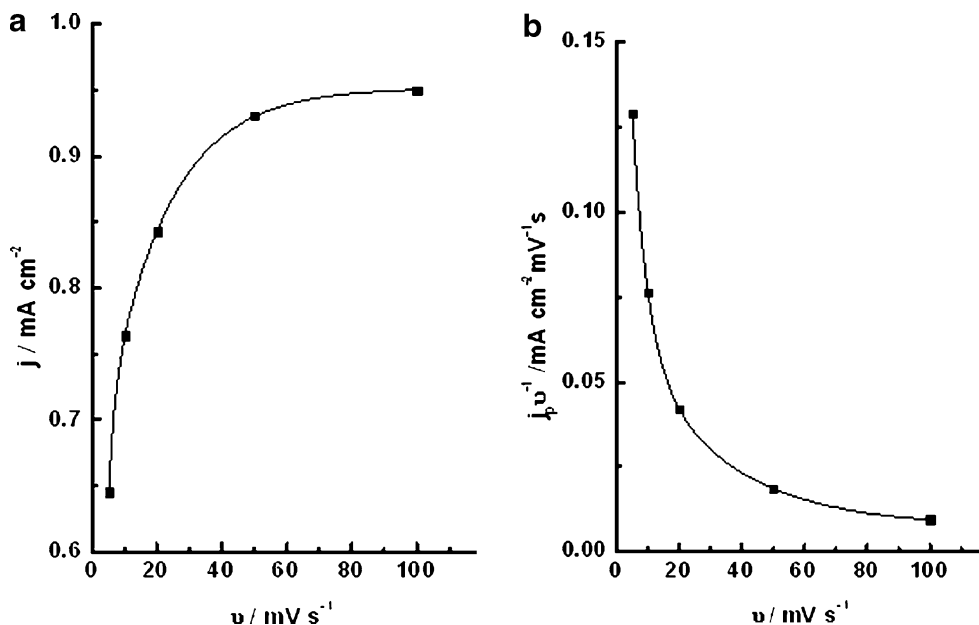
Fig. 10 Cyclic voltammograms of AuZG-1 electrode in *x* M C₂H₅OH +0.5 M NaOH. Scan rate 50 mV s⁻¹
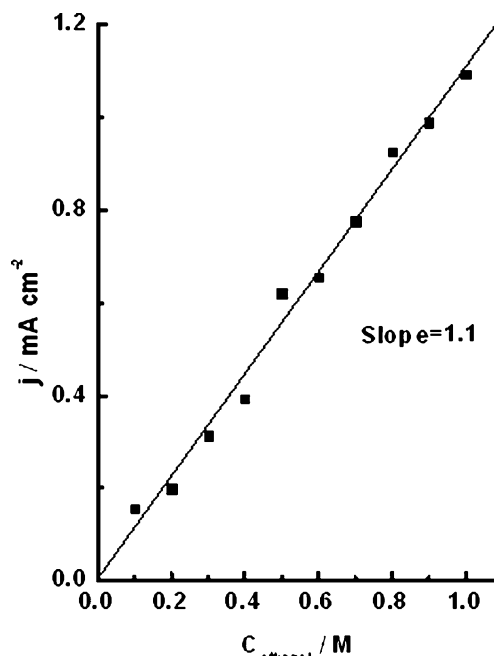
Fig. 11 Dependence of ethanol oxidation current peak on the ethanol concentration

covering the concentration range under study are presented in Fig. 11. A straight line passing through the origin with a slope equal unity is shown, indicating that the process is purely diffusion controlled.

The influence of the scan rate on the activity of AuZG electrode towards ethanol oxidation has also been studied. The results obtained for AuZG-1 electrode in 0.5 M ethanol+ 0.5 M NaOH are presented in Fig. 12. The peak current was found to be proportional to the scan rate up to 20 mV s^{-1}, showing a normal behavior for a surface-adsorbed substance. However, at scan rate of >20 mV s^{-1}, deviation from linearity is observed. The relationship between j_p–v and v (Fig. 12b) decreases as the scan rate increases. This indicates that the reaction between Au particles trapped in zeolite layer and ethanol molecules depends on the rate of diffusion of ethanol through zeolite pores in order to reach the Au particles. The decrease in the scan rate allows more ethanol molecules to reach these atoms, leading to obtainment of higher oxidation rate.

Conclusions

Modification of zeolite–graphite electrode by gold atom has been done by a simple immersion technique which allowed the possibility of controlling a variety of metal loading on the electrode surface. AuZG electrodes show a better activity as well as poisoning tolerance during ethanol oxidation in alkaline medium in comparison with Au or Au/G electrodes. The order of activity was found to be: AuZG>Au/G>Au. The whole oxidation reaction was

found to be diffusion-controlled process depending on the diffusion of ethanol molecule through the zeolite layer to reach the Au particles.

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