

Electrocatalytic oxidation of methanol on a nickel electrode modified by nickel dimethylglyoxime complex in alkaline medium

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Abstract

Electrocatalytic oxidation of methanol on a nickel disc electrode coated with nickel dimethylglyoxime complex (NiDMG), conditioned by potential recycling in a potential range of 100–700 mV (versus SCE) is studied by cyclic voltammetry in alkaline medium (0.10 M NaOH). The results show that the NiODMG layer formed at the surface of electrode behaves as an efficient electrocatalyst for the oxidation of methanol in alkaline medium via Ni(III) species with the cross exchange reaction occurring through out the layer at a low concentration of methanol. A plausible mechanism was proposed for catalytic oxidation of methanol at this modified electrode. Moreover, the effects of various parameters such as oven temperature, ligand concentration, potential scan rates, methanol concentration and media temperature on the electro-oxidation of methanol were investigated.

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1. Introduction

The electro-oxidation of methanol is a research topic of great concern for the development of high performance methanol fuel cells [1,2]. In this respect, a great deal of interest exists in the development of materials with capability for the electrocatalytic oxidation of methanol, in order to decrease the typically large over potentials encountered in its direct oxidation at most unmodified electrode surfaces.

The mechanism and kinetics of methanol oxidation have been studied under a wide range of conditions and on various electrodes including Pt [3], binary and ternary alloys [4,5], modified electrodes [6,7], nano-composites [8,9] and nickel [10–12]. It has been shown that the over potential for electro-oxidation of methanol depends strongly on the

electrode material, its physicochemical state and the involved substrates. Pt electrodes have been reported to be most active for this reaction in acidic medium, but their activity is not satisfactory high [13,14]. One promising approach for minimizing over voltage effects is through the use of an electrocatalytic process at chemically modified electrodes [15,16]. In this context, preparation of modified electrodes with Ni-containing modifiers and its application in catalytic oxidation of organic molecules have received considerable attention [17,18].

In the early works, it was shown that the nickel compounds are capable to form conducting polymeric films at the electrode surface, which are used as modifier due to its reactivity in alkaline solutions as a nickel hydroxide electrode [19,20]. In the present work, the nickel electrode is modified with dimethylglyoxime and the efficiency of this electrode, toward the electrocatalytic oxidation of methanol in alkaline medium, is investigated.

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2. Experimental

2.1. Reagents and apparatus

Sodium hydroxide, dimethylglyoxime and methanol used in this work were analytical grade of Merck origin and were used without further purification. Ni wire (99.99%, 2 mm in diameter) was obtained from Aldrich. All solutions were prepared by doubly distilled water.

The electrochemical experiments were carried out using a Radiometer Model DEA332 digital electrochemical analyzer equipped with an IMT 102 electrochemical interface and a personal computer was used for data storage and recording. Cyclic voltammetric experiments were done in a conventional three-electrode cell using a nickel disc as working electrode (with 2 mm in diameter). Auxiliary electrode was a platinum wire and reference electrode was a saturated calomel electrode.

Infrared spectra in the region of 400–4000 cm^{-1} were recorded in KBr pellets using a BRUCKER vector 22 FT-IR spectrophotometer. The spectrum obtained after multiple scans was a plot of transmittance percent against wave number.

2.2. Modified electrode preparation

The nickel disc electrode was fitted into a Teflon exposing circular. The surface of the electrode for each experiment was mechanically polished with 600-grit sand-paper and then with 0.05 μm α -alumina powder. The polished surface rinsed with acetone and then with doubly distilled water.

The preparation of nickel dimethylglyoxime-modified electrode consists of the following steps: 150 μL (three droplets) of a 0.010 M solution of dimethylglyoxime ligand in acetone was gradually deposited on the surface of working electrode. The electrode was dried every time in an air oven at 160 $^{\circ}\text{C}$ ($\pm 2^{\circ}\text{C}$) for 30 min and then rinsed with water. The prepared electrode was conditioned in 0.10 M NaOH solution by potential cycling between 100 and 700 mV (versus SCE) at a sweep rate 100 mV s^{-1} , for about 50 cycles of potential scans. These parameters were obtained experimentally as optimum values for complete transformation of NiDMG to NiODMG and maximum activation of electrode surface towards electrocatalytic oxidation of methanol.

3. Results and discussion

3.1. Parameters affecting the electrode modification

3.1.1. Effect of ligand concentration

The effect of the DMG concentration on the peak heights of methanol oxidation in a solution containing 0.10 M NaOH + 0.10 M methanol and in the various ligand

concentration range (0.010–0.200 M) was investigated (Fig. 1). As can be seen, at 0.010 M of ligand concentration, the Electro-catalytic oxidation of methanol increases and shows a maximum peak current.

Surface-bonded hydroxyl radicals play a fundamental role in the catalysis oxidation of methanol. The surface of these bonded radicals is hydroxide ions in NaOH solution [21]. When all of the electrode surface is covered by NiDMG complex, the radicals cannot bond on the surface and the electrode was not active for electrocatalytic oxidation of methanol. Accordingly, on the basis of the above-mentioned results, an optimum ligand concentration of 0.010 M is proposed for the methanol oxidation (as shown in Fig. 1). At this concentration, from obtained the optimum number of ligand droplet, we change the number of ligand deposited droplet and observed that with increasing of ligand droplet number, the peak current height corresponding oxidation of methanol increased up to three droplet (Fig. 2).

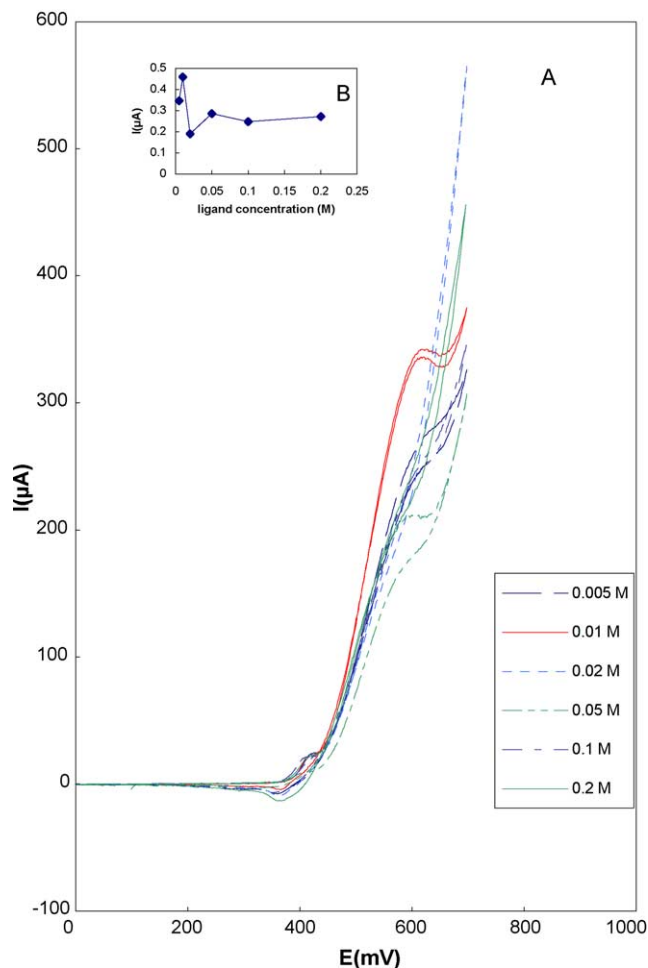


Fig. 1. (A) Cyclic voltammograms obtained in 0.10 M NaOH for Ni/NiODMG electrodes in the presence of 0.10 M methanol with various DMG concentrations in range 0.0050–0.20 M in modification step. (B) Variation of anodic peak currents obtained with DMG concentration. (Oven temperature: 160 $^{\circ}\text{C}$, volume of ligand: 150 μL , scan rate: 20 mV s^{-1} .)

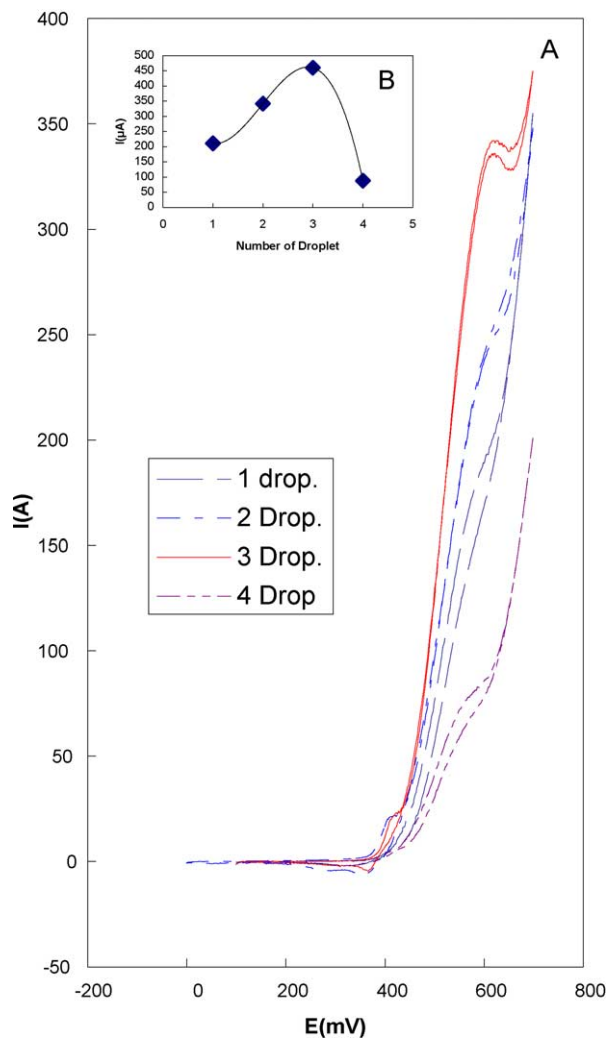


Fig. 2. (A) Cyclic voltammograms obtained in 0.10 M NaOH for Ni/NiODMG electrodes in the presence of 0.10 M methanol with various droplet of deposited complex in modification step. (B) Variation of anodic peak currents obtained with number droplet of deposited complex. (Oven temperature: 160 °C, concentration of ligand: 0.010 M, scan rate: 20 mV s⁻¹.)

3.1.2. Effect of oven temperature

The effect of the oven temperature on the electrode modification process via studies of peak current of the methanol oxidation in a solution containing 0.10 M NaOH, 0.10 M methanol (used 0.010 M DMG in the electrode modification process) was investigated in the range of oven temperature 110–180 °C and is shown in Fig. 3. A linear increase in the peak current with increasing the oven temperature is observed up to 160 °C. This is indicating an enhancement of the methanol oxidation rate with oven temperature in the electrode modification process. No significant enhancement was observed in higher temperatures.

It was shown that the chemical oxidation of nickel is a spontaneous reaction ($\Delta G = -44.3831 \text{ kJ mol}^{-1}$). Consequently, formation of Ni(II) accelerated with increasing the oven temperature. When temperature goes up to 160 °C,

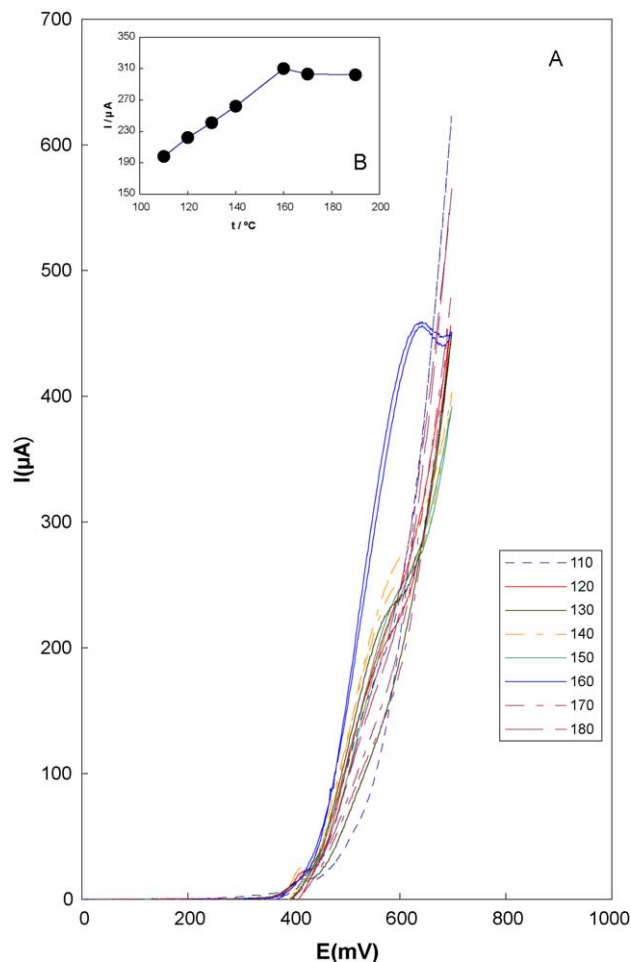


Fig. 3. (A) Cyclic voltammograms obtained in 0.10 M NaOH for Ni/NiODMG electrodes in the presence of 0.10 M methanol with various oven temperatures in modification step. (B) Variation of anodic peak currents obtained with oven temperature. (Concentration of ligand: 0.010 M, volume of ligand: 150 μL , scan rate: 20 mV s⁻¹.)

all of surface atoms oxidized and formed the complex. Therefore, in this temperature, formation of the complex is completed, and increasing oven temperature has not any effect on the efficiency-modified electrode. Although, it has been reported that, a temperature of 150 °C is needed for the effective drying of NiDMG at surface electrode [22]. On the basis of the FT-IR spectrum (as shown in Fig. 4) and comparing with the results of previous reported [23], it can be concluded that the NiDMG complex is formed in these conditions at the surface of electrode. Ultimately, in preparation of modified electrode (Ni/NiODMG), optimum value of parameters affecting the electrode modification is used (ligand concentration: 0.01 M, number of ligand droplet: 3 (150 μL), oven temperature: 160 °C). Then, the modified electrode washed with doubly distilled water and was conditioned in 0.10 M NaOH solution by potential cycling from 100 to 700 mV (versus SCE) at sweep rate of 50 mV s⁻¹ for about 33 min (100 cycles of potential scans), which was found adequate to obtain the modified electrode.

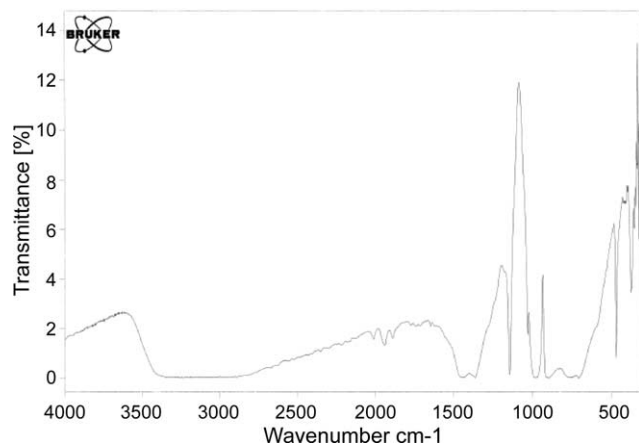


Fig. 4. FT-IR spectra of NiODMG complex formed at surface of modified electrode in modification condition.

This time was obtained experimentally as optimum value for complete transformation of NiDMG to NiODMG and maximum activation of electrode surface towards electrocatalytic oxidation of methanol (see the inset of Fig. 5).

3.2. Electrocatalytic oxidation of methanol

The modifier layer NiODMG at the electrode surface acts as a catalyst for the oxidation of methanol in 0.10 M NaOH solution. Fig. 5 shows the behavior of this electrode in absence and presence of 0.1 M methanol. It obviously seen that the oxidation occurred in two regions of potential. The first region corresponds to that where Ni(III) species begin to produce [10,24–26]. At that potential, methanol oxidation appears as an increase in $I_{p,a}$ accompanied by a decrease in cathodic peak current in the negative sweep. This indicates clearly that the applied modifier in this process participates directly in the electrocatalytic oxidation of methanol. In the second region of potential, where only Ni(III) species exists at the electrode surface, a new anodic peak (b) with a large peak current with respect to that of the former one is appeared. The height of this peak increases linearly with methanol concentration in solution, indicating that it pertains to the process in which methanol is involved. Moreover, the efficiency of the prepared NiODMG for methanol oxidation, characterized by anodic peak current density is significantly high in comparison with other modified electrodes reported in the literature [16,19,27].

The appearance of the new anodic peak (b) at more positive potentials can lead to the conclusion that methanol oxidation takes place mainly after the oxidation of Ni(II) to Ni(III) [28,29]. On the other hand, there is a separation of the Ni(II)/Ni(III) oxidation peak from that for methanol oxidation. On the basis of this observation, the catalytic role of Ni(III) for methanol oxidation is obvious as proposed previously by Fleischmann et al. [30].

On the basis of the other works [25,31] and in the light of present study, a possible mechanism can present with an

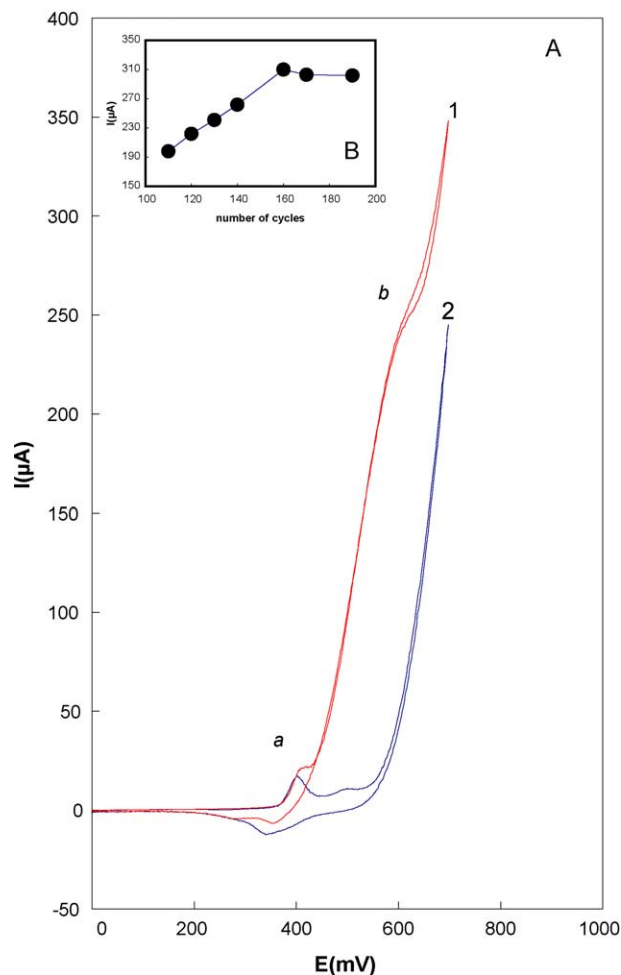
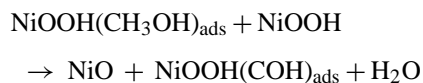
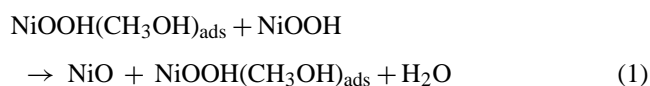
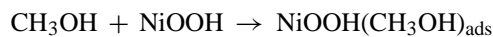


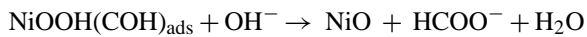
Fig. 5. (A) Cyclic voltammograms obtained in 0.10 M NaOH for Ni/NiODMG electrode: (1) in the presence and (2) in absence of 0.10 M methanol. (B) Inset shows the cyclic voltammograms recorded during the varied numbers of cycles of potentials; scan rate: 20 mV s⁻¹.

overall reaction leading to formate anions:



This mechanism may be written as follows, taking into account that the mechanism of electro-oxidation does not change with temperature variation within the explored temperature range:





In the presented mechanism, Eq. (1) indicates the rate-determining step.

The effect of various factors on the oxidation of methanol at NiODMG was studied. The obtained results can be presented as follow.

3.2.1. Effect of methanol concentration

Fig. 6 shows the effect of methanol concentration on the anodic peak current at Ni/NiODMG electrode in 0.10 M NaOH. It is clearly observed that as the methanol concentration increases, the peak height increase linearly with methanol concentration up to 0.40 M. It can be assumed that the increase is due to the presence of a diffusion-controlled process that appears to play an important role at low methanol concentrations. While the methanol concentration exceeds this limit, the rate of the whole oxidation process seems to be limited by that of the catalytic process in origin and its

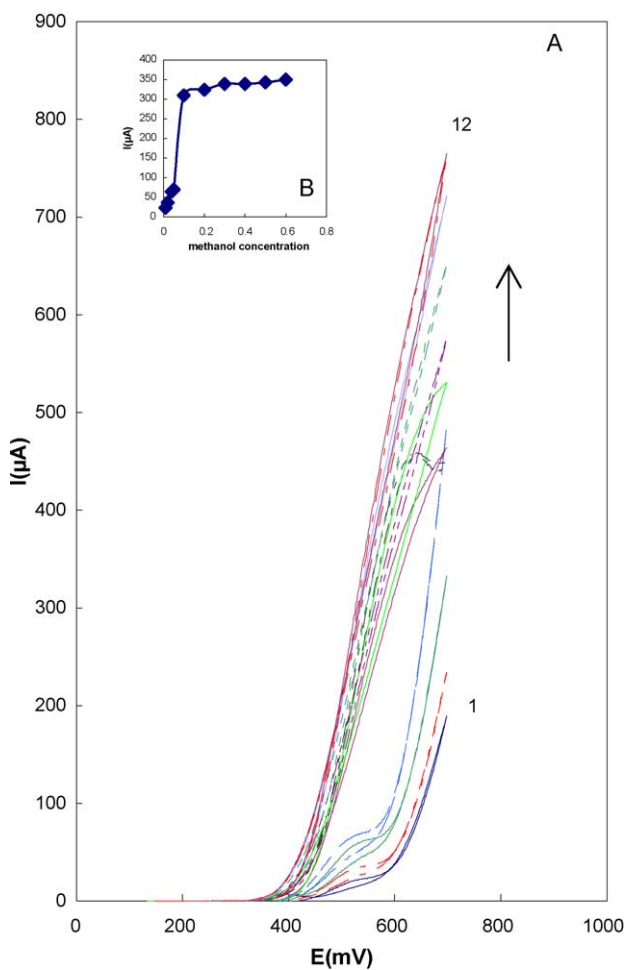


Fig. 6. Plot of anodic peak currents as a function of methanol concentration for Ni/NiODMG electrode: (1) 0.10 M, (2) 0.020 M, (3) 0.040 M, (4) 0.050 M, (5) 0.10 M, (6) 0.20 M, (7) 0.30 M, (8) 0.40 M, (9) 0.50 M, (10) 0.60 M, (11) 0.70 M and (12) 0.80 M (scan rate: 20 mV s^{-1}).

rate depends on the reaction between methanol and Ni(III) species, which is present in the film.

3.2.2. Effect of scan rate on the anodic peak heights

The effect of scan rate on the peak current ratio at modified electrode (Ni/NiODMG) in 0.10 M NaOH + 0.10 M methanol is shown in Fig. 7. This curve shows that the anodic current for methanol oxidation decreases rapidly with increasing the potential scan rate. Indeed, the time window for methanol oxidation process at higher scan rates becomes very narrow avoiding the facile electron transfer between substrate and catalytic sites. However, the peak currents of the oxidation of NiO and the reduction of NiOOH enhanced with increasing the scan rate. Therefore, it can be concluded that the NiO/NiOOH transformation process is much faster than the methanol oxidation. Direct reaction between methanol and NiOOH (that formed on the electrode surface) produces NiO leading to a little increase in the anodic peak current.

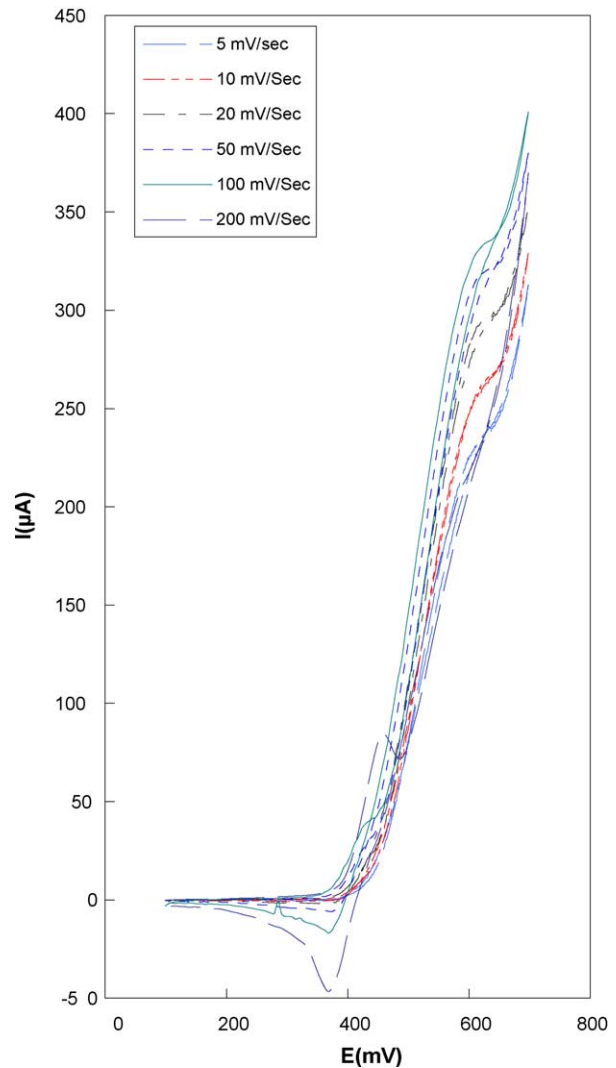


Fig. 7. Variation of anodic peak currents with scan rates in the presence of 0.10 M methanol for Ni/NiODMG electrode.

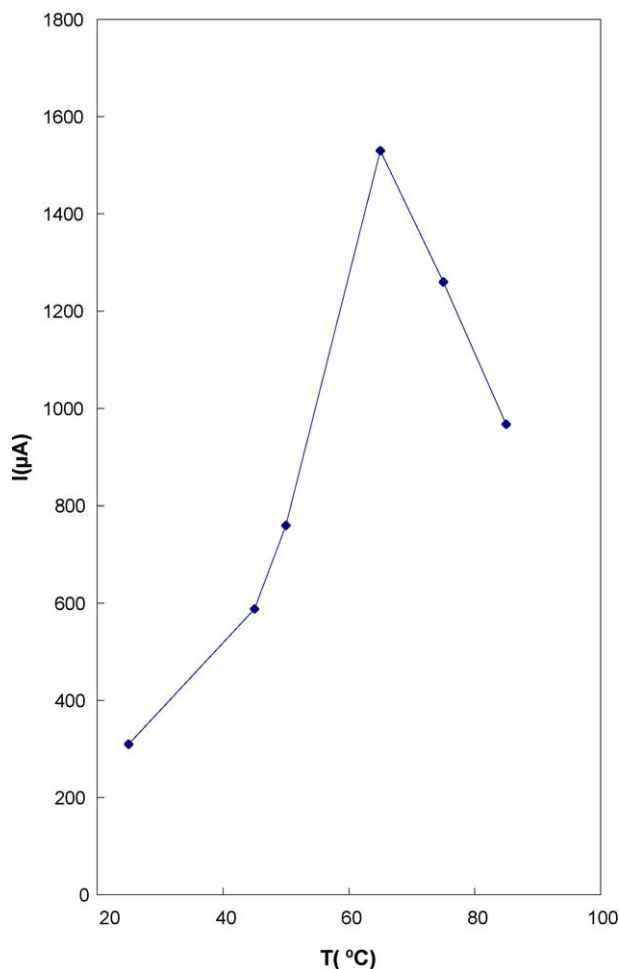


Fig. 8. Medium temperature effect on cyclic voltammograms of methanol oxidation on Ni/NiODMG electrode in the range 30–85 °C (scan rate: 20 mV s⁻¹).

At higher potentials, the whole catalytic sites are in NiOOH form, which cause a considerable growth in the anodic current of peak corresponding to oxidation of methanol. The amount of NiOOH formed on the electrode surface decreases in the reverse scan due to its chemical reaction with methanol, which appears as a decrease of cathodic peak height.

3.2.3. Effect of medium temperature

The effect of medium temperature on the anodic current is shown in Fig. 8. It is found that the anodic current at the Ni/NiODMG electrode is not affected by temperature variations, most probably due to the inactive nature of the electrode matrix for the electron transfer process. A linear increase in the peak current with increasing medium temperature is observed for this electrode up to 65 °C, indicating an enhancement of the kinetics of methanol oxidation with the temperature. The decrease of peak current in higher temperatures can be attributed to the progressive evaporation of methanol with increasing temperature. By assuming that no azeotrope is formed in the methanol/water mixture [31], it

is expected that a progressive decrease in peak current should appear during the temperature elevation, because of a loss in methanol concentration. However, the linear increasing of the peak current, which is observed in practice in temperatures till 65 °C can be correlated to the acceleration of the electrode reaction kinetics proportionally to temperature increase. Accordingly, on the basis of the above results, an optimum temperature of 60 °C is proposed for methanol oxidation at Ni/NiODMG electrode in 0.10 M methanol + 0.10 M NaOH (the boiling point of methanol is 64.5 °C).

4. Conclusion

This work presents the electrocatalytic oxidation of methanol on nickel dimethylglyoxime-modified nickel electrode (Ni/NiODMG) in alkaline solutions. It is concluded that the electro-oxidation of methanol that starts around 610 mV (versus SCE) occurs through a mediated electron transfer mechanism catalyzed by Ni(III) species, which form in the same potential region. The kinetics of the reaction based on the above mechanism has been developed and the optimum temperature for modification, optimum methanol concentration and optimum temperature have been obtained.

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References

- [1] S. Wasmus, A. Kűver, J. Electroanal. Chem. 461 (1999) 14–31.
- [2] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111–116.
- [3] H. Nonaka, Y. Matsumura, J. Electroanal. Chem. 520 (2002) 101–110.
- [4] C.L. Green, A. Kucernak, J. Phys. Chem. 106B (2002) 1036–1047.
- [5] A.S. Arico, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano, Vantonucci, J. Power sources 55 (1995) 159–166.
- [6] M. Jafarian, M.G. Mahjani, H. Heli, F. Gopal, H. Khajesharifi, M.H. Hamedi, Electrochim. Acta 48 (2003) 3423–3429.
- [7] S.M. Golabi, A.N. Golikand, Electroanalysis 15 (2003) 278–286.
- [8] F.E. Jones, S.B. Milen, B. Gurau, E.S. Smotkin, S.R. Stock, C.M. Lukehart, J. Nanosci. Nanotechnol. 2 (2002) 81–85.
- [9] J. Luo, M.M. Maye, Y. Lou, L. Han, M. Hepel, C.J. Zhong, Catal. Today 77 (2002) 127–138.
- [10] A.A. Elshafei, J. Electroanal. Chem. 471 (1999) 89–95.
- [11] M.S. Kim, T.S. Hwang, K.B. Kim, J. Electrochem. Soc. 144 (1997) 151–157.
- [12] M.A. Abdel Rahim, R.M. Abdel Hameed, M.W. Khalil, J. Power Sources 134 (2004) 160–169.
- [13] C. Lamy, J.M. Leger, J. Clavilier, R. Parsons, J. Electroanal. Chem. 150 (1983) 71–77.
- [14] A. Kucernak, JiangF J.H., Chem. Eng. J. 93 (2003) 81–90.

- [15] B. Bittins-Cattaneo, T. Iwasita, J. Electroanal. Chem. 238 (1987) 151–161.
- [16] S.M. Golabi, A.N. Golikand, Electroanalysis 16 (2004) 199–209.
- [17] C. Lin, A.B. Bocarsly, J. Electroanal. Chem. 300 (1991) 325–345.
- [18] E.Y. Lee, D. Hong, H.W. Park, M.P. Suh, Eur. J. Inorg. Chem. (2003) 3242–3258.
- [19] A. Ciszewski, G. Milczarek, J. Electroanal. Chem. 426 (1997) 125–130.
- [20] A. Ciszewski, G. Milczarek, J. Electroanal. Chem. 469 (1999) 18–26.
- [21] S. Chen, M. Schell, J. Electroanal. Chem. 478 (1999) 108–117.
- [22] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd ed., Longman, London, 1975, p. 479.
- [23] K.O. Xavier, J. Chacko, K.K. Mohammed Yusuff, Appl. Catal. A: Gen. 258 (2004) 251–259.
- [24] R.-S. Schebler-Guzam, J.R. Vielche, A. Arvia, J. Electrochem. Soc. 125 (1978) 1578–1582.
- [25] R.-S. Schebler-Guzam, J.R. Vielche, A. Arvia, Corros. Sci. 18 (1978) 441–449.
- [26] A. Seghioure, J. Chevalet, A. Barboun, F. Lantelme, J. Electroanal. Chem. 442 (1998) 113–123.
- [27] A. Ciszewski, G. Milczarek, J. Electroanal. Chem. 413 (1996) 137–142.
- [28] P.M. Robertson, J. Electroanal. Chem. 111 (1980) 97–104.
- [29] J. Taraszewska, G. Roslonek, J. Electroanal. Chem. 364 (1994) 209–213.
- [30] M. Fleischmann, K. Korinek, D. Pletcher, J. Electroanal. Chem. 31 (1971) 39–49.
- [31] S. Ohi, Vapor–Liquid Equilibrium Data, Physical Science Data Series, vol. 37, Elsevier, Amsterdam, 1989, p. 94.