

Electrocatalytic Oxidation of Methanol on Pt/NiZn Electrode in Alkaline Medium¹

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Abstract—In this study, a platinum electrode was coated with NiZn layer (Pt/NiZn) in a nickel-zinc bath by electrodeposition for use as anode material for methanol electrooxidation in alkaline solution. The electrode prepared was etched in a concentrated alkaline solution (30% NaOH) to produce a porous and electrocatalytic surface suitable for use in the methanol electrooxidation (Pt/NiZn). The surface morphologies and compositions of coating before and after alkaline leaching were determined by energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) techniques. The effect of NiZn coated platinum electrode for methanol electrooxidation was investigated in 1 M NaOH solution by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. Methanol electrooxidation on Pt/NiZn electrode was studied at various temperatures and potential scan rates. The results showed that Pt/NiZn electrode behaved as an efficient catalyst for the electrooxidation of methanol in alkaline medium.

Keywords: methanol electrooxidation, alkaline medium, electrocatalysis, electrodeposition

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INTRODUCTION

Direct alcohol fuel cells based on liquid fuels such as methanol have attracted enormous attention as power sources for portable electronic devices and transportation as alcohol has much higher energy density than gaseous fuels such as hydrogen and natural gas [1, 2]. The literature on electrochemical oxidation of alcohols can be roughly grouped into two sets: Fuel cells and homogenous catalysis [3]. Work on fuel cells primarily focuses on surface science/electrochemistry approach; single molecule catalysts are generally not considered [3].

Direct methanol fuel cells (DMFC) can become commercially feasible only if breakthroughs are achieved in reducing the loading of precious metal catalyst by methanol oxidation reaction intermediates [4]. Methanol, as a fuel, is a relatively highly active and easily transported and converted into energy from the liquid state. Although the DMFC has a lower power density (W m^{-2}) than the hydrogen fuel cell, the high theoretical energy storage capacity of methanol (5019 A h kg^{-1}) has the potential to increase the energy density of the DMFC system above that of competing electrochemical power sources [5].

Methanol oxidation in alkaline media is kinetically faster than in acidic media [6, 7]. The anode surface is covered by OH and CO species adsorbed on the surface. Cathode kinetics is also improved in alkaline media [8]. The disadvantage of alkaline solution is its progressive carbonation with CO_2 which has been the reason for the lack of interest in investigation of methanol oxidation in alkaline media [9, 10]. Thus, to avoid the carbonation alkaline membranes should be used [9]. Varcoe et al. [11] have reported the development of a novel alkaline membrane for DMFCs and showed reasonable performance stability.

The formation of intermediate organic poisoning species during the course of methanol oxidation reaction (MOR) on noble metals and their alloy electrodes in aqueous solution of alkaline and acid is considered to be a common phenomenon and has been poisoning a problem for developing DMFC anodes. These intermediate organic poisoning species has been found to exist in the form of $(\text{CHO})_{\text{ads}}$ in alkaline solution and in the form of linearly bonded $=\text{C}=\text{O}$ in acid solution on smooth Pt and Pt-based alloy electrodes [12]. The MOR mechanistic pathways in alkaline solutions are as follows [12]:



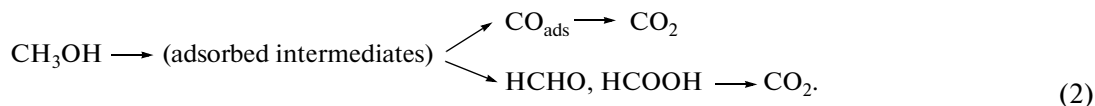
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Pt and Pt-based catalysts have been extensively used as the electrocatalysts for the oxidation of methanol [13–15]. Platinum has been recognized as an important electrocatalyst in the direct oxidation of small organic compounds [16]. Numerous modifications of Pt electrodes have been carried out in order to enhance the electrocatalytic oxidation process. This was achieved using various metals either by alloying, novel immersion techniques, or underpotential deposition [17, 18]. However transition metals (Cr, Ni, Co) alloyed with platinum as well as manganese oxides

[19, 20] are also found to be efficient catalysts to decrease the CO poisoning effect. Further these catalysts are effective to reduce the cost compared to pure platinum based electrodes. Nickel is also known to promote breaking of the C–H bond of methanol at the anode and the O=O bond rupture during the cathodic reduction of O₂ [21].

The total oxidation process consists of a pattern of parallel reactions which can, in principle, be formulated as follows [22]:



In this study, the electrooxidation of methanol was investigated using platinum and Pt/NiZn electrodes in 1 M NaOH solution. CV and EIS methods were used to investigate the reaction kinetics.

EXPERIMENTAL

The bath composition for NiZn coating was 30.00% NiSO₄ · 7H₂O, 1.00% NiCl₂ · 6H₂O, 1.25% H₃BO₃, 15.00% ZnSO₄ · 7H₂O, pH 5.6–6.2. Deposition was carried out by applying 20 mA cm⁻² constant current density at 298 K under stirring conditions and NiZn deposit with 10 μm thickness was achieved (Pt/NiZn*). The thickness of NiZn co-deposit was calculated by assuming an average alloy density of 7.5 g cm⁻³ and average atomic weight of 60 g mol⁻¹. The electrode prepared was immersed in 30.0% NaOH solution at room temperature during 24 h and more active zinc metal leached out from the surface to increase porosity of electrodes. The alkaline leached electrode was named as Pt/NiZn.

Before each experiment, the surface of platinum was immersed in HNO₃ : H₂O (1 : 1) and continuously washed with doubled distilled water. Then Pt was cleaned electrochemically using Bulk Electrolysis with Coulometry technique until obtain standard voltammogram of Pt.

The electrochemical measurements were carried out using a CHI 604 A.C. Electrochemical Analyzer (Serial Number 64721A) under computer control. A double-wall one-compartment cell with a three-electrode configuration was used. A platinum sheet with 2 cm² surface area and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. All potential values were referred to this reference electrode. Pt and Pt/NiZn electrodes were used as working electrodes. EIS measurements were performed at methanol oxidation peak potential which was determined from corresponding CV. The fre-

quency range was between 10⁵–10⁻³ Hz and amplitude was 0.005 V.

The test solutions used in this study were 1 M NaOH (Merck) solution with and without addition of various methanol concentrations (Merck). All the tests were carried out at 298 K and the test solutions were opened to the air. The tests were prepared by using bidistilled water.

The elemental analysis of NiZn surface before and after leaching was determined by EDX analysis. The surface morphologies were investigated by SEM technique using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10 kV EHT.

RESULTS AND DISCUSSION

The SEM images of NiZn coating before and after leaching are given in Fig. 1. It can be seen from Fig. 1a that the surface of Pt was fully covered by the NiZn layer. The coating is compact and has a porous structure. However, the morphology of surface changed significantly after leaching of Zn from the deposit (Fig. 1b). A great number of cracks and pores appeared leading a high surface area available for the methanol oxidation reaction.

Figures 2a and 2b show EDX spectrums obtained from the surface of NiZn coating before and after leaching process, respectively. The EDX analysis of Pt/NiZn* (as deposited) electrode reveals that the layer plated is made up of Ni and Zn elements with percentages of 10.94 wt % Ni and 89.06 wt % Zn. However, the metal composition of surface altered after the leaching of zinc from the surface of electrode and Zn content was decreased considerably. The surface composition was found to be 60.77 wt % Ni, 36.57 wt % Zn and 2.66 wt % Pt after leaching out.

Figure 3 shows voltammogram recorded for the Pt electrode at 298 K in 1.00 M NaOH at 0.100 V s⁻¹ scan

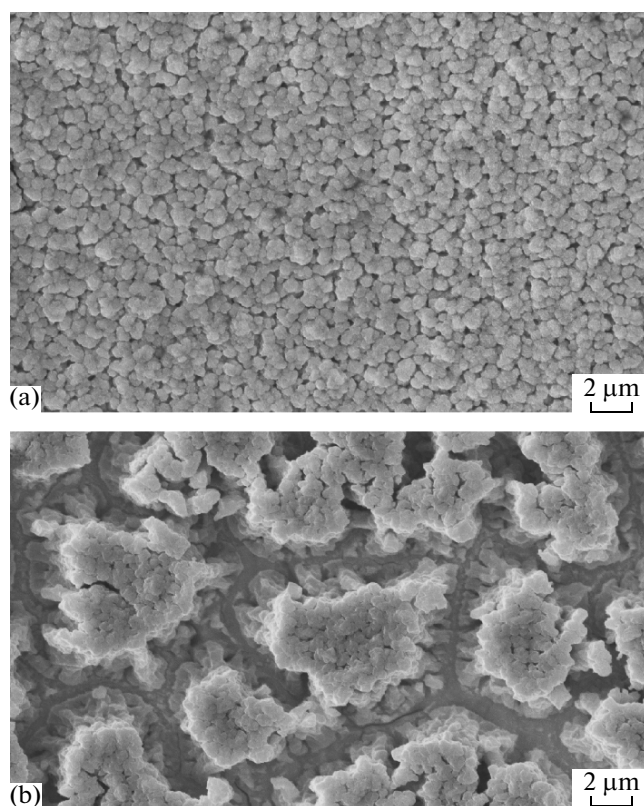


Fig. 1. SEM images of NiZn coating before (a) and after (b) zinc leaching process.

rate. The peaks named as *A* and *A'* are associated with the hydrogen adsorption/desorption process, while the anodic peaks, *B* that appeared at more positive potentials were related to formation of platinum oxides. The region between nearly -0.550 and -0.500 V is the double layer region. On the negative scan, the reduction of platinum oxides were observed between -0.100 and -0.500 V (*B'*).

The NiZn coated Pt electrodes before and after alkaline leaching of Zn were characterized by CV. The CVs of Pt/NiZn* (as deposited) and Pt/NiZn (after leaching) electrodes were recorded in 1 M NaOH solution at 298 K between the hydrogen and oxygen evolution potential range and the diagrams obtained are presented Figs. 4.1 and 4.2, respectively. As it was shown in Fig. 4, the CVs of NiZn coatings correspond to the well-known formation and reduction of the metal hydroxides and oxides. Three well-defined anodic peaks during the forward scan and one cathodic peak in the backward scan were observed, in the case of Pt/NiZn* electrode. These anodic peaks correspond to formation of Zn(OH)_2 at -1.20 V, Ni(OH)_2 at -0.80 V and NiOOH at 0.60 V, respectively. After leaching out Zn from the surface, Zn(OH)_2 peak is not seen in Fig. 4.2. The NiOOH formation peak of the Pt/NiZn* electrode is larger than

those of the Pt/NiZn* electrode, which is probably due to the increasing surface area.

In Fig. 5, CVs of Pt and Pt/NiZn (after leaching) electrodes in 1 M NaOH + 0.25 M CH_3OH solution were given. It is clear from Fig. 5 that the methanol electrooxidation activity of Pt/NiZn is significantly higher than that of Pt electrode. The enhanced performance of Pt/NiZn might be resulted from the synergistic effect of metals as well as enhanced surface area. The catalytic activity of Pt for methanol oxidation can be improved by co-deposition of Ni and Zn. The zinc was leached out and resulting high surface area is also responsible for functioning of the anode as good electrocatalyst.

Figure 6 shows the effect of methanol concentration on the electrooxidation activity of Pt electrode in 1 M NaOH solution. The peak observed during the forward scan is due to the methanol oxidation, while that observed during the forward scan is associated with the removal of carbonaceous intermediate [23–26]. Figure 7 shows the CVs of Pt/NiZn electrode obtained in 1 M NaOH solution in the presence of various concentrations of methanol. The most obvious voltammetric characteristics of methanol oxidation at the modified electrode is that the CVs recorded display a

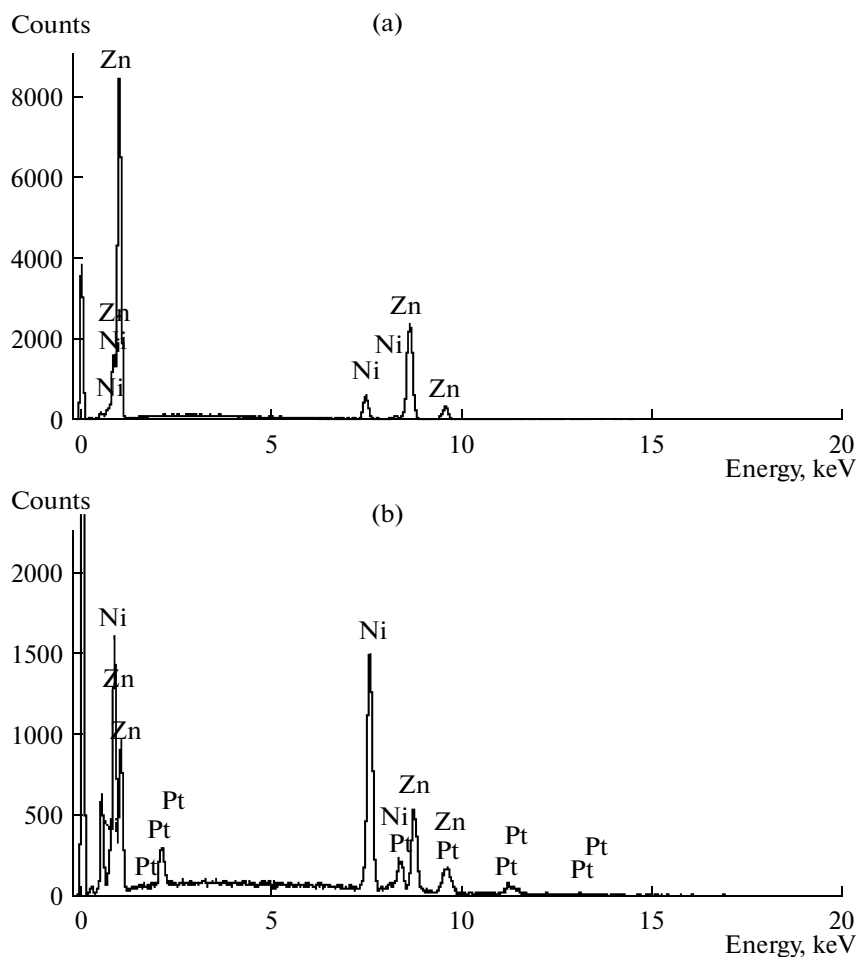


Fig. 2. Energy dispersive X-ray spectra obtained from the surface of NiZn coating before (a) and after (b) zinc leaching process.

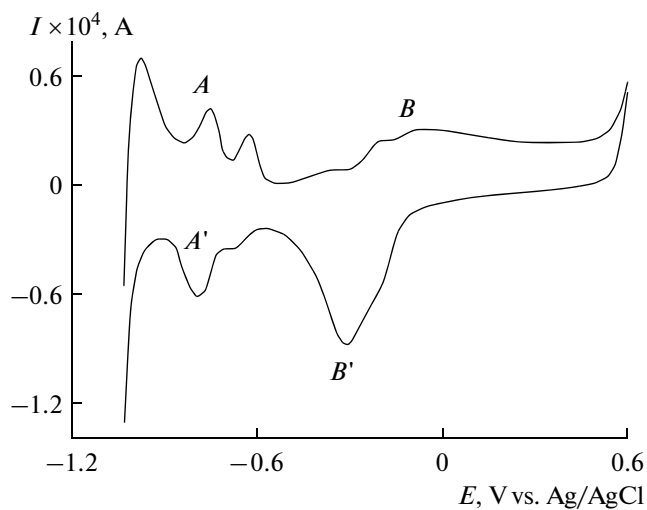


Fig. 3. Cyclic voltammogram of Pt electrode in 1 M NaOH solution at 0.100 V s^{-1} scan rate.

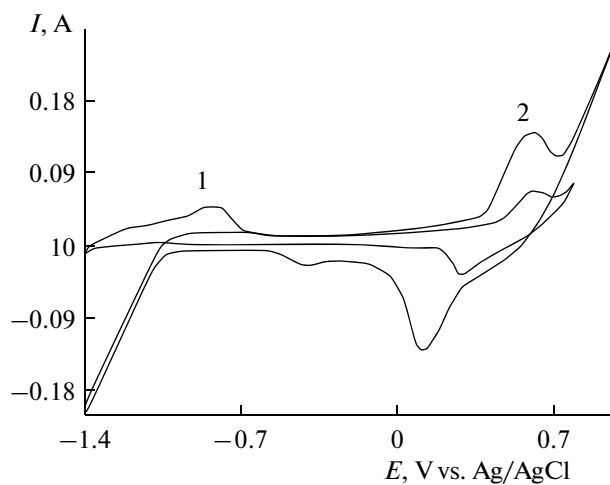


Fig. 4. Characterization curves of (1) Pt/NiZn, (2) Pt/NiZn electrode.

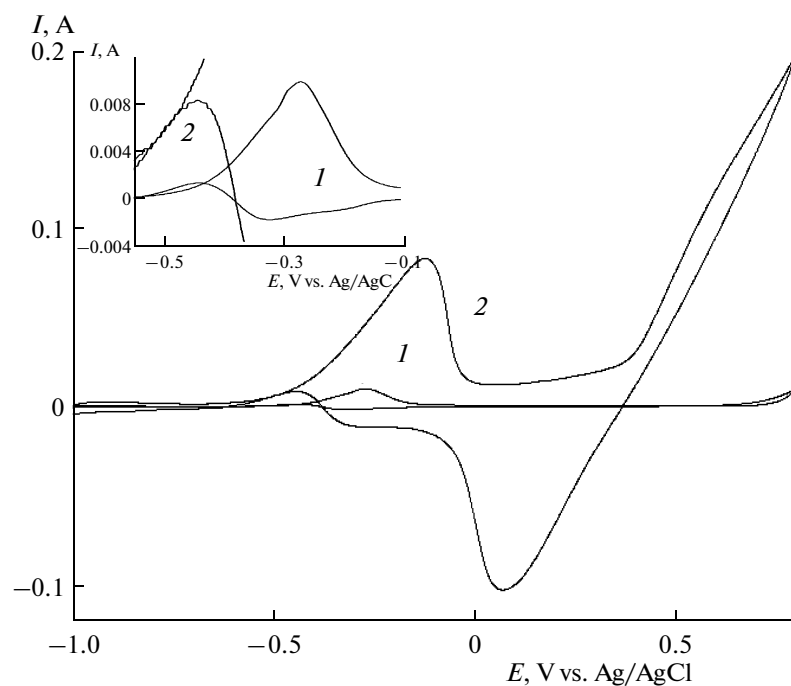


Fig. 5. Cyclic voltammograms of methanol electrooxidation on Pt (1) and Pt/NiZn (2) electrode in 1 M NaOH solution containing 0.25 M methanol at 0.100 V s^{-1} scan rate.

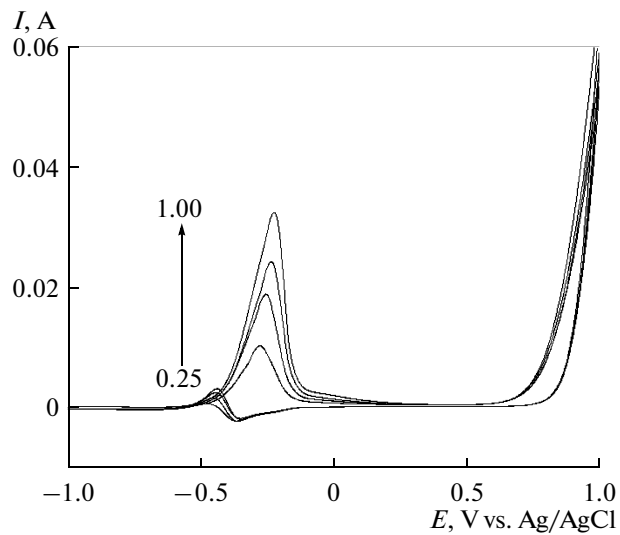


Fig. 6. Cyclic voltammograms of the Pt electrode in 1 M NaOH solution in the presence of 0.25, 0.50, 0.75 and 1.00 M of methanol in the solution at 0.100 V s^{-1} scan rate.

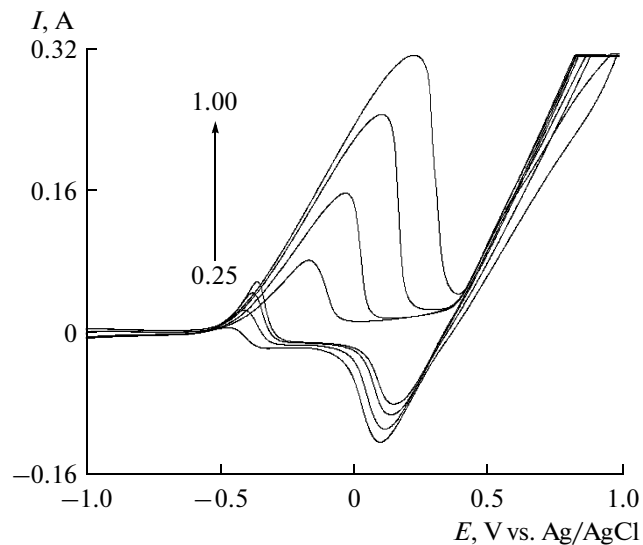


Fig. 7. Cyclic voltammograms of the Pt/NiZn electrode in 1 M NaOH solution in the presence of 0.25, 0.50, 0.75 and 1.00 M of methanol in the solution at 0.100 V s^{-1} scan rate.

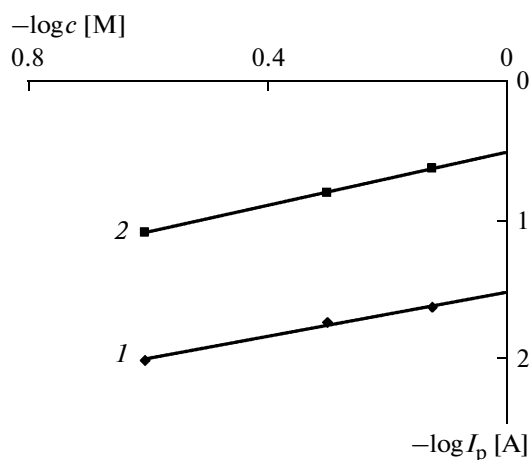


Fig. 8. $\log I_p$, $\log c$ curves obtained on Pt (1) and Pt/NiZn (2) electrodes at 0.100 V s^{-1} scan rate.

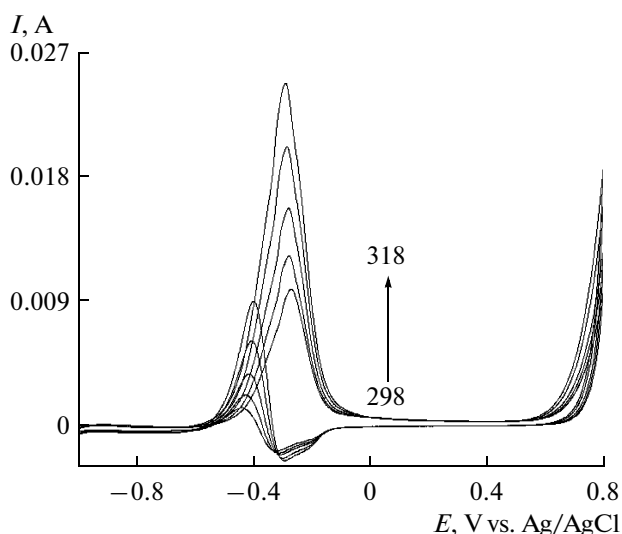


Fig. 9. Cyclic voltammograms of methanol electrooxidation on Pt electrode in 1 M NaOH solution containing 0.25 M methanol at 298, 303, 308, 313 and 318 K temperatures, at 0.100 V s^{-1} scan rate.

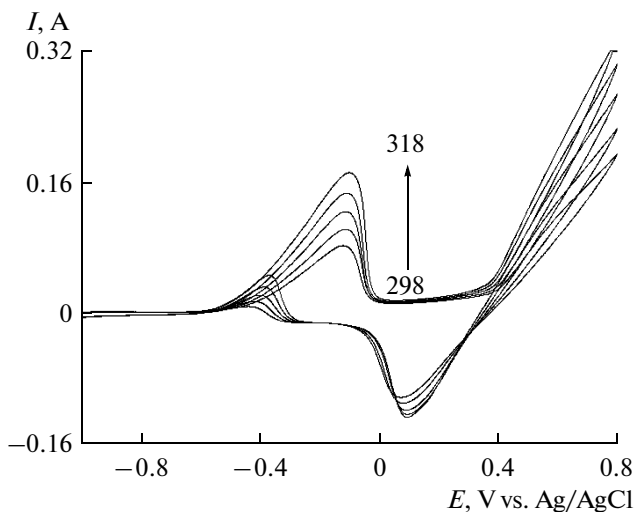


Fig. 10. Cyclic voltammograms of methanol oxidation on Pt/NiZn electrode in 1 M NaOH solution containing 0.25 M methanol at 298, 303, 308, 313 and 318 K temperatures, at 0.100 V s^{-1} scan rate.

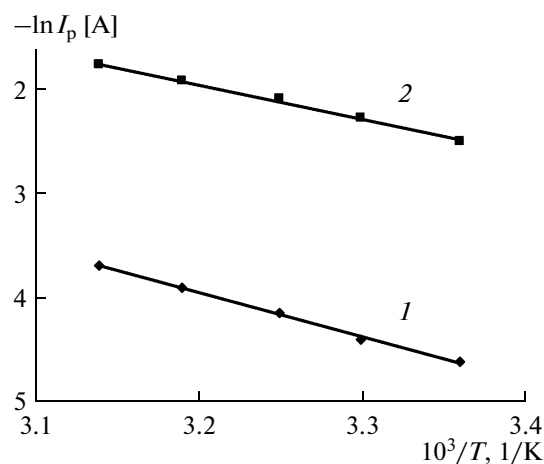


Fig. 11. $1/T$, $\ln I_p$ curves obtained in 1 M NaOH solution containing 0.25 M methanol on Pt (1) and Pt/NiZn (2) electrodes at 0.100 V s^{-1} scan rate.

large oxidation peak in the forward anodic scan and a cathodic peak in the backward cathodic scan.

The plot of peak current density of methanol oxidation at the Pt and Pt/NiZn electrodes with their bulk concentration up to a value of 0.25 M produces straight line relations (Fig. 8). The slope of these straight lines is equal to the order of reaction with respect to methanol according to the relations [17]:

$$\begin{aligned} \text{Rate} &\equiv I = kc^n, \\ \log I &= \log k + n \log c, \end{aligned} \quad (3)$$

where I is the peak current density, k is the reaction rate constant, c is the bulk concentration of methanol, and n is the reaction order. Reaction rate constant values of Pt and Pt/NiZn electrodes are 0.0312 and 0.3105, respectively. It is seen that the reaction rate constant (k) calculated on Pt/NiZn electrode is bigger than that was calculated on Pt electrode.

The temperature dependence for methanol electrooxidation was determined in the temperature range from 298 to 318 K by means of CV. Figures 9 and 10 show CVs of Pt and Pt/NiZn electrodes in 1 M NaOH + 0.25 M methanol solution at various temperatures. In

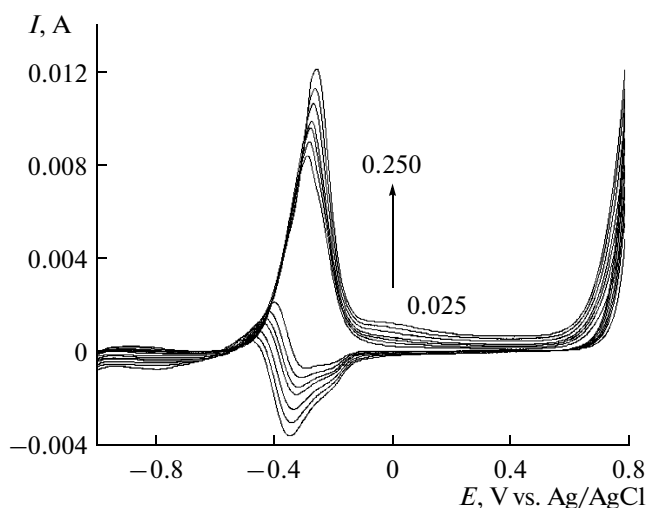


Fig. 12. Cyclic voltammograms of methanol oxidation on Pt electrode in 1 M NaOH solution containing 0.25 M methanol at 0.025, 0.050, 0.075, 0.100, 0.150, 0.200 and 0.250 V s⁻¹ scan rate.

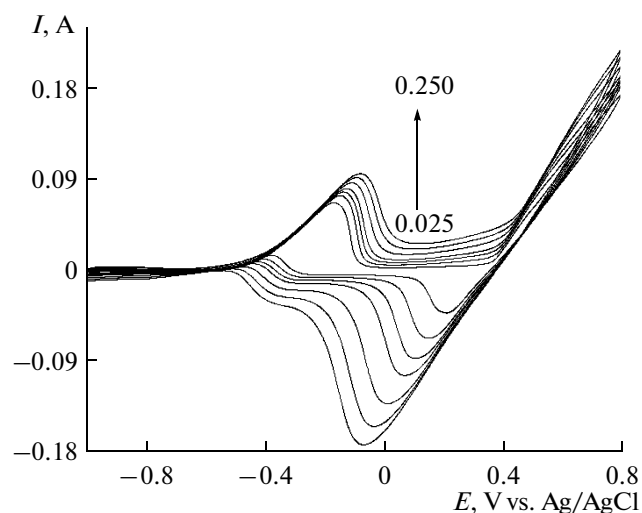


Fig. 13. Cyclic voltammograms of methanol oxidation on Pt/NiZn electrode in 1 M NaOH solution containing 0.25 M methanol at 0.025, 0.050, 0.075, 0.100, 0.150, 0.200 and 0.250 V s⁻¹ scan rate.

both electrodes, peak currents increased with the increase of temperature. Figure 11 represents Arrhenius plots obtained in the case of Pt and Pt/NiZn electrodes. Activation energies (E_a) determined for Pt and Pt/NiZn electrodes are 35.18 and 27.49 kJ mol⁻¹, respectively. The E_a was decreased at NiZn coated Pt electrode indicates better catalytic activity for the methanol electrooxidation.

Figures 12 and 13 show the CVs of Pt and Pt/NiZn electrodes in 1 M NaOH solution at various scan rates (0.025–0.250 V s⁻¹). Both Pt and Pt/NiZn electrodes's methanol oxidation peak currents increased with the increase of scan rate.

The Nyquist plots of Pt and Pt/NiZn electrodes obtained in 1 M NaOH + 0.25 M CH₃OH solution at 298 K are shown in Fig. 14. The effective charge transfer resistance was used to determine the efficient electrode for methanol oxidation reaction. The impedance plots wrap around the origin anti-clockwise and the capacitive arcs flip to the second quadrant with the real component of the impedance becoming negative, which is probably due to the passivation of electrode surface [27]. As it can be seen clearly from Fig. 14, the diameter of semi circle which corresponds to charge transfer resistance reduced considerably at Pt/NiZn electrode in comparison to that observed for Pt electrode. This result suggests that the Pt/NiZn offers better catalytic surface for the oxidation of methanol in NaOH which may be result of increasing effective surface area for the charge transfer reaction [27, 30].

CONCLUSIONS

The methanol electrooxidation on Pt and Pt/NiZn electrodes was investigated in 1 M NaOH solution with the addition of various concentrations of metha-

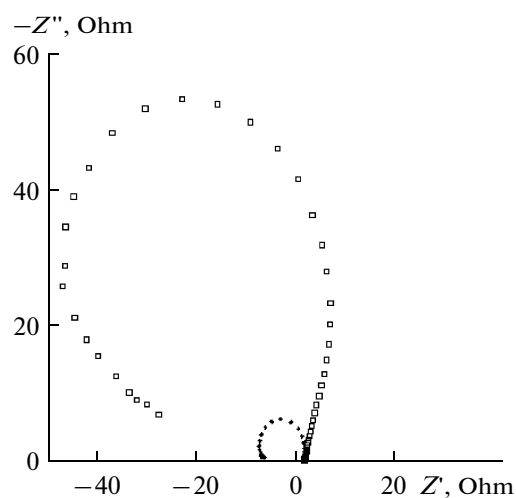


Fig. 14. Impedance diagrams obtained on Pt and Pt/NiZn electrodes in 1 M NaOH solution containing 0.25 M methanol.

anol. It was found that the reaction rate constant was increased and activation energy was decreased when a thin NiZn was prepared on the Pt electrode in comparison with uncoated Pt. The methanol electrooxidation on Pt/NiZn electrode was faster than on Pt electrode. The better methanol electrooxidation activity of Pt/NiZn electrode was associated with the increasing surface area and synergistic effect of metals.

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