

Short communication

A systematic study on the effect of OH^- and Ni^{2+} ions on the electro-catalytic oxidation of methanol at Ni-S-1 electrode

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Received 25 February 2005; accepted 14 March 2005

Available online 31 May 2005

Abstract

The effect of varying nickel ions as well as OH^- ions concentration on the electrochemical oxidation of methanol on nickel impregnated silicalite-1 (Ni-S-1) electrodes was investigated. The study of nickel ions concentration effect was carried out in two different ways: by varying the soaking time in one and the same concentration of NiSO_4 solution, or by fixing the soaking time in different concentrations of NiSO_4 solution. The results showed that for electrodes pre-soaked in 1.0 M NiSO_4 solution for 90 s, increasing the OH^- ions concentration results in increasing the oxidation current density of methanol. On the basis of this result, high concentration of KOH is preferable as a medium for methanol oxidation at the Ni-S-1 electrode in presence of nickel ions. On the other hand, at a certain OH^- ions concentration, the peak height of methanol oxidation increases with increasing Ni ions concentration up to a certain value after which no effect was observed. A first order reaction kinetics with respect to both nickel ions and OH^- ions was estimated for the oxidation of methanol.

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Keywords: Nickel-zeolite; Impregnated silicalite-1; Electro-catalyst; Methanol oxidation; Alkaline solution

1. Introduction

Fuel cells are being considered as an important technology that can be used for various power applications. They are devices in which the energy of a chemical reaction is converted directly into electricity. In direct methanol fuel cells (DMFC), methanol is used as a fuel. It is electrochemically oxidized at the anode electro-catalyst to produce electrons which travel through the external circuit to the cathode electro-catalyst where they are consumed together with oxygen in a reduction reaction. The main problem facing the performance of the DMFC is the choice of a suitable catalyst for the complete oxidation of methanol to CO_2 and H_2O . For this purpose, intensive efforts have been carried out in order to prepare efficient catalysts for this reaction. Several possible solutions to this problem were adopted by various research groups [1]. These solutions involve the prepara-

tion and development of a number of catalysts based on: platinum binary [2,3] and ternary [3] or quaternary [4,5] alloys, carbon-supported electrodes [1,2,6,7], platinized expanded graphite [8] and modified-zeolite electrodes [9], . . . , etc. Some of these electro-catalysts are used as a cathode catalyst to enhance the performance of the direct methanol fuel cells [10]. It seems that the method of catalyst preparation [11] and the preparation conditions [7,12,13] greatly affect the performance of the catalyst for methanol electro-oxidation.

The use of zeolites as supported electrodes represents one of the solutions that overcome the problem of catalytic oxidation of methanol. Zeolites are crystalline microporous solids that contain many channel-networks providing molecular-sized cages and passageways for excellent steric control of reaction paths. For catalytic purposes, modification of zeolites is, therefore, carried out with some metals. The pore geometry is considered as the main reason for the different activity of zeolite-based catalysts. Transition metal-containing zeolites were found to exhibit a high cat-

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alytic activity. Ni-containing zeolites [14], Ti-zeolites [15], Pt- and Pt–Ru-zeolites [16] have been used for catalytic purposes.

Our previous work [9] involved the use of Ni impregnated zeolite, Ni-silicalite-1 (Ni-S-1 electrode), for the electrochemical oxidation of methanol in KOH solution. The study revealed that the catalytic activity was greatly enhanced by soaking the electrode in NiSO₄ solution for some time. The present investigation describes the effect of Ni ions as well as the hydroxyl ions concentrations on the catalytic behaviour of Ni-S-1 electrodes towards the electro-oxidation of methanol and the conditions that provide the highest catalytic activity.

2. Experimental technique

Silicalite is a crystalline material with a special structure and contains 100% SiO₂. The silicalite-1 (1 SiO₂: 0.437 TPAOH: 26H₂O), used as a substrate, is of a MFI-type zeolite structure [17,18], it has been synthesized in Institut für Technische Chemie, Technische Universität Dresden, Dresden, Germany. It has a surface area (N₂-adsorption) of 466 m² g⁻¹ and the volume of the micropores is 0.182 cm³ g⁻¹. The preparation of nickel-silicalite-1 catalyst was performed by the impregnation technique. Details of the preparation method are described elsewhere [9].

The Ni-S-1 electrode was mixed with activated carbon black (high surface area acetylene black as P1042, Stickstoffwerk Piesteritz, Germany) in the ratio of 1:3, respectively, in a water bath at around 80 °C with constant stirring for 3 h. This step was particularly necessary to ensure that the zeolite component of the catalyst becomes fully conducting prior to the electrochemical tests. A 10 wt% suspensions of PTFE (used as suspension, Dyneon TF5032) and an appropriate amount of isopropyl alcohol were used together with the Ni-S-1 to form a paste. The resulting paste was spread over a gold plated stainless steel mesh of 0.38 cm² apparent surface area and pressed under 4 t cm⁻² pressure for a period of 5 min. The electrode discs obtained were then dried in an air oven at 110 °C for 1 h, and subsequently, heated at 300 °C for 15 min.

The electrochemical measurements were performed using an Amel 5000 system (supplied by Amel instrument, Italy) driven by a PC for data processing. The PC was interfaced with the instrument through a serial RS-232C card. Amel Easyscan software was used in connection with the PC to control the Amel 5000 system. A conventional 3-electrode glass cell with a Pt sheet as a counter electrode and Hg/HgO/1.0 M NaOH (MMO) as a reference electrode was used. Chemicals were obtained from BDH (NiSO₄ analytical reagent and AR methanol). They were used without further purification and solutions were prepared using triply distilled water. All experiments were carried out at room temperature of 30 ± 2 °C.

3. Results and discussion

It was found previously that Ni-silicalite-1 electrode is electrochemically inactive towards methanol oxidation in alkaline medium unless it has been soaked in NiSO₄ solution for some time [9]. In this work [9], different electrodes were prepared by mixing the Ni-S-1 paste with carbon in the mass ratios of 1:1, 1:3 and 1:5, respectively, and were examined in the electro-oxidation of methanol in KOH solution but they were inactive. The activity was enhanced by soaking the electrode in a nickel sulphate solution for some time. On the bases of these results [9], it was proposed that the catalytic oxidation reaction of methanol takes place once the oxy-hydroxide species [NiOOH] starts to be electrochemically formed by the anodic oxidation of nickel hydroxide [Ni(OH)₂] at the electrode surface. The Ni(OH)₂/NiOOH transformation preferably occurred at the Ni sites in the zeolite matrix's surface, i.e., bonded Ni species act as an electron relay to the Ni²⁺/Ni³⁺ redox system. This suggests that the electro-oxidation of methanol undergoes Faradaic change through the reduction of Ni(III) to Ni(II). On the basis of this result and in the present investigation, in order to use this electrode for the catalytic oxidation of methanol in KOH solutions, it was first soaked in NiSO₄ solution for various time intervals. In KOH solution, the soaked Ni ions at the electrode surface will be converted into Ni(OH)₂ species. Fig. 1 illustrates the cyclic voltammetric curves recorded at a scan rate of 10 mV s⁻¹ in blank KOH solutions of various concentrations

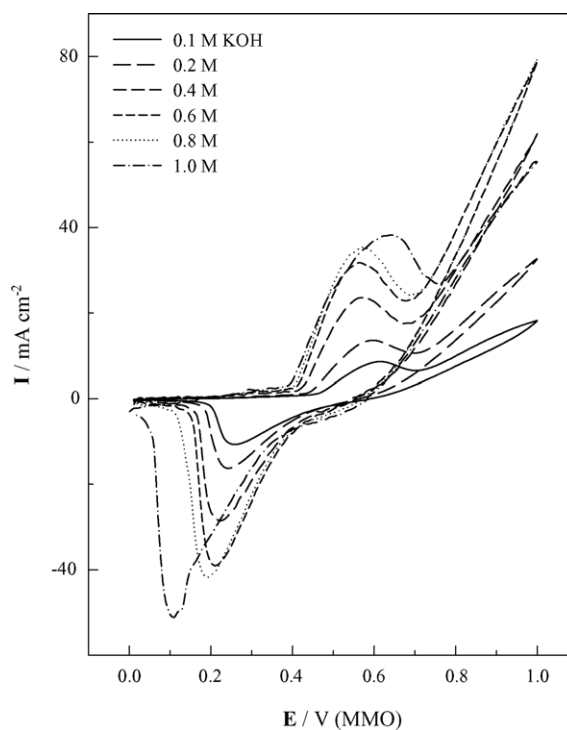


Fig. 1. Effect of KOH concentration on the cyclic voltammetric behaviour of Ni-silicalite-1 electrode at a scan rate of 10 mV s⁻¹ (the electrode was pre-soaked in 1.0 M NiSO₄ solution for 90 s).

ranging from 0.1 to 1.0 M. Before these experiments, the electrode was pre-soaked in 1.0 M NiSO₄ solution for 90 s. In this figure, two peaks appear in the voltammogram, one in the anodic direction at a potential value of about 0.60 V which represents the oxidation of nickel hydroxide [Ni(OH)₂] to nickel oxy-hydroxide [NiOOH] and the other in the cathodic direction at about 0.2 V represents the reduction of the produced oxy-hydroxide to the hydroxide. It is clear in Fig. 1 that the redox peak heights increase with the increase of KOH concentration. This is expected as the amount of nickel hydroxide [Ni(OH)₂] increases with increasing the KOH concentration in accordance with the following equation:



In each KOH solution and after recording the cyclic voltammogram, the electrode was introduced into another cell containing 0.25 M methanol solution in the desired KOH concentration, and then a cyclic voltammogram was recorded at 10 mV s⁻¹. The resulting CV's are shown in Fig. 2. Considerable anodic current density for the methanol oxidation was observed in each case. The current density increases rapidly with OH⁻ concentration at the same methanol concentration. As the OH⁻ activity is determinant for the formation of the oxy-hydroxide which is the main species enhances methanol oxidation, one expects a strong dependence of the peak current density of methanol oxidation on the activity of OH⁻. Cathodic peak are also observed in the voltammograms of Fig. 2, however, their current density values are much smaller than the anodic one as a result of the oxy-hydroxide reduction.

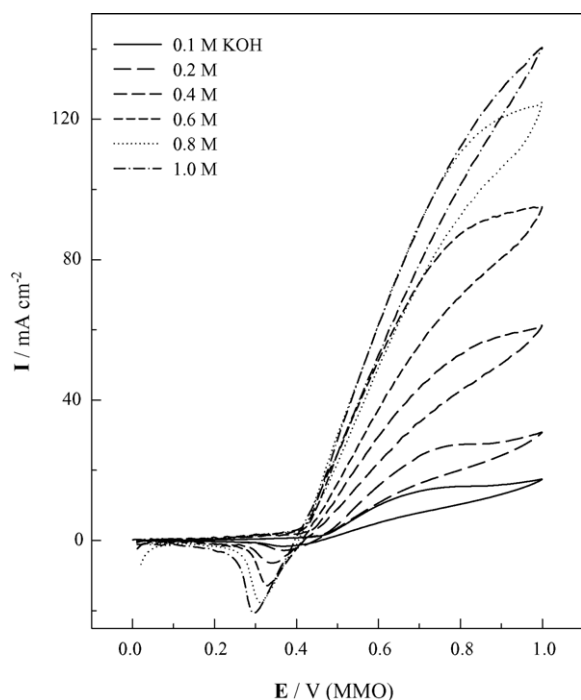
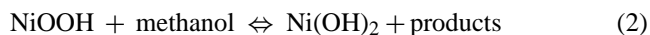


Fig. 2. Effect of KOH concentration on the oxidation methanol at Ni-silicalite-1 electrode at a scan rate of 10 mV s⁻¹ (in each KOH solution, the electrode was pre-soaked in 1.0 M NiSO₄ solution for 90 s).

The relative decrease of the cathodic peak height in presence of methanol is attributed to the partial consumption of nickel oxy-hydroxide species for the oxidation of methanol with the formation of nickel hydroxide in accordance with the following reaction:



Charges under the cathodic peaks of the voltammograms of Fig. 1 (in absence of methanol) and of Fig. 2 (in presence of methanol) are estimated and represented in Fig. 3 as a function of KOH concentration. Comparing the average value of the charge in both cases, it is noted that in presence of methanol, the charge under the cathodic peak is reduced to about 18.7% of its value in absence of methanol. This leads to the conclusion that about 81.3% of the NiOOH species produced during the anodic oxidation of Ni(OH)₂ in the anodic half cycle are consumed in the oxidation of methanol (Eq. (2)). The anodic peak potential for methanol oxidation (see Fig. 2) is naturally shifted to the positive direction as a result of an IR drop arising from a current density value more than 140 mA cm⁻².

Soaking time in 1.0 M NiSO₄ was found to affect the peak current density and the peak potential of the anodic oxidation of methanol. Cyclic voltammograms were recorded for electrodes that were soaked for various time intervals. Fig. 4 shows such voltammograms in 0.8 M KOH solution containing 0.25 M MeOH for electrodes pre-soaked in NiSO₄ solution for time intervals in the range of 10–300 s. The current

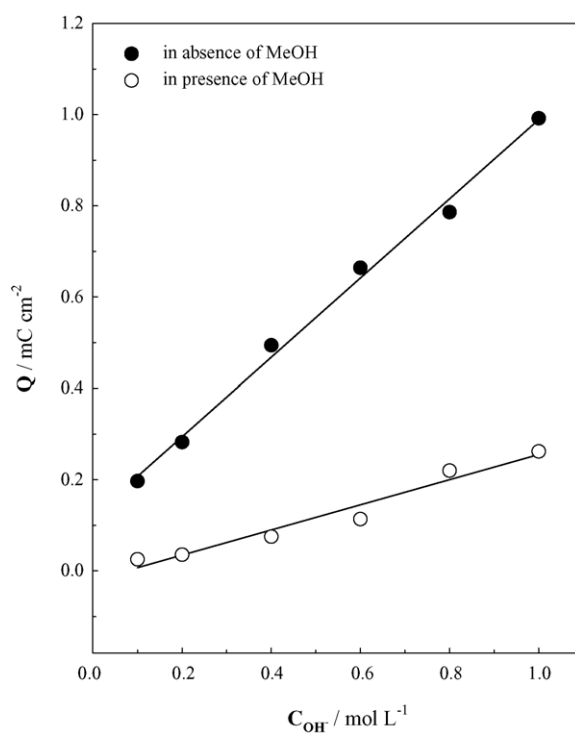


Fig. 3. Variation of the charges under the cathodic peaks of the voltammograms of the Ni-S-1 electrodes in KOH solutions in absence and in presence of methanol with KOH concentrations at a scan rate of 10 mV s⁻¹.

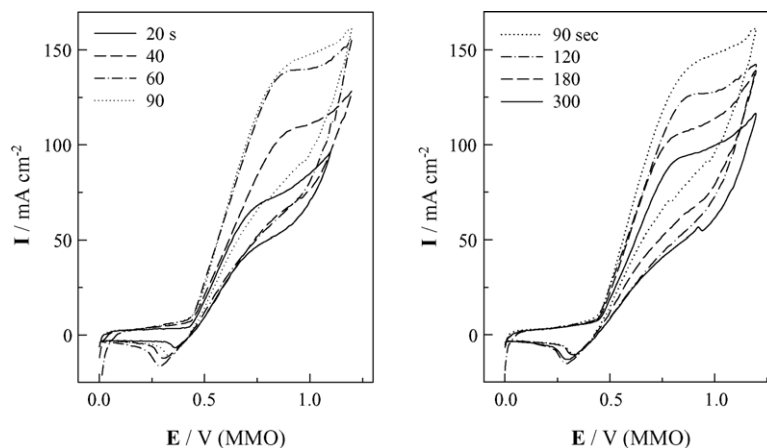


Fig. 4. Effect of soaking time in 1.0 M NiSO_4 solution on the voltammetric behaviour of Ni-S-1 electrode in 0.25 M MeOH + 0.8 M KOH solution at a scan rate of 10 mV s^{-1} .

densities of methanol oxidation were found to increase as a result of longer soaking time up to 90 s and then they decrease again. It seems that there would be a certain maximum concentration of Ni ions on the electrode surface, after which the catalytic activity decreases. Fig. 5 shows the effect of soaking time on the peak current density for methanol oxidation in two different KOH concentrations, 0.2 and 0.8 M. These results suggest that the crucial factor for the methanol oxidation is the formation of the nickel oxy-hydroxide $[\text{NiOOH}]$ species, and any conditions favoring this process lead to enhancing methanol oxidation. The effect of nickel ions concentration

was also examined by fixing the soaking time of the electrode at 90 s in various concentrations of NiSO_4 solution. The relation between the concentration of NiSO_4 in the soaking bath and the peak current density of methanol oxidation in 0.2 and 0.8 M KOH solution is represented in Fig. 6. This result shows that, in both KOH solutions, the peak height of methanol oxidation increases by increasing the NiSO_4 concentration in the soaking bath up to 0.5 M after which no appreciable change in the peak height was observed. On the basis of this result, one may conclude that soaking the electrode in 0.5 M NiSO_4 solution for 90 s is quite enough to saturate the electrode

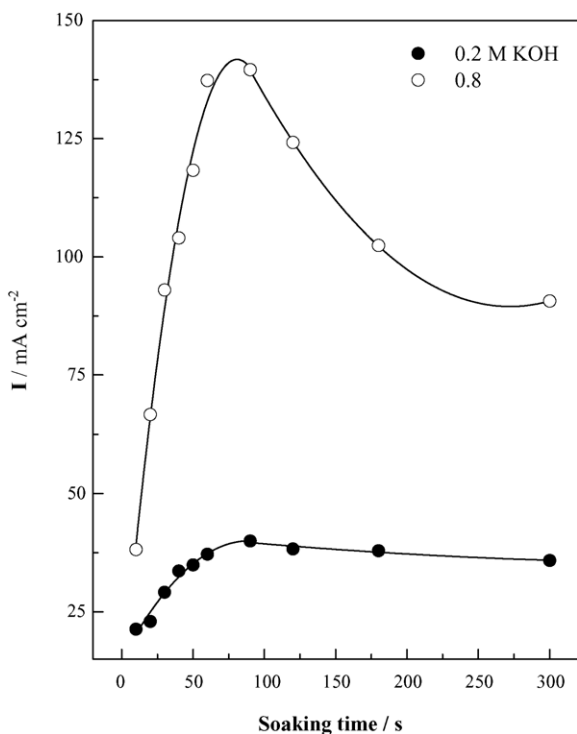


Fig. 5. Relation between soaking time in 1.0 M NiSO_4 solution and the peak current density of methanol oxidation in 0.2 and 0.8 M KOH solutions.

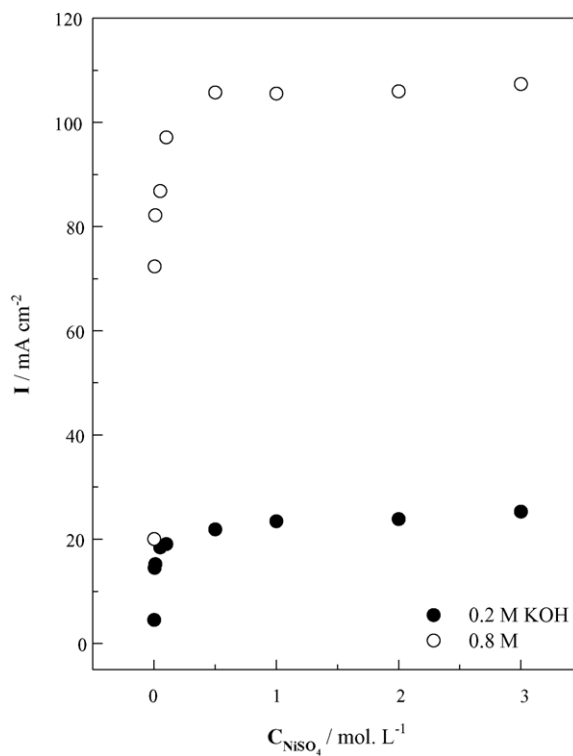


Fig. 6. Relation between NiSO_4 concentration in the soaking bath and the peak current density of methanol oxidation in 0.2 and 0.8 M KOH solutions.

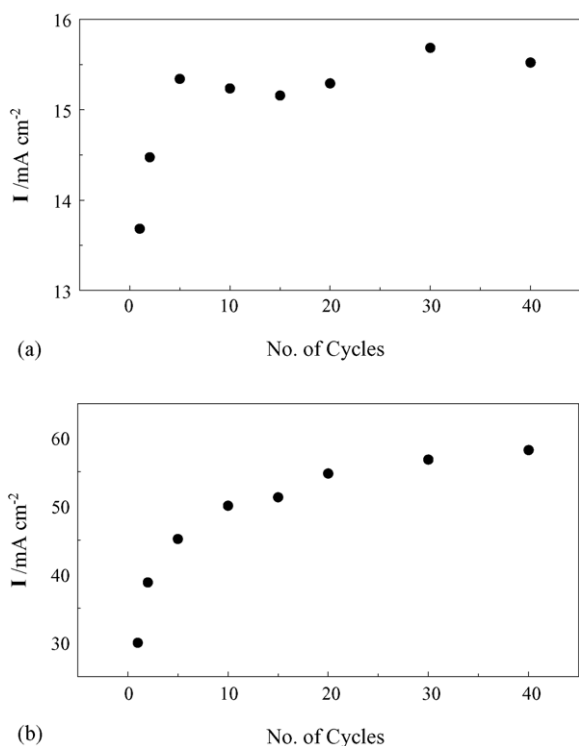
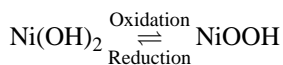


Fig. 7. Variation of the oxidation peak height of the Ni(II)/Ni(III) transformation with the number of potential cycles in 0.2 KOH (a) and in 0.8 KOH (b) solutions.

surface by incorporated nickel ions that enhance the methanol oxidation process.

A set of experiments was carried out to examine the stability of the Ni-S-1 electrode (pre-soaked in NiSO₄ solution) on repeated potential cycling in KOH solution in absence and in presence of methanol. In absence of methanol, after soaking the electrode in 1.0 M NiSO₄ solution for 90 s, the electrode was transferred into a cell containing 0.2 M KOH solution in which repeated potential cycling was carried out. The experiment was repeated using 0.8 M KOH solution. Fig. 7 represents the variation of the peak height of nickel oxy-hydroxide formation with the number of potential cyclization in KOH solution. It is noted from these results that continuous potential cycling of the pre-soaked Ni-S-1 electrode in KOH results in continuous formation of the nickel oxy-hydroxide species according to the following reaction:



In 0.2 M KOH, the formation rate of the nickel oxy-hydroxide species in the first five cycles, as denoted from the value of oxidation peak height, increases with relatively high rate after which it reaches almost a steady value up to 40 cycles. In highly concentrated KOH solution, 0.8 M, a nearly regular increase in the oxidation peak current density was observed along the 40 cycles. This result leads to the assumption that high concentration of KOH is more preferable

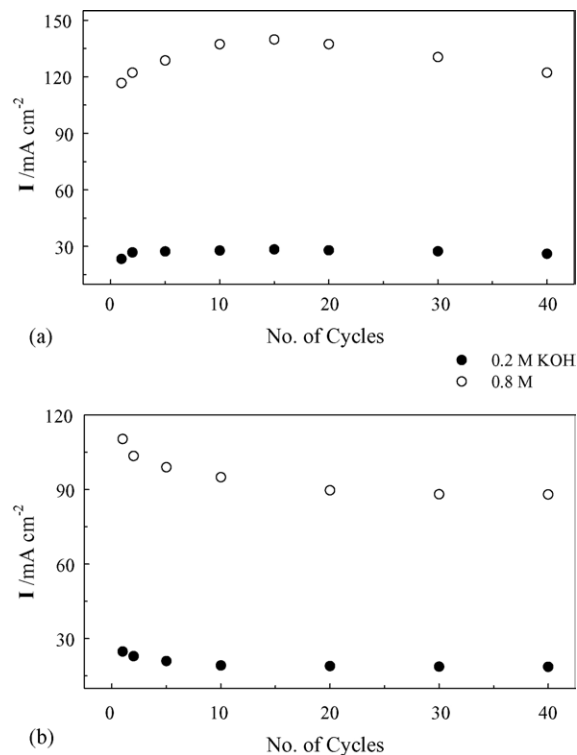


Fig. 8. The dependence of the peak current density of methanol oxidation at the Ni-S-1 electrode in 0.2 and 0.8 M KOH on the number of potential cycles according to the first procedure (a) and the second one (b).

as a medium for methanol oxidation at the Ni-S-1 electrode in presence of nickel ions. This is due to the continuous supply of NiOOH by repeated potential cyclization in presence of OH⁻ ions.

On the other hand, repeated potential cycling of the pre-soaked Ni-S-1 electrode in KOH solution in presence of 0.25 M methanol showed different behaviour, see Fig. 8. The study was carried out in two different procedures: in the first procedure, the electrode was soaked in 1.0 M NiSO₄ solution for 90 s and was then transferred into a cell containing 0.2 M KOH solution. In this solution, the potential of the electrode was scanned one cycle at a scan rate of 10 mV s⁻¹ (from 0.0 to 1.0 V in the anodic direction and then the scan was reversed in the cathodic direction to 0.0 V). After this cycle in KOH solution, a 0.25 M methanol was added to the cell after which another one potential sweep was carried out. The experiment was repeated on another pre-soaked Ni-S-1 electrodes but a number of potential sweeps of 2, 5, 10, 15, . . . and 40 cycles in KOH was carried out before adding MeOH and a single potential sweep was recorded. The same procedure was also performed using 0.8 M KOH solution. The process carried out in this manner was intended to increase the amount of nickel oxy-hydroxide species on the electrode surface which helps to oxidize methanol. Fig. 8a shows the variation of the peak height of methanol oxidation with the number of cycles in both KOH solutions (0.2 and 0.8 M solutions). The effect is quite clear in 0.8 M KOH solution. In this solution, the

peak height of methanol oxidation increases with potential cyclization up to 15 cycles after which it decreases. It was assumed that the increase of methanol oxidation peak height during the first 15 cycles could be attributed to the increase in the amount of nickel oxy-hydroxide (NiOOH) formed during potential cyclization in KOH. Along this procedure, two opposing operations could exist. The first one is the continuous formation of nickel oxy-hydroxide as a result of potential cyclization in KOH solution that helps methanol oxidation. The second one is the repeated oxidation of methanol on the electrode surface which causes the formation of intermediate products that might accumulate on the electrode surface and retard the methanol oxidation process. The effect of the second operation is obviously clear after 15 cycles where a decrease in the peak height of methanol oxidation is observed.

In the second procedure, repeated potential sweep of the pre-soaked Ni-S-1 electrode in both 0.2 and 0.8 M KOH solutions containing 0.25 M MeOH was carried out. The variation of methanol oxidation peak current density with the number of potential sweeps is represented in Fig. 8b. This figure showed a regular decrease of the peak height of methanol oxidation with potential cyclization along the 40 cycles. After 40 cycles in 0.2 M KOH containing MeOH, the peak height of methanol oxidation decreases to about 75% from its value in the first cycle, while it decreases to about 80% in 0.8 M KOH containing MeOH. This also confirms the assumption that the oxidation reaction of methanol is more efficient at higher concentrations of KOH solutions.

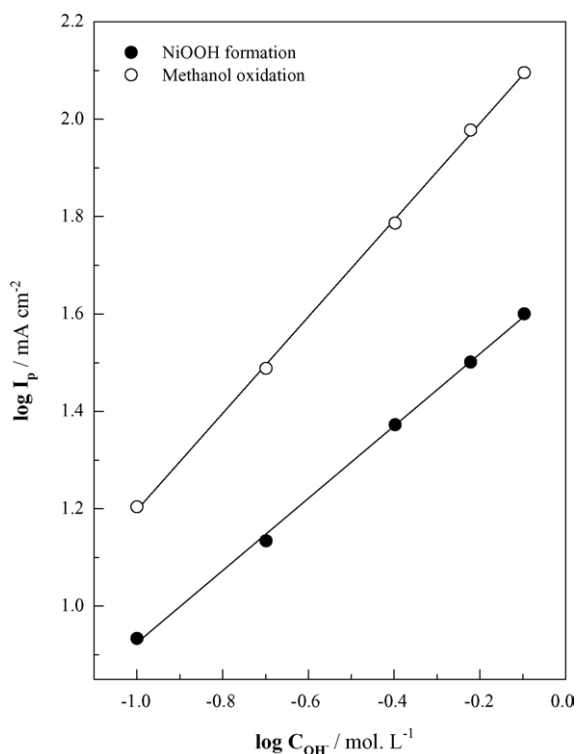


Fig. 9. Dependence of the oxy-hydroxide [NiOOH] formation and the methanol oxidation on the concentration of OH^- ions.

Quantitative estimations of the dependence of the oxy-hydroxide [NiOOH] formation (Fig. 1) and the methanol oxidation (Fig. 2) on the concentration of OH^- ions are shown in Fig. 9 on log–log plots. Straight lines were obtained in both cases with slopes of 0.74 for the oxy-hydroxide formation and 0.99 for methanol oxidation. This result suggests that the methanol oxidation reaction is a first order with respect to the OH^- concentration which confirms the control of the reaction (2) over the entire methanol oxidation process. More evidence for this view is also shown from the weak dependence on the methanol concentration on the oxidation process.

4. Conclusion

In spite of the results which show that the nickel impregnated silicalite-1 electrode is not electrochemically active towards methanol oxidation in alkaline medium unless it has been soaked in nickel ions-containing solution [9], the present investigation proved that increasing nickel ions in the soaking solution improves the electro-catalytic behaviour of the electrode for methanol oxidation until a certain limit. There would be a certain maximum concentration of Ni in the zeolite matrix, after which the catalytic activity decreases. Increasing the concentration of OH^- ions leads to an increase in the anodic peak height of methanol oxidation to a great extent as the OH^- activity is determinant for the formation of the oxy-hydroxide which is the main species that enhances methanol oxidation. A reaction order for methanol oxidation of about one was estimated with respect to both the nickel ions and the OH^- ions concentration. A weak dependence of methanol peak current density on methanol concentration is observed that leads to the conclusion that such reaction is greatly affected only by the amount of nickel as well as the hydroxide ions.

References

- [1] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, *J. Appl. Electrochem.* 34 (2004) 439.
- [2] W.J. Zhou, S.Q. Song, W.Z. Li, Z.H. Zhou, G.Q. Sun, Q. Xin, S. Douvartzides, P. Tsiakaras, *J. Power Sources* 140 (2005) 50.
- [3] K.-W. Park, J.-H. Choi, B.-K. Kwon, S.-A. Lee, Y.-E. Sung, H.-Y. Ha, S.-A. Hong, H. Kim, A. Wieckowski, *J. Phys. Chem. B* 106 (2002) 1869.
- [4] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangpani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735.
- [5] B. Garau, R. Vishwanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Somtkin, *J. Phys. Chem. B* 102 (1998) 9997.
- [6] D. Paneva, T. Tsoncheva, E. Manova, I. Mitov, T. Ruskov, *Appl. Catal. A Gen.* 267 (2004) 67.
- [7] T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, *J. Catal.* 229 (2005) 176.
- [8] A. Bhattacharya, A. Hazra, S. Chatterjee, P. Sen, S. Laha, I. Basumallick, *J. Power Sources* 136 (2004) 208.
- [9] M.W. Khalil, M.A. Abdel Rahim, A. Zimmer, H.B. Hassan, R.M. Abdel Hameed, *J. Power Sources*, in press.

- [10] H.B. Yu, J.-H. Kim, H.-I. Lee, M.A. Scibioh, J. Lee, J. Han, S.P. Yoon, H.Y. Ha, J. Power Sources 140 (2005) 59.
- [11] M.A. Abdel Rahim, R.M. Abdel Hameed, M.W. Khalil, J. Power Sources 134 (2004) 160.
- [12] T. Tsoncheva, S. Vankova, O. Bozhkov, D. Mehandjiev, J. Mol. Catal. A Chem. 225 (2005) 245.
- [13] J. Zeng, J.Y. Lee, J. Power Sources 140 (2005) 268.
- [14] B.I. Mosqueda-Jimenez, A. Jentys, K. Seshan, J.A. Lercher, J. Catal. 218 (2003) 348.
- [15] A. Zimmer, D. Monter, W. Reschetilovski, J. Appl. Electrochem. 33 (2003) 933.
- [16] P.V. Samant, J.B. Fernandes, J. Power Sources 125 (2004) 172.
- [17] R.W. Grose, E.M. Flanigen, Union Carbide Corporation, US Patent 4,061,724 (1977).
- [18] E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner, J.V. Smith, Silicalite, a new hydrophobic crystalline silica molecular sieve, Nature 271 (1978) 512.