Ni Modified MCM-41 as a Catalyst for Direct Methanol Fuel Cells

H.B. Hassan^{*}, M.A. Abdel Rahim, M.W. Khalil and R.F. Mohammed

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt *E-mail: <u>Hanaa20055@hotmail.com</u>

Received: 11 September 2013 / Accepted: 28 October 2013 / Published: 8 December 2013

Electrodes made from Mobil catalytic materials number 41 (MCM-41) modified with nickel were successfully prepared by mixing Ni–MCM-41 powders with conducting carbon black in an appropriate ratio. The chemical composition and the phase structure of the prepared catalyst were investigated by energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). On the other hand, the surface morphology was investigated using scanning electron microscope (SEM) and transmission electron microscope (TEM). For fuel cell applications, the electrochemical measurements demonstrated that the fabricated electrodes displayed a considerable catalytic activity towards the electrooxidation of methanol in 1.0 M NaOH solution. In addition, their catalytic performance as a function of the amount of Ni–MCM-41 powder and carbon black ratio was investigated. Chronoamperometric measurements revealed a good catalytic stability as well as good catalytic efficiency towards methanol electrooxidation. A comparison was made between the catalytic activity of Ni(II) modified Ni–MCM-41, NiS-1 and TS-1 catalysts as a function of channel pore size.

Keywords: Electrocatalysts, DMFC, Electrooxidation, Fuel Cells, Ni-MCM-41, Mesoporous Materials, Methanol.

1. INTRODUCTION

Nowadays the development of new, more active and selective catalysts is a real challenge for a catalytic science. The environmentally friendly zeolites were used for many decades [1-5]. At the beginning of the 90's, the discovery of a new family of mesoporous materials called M41S (Mobil catalytic material, number 41), opened new possibilities to prepare catalysts for reactions of relatively large molecules. MCM-41 is the most important member of silica-based mesoporous molecular sieves family was described by Mobil oil scientists led by Kresge [6]. The mesopore size is in the range of 2–50 nm. The large surface area and pore size of these substances make it attractive for many applications in the field of adsorption and catalysis involving large organic molecules [7, 8]. Ideally,

MCM-41 pore structure consists of hexagonal arrays of non-intersecting uniform channels of controlled size, the long-range order is in the pore structure rather than in the solid itself, which may be virtually amorphous. It is evident that the pores are not of an intracrystalline nature, as in a zeolite. Incorporation of elements such as Al or Ni into the framework positions of the siliceous MCM-41 gives acidic properties [9-11]. Because of its uniform size and shape of mesopores, as well as its thermal stability MCM-41 has attracted considerable interest as a catalyst support [9, 12]. It was reported that M41S materials were used as potential catalysts for catalytic ozonation processes for potable water treatment purposes [13]. Also, Ni/MCM41 materials could be of good use in a hydrogen-storage capacity and hydrogen production from gasification of wood sawdust [14, 15]. Moreover, Fe(III)-, Co(II)- and Ni(II)-impregnated MCM41 were used for wet oxidative destruction of 2,4-dichlorophenol in water [16].

So far no work has been reported on the application of Ni modified MCM-41 catalyst as anodes for fuel cell applications. Although, it seems that Ni–MCM-41 would be a good catalyst for electrooxidation processes because of its relatively high surface area and the presence of a transition metal element such as Ni. A similar work was carried out by our group on nickel silicalite (NiS-1) and titanium silicalite (TS-1) catalysts which showed a good catalytic activity towards methanol oxidation in alkaline solutions [1, 2]. On the same line, the objective of this study is to investigate the catalytic activity of Ni–MCM-41 as anodes towards electrooxidation of methanol for fuel cell applications. Also, the catalytic activity as a function of channel pore size is investigated and compared for Ni modified Ni–MCM-41, NiS-1 and TS-1 catalysts.

2. EXPERIMENTAL TECHNIQUE

2.1. Electrode preparation

Ni–MCM-41 catalyst is obtained by modification of MCM-41 material by 5 wt.% Ni via impregnation method in Institut fur Technische Chemie, Technische Universtat Dresden, Dresden, Germany. MCM-41 displays a very large specific surface area of approximately 1000 m² g⁻¹ [17]. The resulting 5 wt.% Ni–MCM-41 powder was used in the present study. It was mixed with activated carbon black (high surface area acetylene black as P1042, Stickstoffwerk Piesteritz, Germany) in 1:1 and 1:3 ratios. The mixture was then heated in a water bath at 80°C with constant stirring for 3h. Mixing with carbon black, in the present work, was particularly necessary to increase the conductivity of the Ni–MCM-41 materials. Subsequently and using a micropipette, 10 wt.% suspension of PTFE (used as suspension, Dyneon TF5032) was slowly added to it with constant stirring over a period of 30 min. An appropriate amount of isopropyl alcohol was added and the slurry was allowed to wet for 2h. The resulting paste was spread over a gold plated stainless steel mesh of an apparent surface area of 1 cm² and pressed under 0.1 t cm⁻² pressure for a period of 5 min. The electrode discs obtained were dried in an air oven at 110°C for 1h and subsequently heated in an air oven at 300°C for 15 min. Electrodes prepared by the above procedure were used as anodes for the electrooxidation of methanol without any further treatments.

2.2. Electrochemical measurements

The electrochemical measurements were performed using Amel 5000 system (supplied by Amel instrument, Italy), driven by a PC for data processing. Amel easyscan software was used in connection with the PC to control the Amel 5000 system. A conventional three-electrode glass cell was used in the electrochemical measurements. The reference electrode to which all potential values are referred, is the Hg/ HgO/ 1.0 M NaOH, $E^{\circ} = 140 \text{ mV } vs$. NHE and a Pt sheet was used as a counter electrode. Chemicals were obtained from Sigma-Aldrich (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 in an aerated solution.

2.3. Surface analysis

Transmission electron microscope (TEM) (Tecnai G20, Super twin, double tilt, FEI), and a scanning electron microscope (SEM) equipped with energy dispersive X-ray system (EDX) model JEOL, JSM- 5410 were used to study the surface morphology of the catalyst and its elemental analysis, respectively. The phase structure of the catalyst was characterized by X-ray diffraction analysis using Bruker AXS X-ray diffractometer with Cu K α_1 target of wavelength 0.15046 nm. The scanning step, rate and range were 0.02°, 0.05°/s and 10- 100°, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Ni-MCM-41 catalyst

SEM images recorded for Ni–MCM-41 powder at different magnification power are represented in Fig. 1(a) and (b). The micrographs show that the powder has a porous structure. The SEM image of the powder mixed with carbon black [Fig. 1(c)] shows a homogenous distribution of both components in the mixture. On the other hand, TEM images of the Ni–MCM-41 powder with different magnification power are presented in Fig. 2(a) and (b). The images illustrated approximately the regular hexagonal array of mesoporous channels of the catalyst in the nano-sized scale. Furthermore, the EDX analysis of Ni–MCM-41 is shown in Fig. 3 that reflects the elemental composition of the powder. One peak for Ni is detected in the figure demonstrating the existence of Ni atoms. According to this figure, it was found that the estimated percent of Ni is about 4.8 wt.%.

Characterization of Ni–MCM-41 with x-ray diffraction yields a diffractogram represented in Fig. 4. The XRD pattern shows the presence of a main broad peak of relatively high intensity at low angle and another peak at 2 θ around 45° characteristic of amorphous/nanocrystalline structure with preferred orientation of Ni (111). These characterizations are in agreement with those found in the literatures [10]



Figure 1. SEM images of: (a), (b) Ni–MCM-41 powder with different magnification power and (c) Ni–MCM-41 powder mixed with carbon black in the ratio of 1:3.



Figure 2(a), (b). TEM micrograph of Ni-MCM-41 powder at different magnification power and the inset figure in (b) represents the diffraction pattern.



Figure 3. EDX analysis of Ni–MCM-41 powder.



Figure 4. XRD pattern of Ni-MCM-41 powder.

3.2. Electrochemical behavior and oxidation of methanol



Figure 5. Cyclic voltammograms of Ni–MCM-41 powder in 1.0 M NaOH in absence and in presence of 2.0 M MeOH at 10 mV s⁻¹.

Figure 5 shows the electrochemical behavior of Ni–MCM-41 powder without mixing with carbon black in 1.0 M NaOH in absence and in presence of 2.0 M methanol at a scan rate of 10 mV s⁻¹. It is clear from the cyclic voltammograms that the conductivity of the electrode is poor as indicated from the relatively very low current density values inherent with the voltammograms. Two small peaks are observed in the voltammograms due to Ni redox species, one in the anodic direction (I_a) at about +500 mV (MMO) and the other in the cathodic half cycle (I_c) at about -300 mV (MMO). It is worth noting that no appreciable oxidation peak was observed upon addition of 2.0 M methanol on the electrode powder in 1.0 M NaOH at 10 mV s⁻¹. This is probably due to the low conductivity inherent with such electrode as well as the lack of catalytic activity.



Figure 6. Cyclic voltammograms of Ni–MCM-41 powder mixed with carbon black in the ratios of 1:1 and 1:3 in 1.0 M NaOH at 10 mV s⁻¹.

The conductivity of the powder is improved upon mixing with carbon black in adequate ratios. Two modified Ni–MCM-41 electrodes were prepared by mixing the powder with carbon black in appropriate ratios of 1:1 and 1:3. The electrochemical response of the fabricated electrodes was studied by cyclic voltammetry in 1.0 M NaOH at a scan rate of 10 mV s⁻¹ and the results are represented in Fig. 6. The polarization started from -500 up to +1200 mV (MMO) in the anodic direction then the scan was reversed to -500 mV (MMO) in the cathodic direction. Two peaks appear in the anodic half cycle of cyclic voltammograms, the first one (I) at about 0 mV (MMO) corresponding to the formation of Ni(OH)₂ [18], and the second peak (II_a) appears at about +580 mV (MMO) due to the transformation of Ni(OH)₂ to NiOOH according to the following reaction [19, 20]:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
 (1)

Besides, there is a small peak in the cathodic direction (II_c) at about +450 mV (MMO) for the reduction of NiOOH to Ni(OH)₂. It is worth noting that the heights of the peak current density of both Ni(II) formation and Ni redox species are higher in case of 1:1 electrode compared to those of 1:3 electrode, as the amount of the Ni-MCM-41 catalyst powder and consequently the amount of Ni in the first electrode is relatively higher than that in the second electrode.



Figure 7. Cyclic voltammograms of Ni–MCM-41 (1:1) (a) and Ni–MCM-41 (1:3) (b) at a scan rate of 10 mV s⁻¹ in different concentrations of NaOH.



Figure 8. Cyclic voltammograms of Ni–MCM-41 (1:1) (a) and (1:3) (b) in 1.0 M NaOH in absence and in presence of 2.0 M MeOH at 10 mV s⁻¹. (c) Represents the effect of repeated potential cyclization upon the peak current density of methanol oxidation at both 1:1 and 1:3 electrodes.

Figure 7 (a, b) illustrates typical cyclic voltammograms of Ni–MCM-41 electrodes (prepared with 1:1 and 1:3 ratios) in different concentrations of NaOH solution at a potential scan rate of 10 mV

 s^{-1} . The current density values of the peaks corresponding to the formation of Ni(OH)₂ (I) and Ni redox species (II_a, II_c) were found to increase with the increase of NaOH concentration. This is expected as a result of increasing the formation of Ni(OH)₂ and Ni(OH)₂/NiOOH transformation in presence of a higher concentration of OH⁻ ions in the solution. The same behavior was observed upon repeated potential cyclization of the working electrode (up to 50 cycles) in one and the same concentration of NaOH (figures are not presented). The increase of peak current density values in this case is also owing to the increase of Ni(OH)₂ formation and Ni(OH)₂/NiOOH transformation in presence of OH⁻ ions under the influence of spending more time in the NaOH solution. Accordingly, the concentration of NaOH has a significant effect on the catalytic activity of the catalyst.

Changes in the voltammetric behavior of the working electrode are observed upon the addition of 2.0 M methanol to the electrolyte. An anodic peak for methanol oxidation was observed in the voltammograms of both 1:1 and 1:3 electrode ratios. Figure 8 represents the electrochemical oxidation of 2.0 M methanol in 1.0 M NaOH at a scan rate of 10 mV s⁻¹. It was found from these voltammograms that the oxidation process for methanol starts with NiOOH formation at a potential value of about +500 mV (MMO) reaching its maximum value at the peak potential in the anodic direction. Another oxidation peak for methanol oxidation was observed in the reverse scan but with a relatively smaller current density. This peak is probably due to the reoxidation of 74 mA cm⁻² was obtained for the oxidation peak current density recorded at 1:3 electrode at +700 mV (MMO). On the other hand, undistiguished oxidation peak is inherent with the 1:1 electrode but an increase of the anodic current was observed [see Fig. 8(a)]. Accordingly a common way was applied to estimate the value of the peak hight, in this case and similar cases, by considering the peak current value at the end of the steady current rise. A value of about 124 mA cm⁻² was estimated at the 1:1 electrode at +890 mV (MMO).

It was found that the electrooxidation of organic compound requires the presence of oxide, hydroxide and/or oxyhydroxide groups [21]. At Ni–MCM-41 electrodes, the oxidation process of methanol starts at a potential value corresponding to the formation of NiOOH species. It is suggested that methanol is oxidized on these electrodes through the reduction of NiOOH to form Ni(OH)₂, i.e., NiOOH acts as electron transfer mediator for the oxidation process according to the following reaction [2]:

$NiOOH + MeOH \leftrightarrow Ni(OH)_2 + products$ (2)

Fleischmann et al. [22] reported that the oxidation reaction of organic compounds with oxides of higher valences is usually the rate-determining step. Based on this assumption, equation (2) is considered the slow step for alcohol oxidation. In addition, the presence of MCM-41 in the catalyst system is essential as it can provide a high surface area for metal dispersion and contains many channels and pores which permit the diffusion of electrolyte inside the electrode and increase the efficiency of oxidation process. Electrode of Ni–MCM-41 powder: carbon black ratio of 1:3 shows the best electrochemical performance as inferred from its relatively lower oxidation potential with respect to that obtained at the 1:1 electrode and the well-defined peak of methanol oxidation. Accordingly, electrodes of 1:3 ratio were used in most of the next studies.

The performance of both 1:1 and 1:3 Ni–MCM-41 electrodes with repeated potential cyclization in presence of 2.0 M methanol was studied and the peak current density of methanol oxidation is plotted as a function of the number of potential cycles in Fig. 8(c). It was found that the value of the peak current density of methanol oxidation increases with repeated potential cycling up to 75 cycles at both electrodes and then is nearly leveled off.



Figure 9. Cyclic voltammograms of Ni–MCM-41 (1:3) in 1.0 M NaOH at various scan rates (a). Variation of the Ip_a and Ip_c of Ni(III)/Ni(II) transformation with scan rate in 1.0 M NaOH (b). Variation of Ip_a of methanol oxidation with the square root of the scan rate (c).

The increase in peak height in the first 75 cycles could be due to the increase of the amount of NiOOH formed with the increase of potential cyclization in the presence of NaOH solution. As NiOOH species acts as the start material for oxidation of methanol. However, as a result of prolonged polarization time (due to repeated potential cyclization) it is expected to have an accumulation of methanol oxidation products at the active centers on the electrode surface. The accumulation of these products at high concentrations could hinder the oxidation of methanol, but in the present study the poisoning effect of the prepared catalyst is very small or negligible, as the catalyst contains many pores and channels which permit easier removal of the oxidation products.

In a set of experiments, the influence of scan rate (v) on the cyclic voltametric features of 1:3 electrode was analyzed. Fig. 9(a) illustrates typical cyclic voltammograms of 1:3 electrode in 1.0 M NaOH solution at various potential scan rates in the range from 5 to 100 mV s⁻¹. With increasing the scan rate, a significant increase in the peak current density of Ni³⁺/Ni²⁺ redox reaction is observed. On the other hand, it is noted that the current density values of the first anodic peak of Ni(OH)₂ formation (I) increased and shifted towards more positive potential values with increasing the scan rate. In addition, the potential of the anodic peak of Ni^{2+}/Ni^{3+} species (II_a) is shifted towards more positive values, while that of the cathodic peak of Ni^{3+}/Ni^{2+} (II_c) is shifted towards more negative values. It was reported that there are four phases produced over the lifetime of a nickel hydroxide electrode, namely α -Ni(OH)₂, β -Ni(OH)₂, β -NiOOH, and γ -NiOOH [23, 24]. All these phases are transformed by time and by increasing potentials to the more stable β -Ni(OH)₂ which is oxidized into β -NiOOH [25]. Therefore, the basic electrochemical reaction at the nickel based electrode in the alkaline solution involves the oxidation of β -Ni(OH)₂ to β -NiOOH [26, 27]. Figure 9(b) shows that both of the anodic and the cathodic current density values of the Ni redox species peaks are directely proportional to the scan rates in the range from 5 to 100 mV s^{-1} indicating the electrochemical activity of the surface redox couple. The effect of varying the scan rate on the anodic peak current density of methanol oxidation was also studied. The results are represented in figure 9(c) that shows a straight line relation between the square root of scan rate and the methanol oxidation peak current density. This behaviour suggests that the overall oxidation of methanol at this electrode is controlled by the diffusion of methanol from solution to the surface active sites.

The dependence of the peak current density values of methanol oxidation on the bulk concentration of methanol was investigated at 1:3 Ni–MCM-41 electrodes. Cyclic voltammograms at a scan rate of 10 mV s⁻¹ were recorded in 1.0 M NaOH solution in presence of various concentrations of methanol ranging from 0.1 to 5 M. The corresponding oxidation peak current density as a function of methanol concentration is presented in Fig. 10. The result indicates a linear dependence of oxidation peak current density on methanol concentration in the studied concentration range. So, a catalytic electrooxidation of methanol on Ni–MCM-41 electrode appears to be possible. Under the present experimental conditions, the order of reaction with respect to methanol concentration was found to be 0.6 as estimated from the slope of the straight line relation of the logarithmic plot between the peak current density of methanol oxidation and the scan rate (see the inset in Fig. 10).

To evaluate the reproducibility and stability of Ni–MCM-41 electrode, three electrodes were prepared of the same 1:3 ratio and their electrochemical behavior towards methanol electrooxidation in

1.0 M NaOH was investigated. A comparison was made of the peak current density values of methanol oxidation at the three electrodes.



Figure 10. Dependence of the anodic peak current density of methanol oxidation on the methanol concentration in 1.0 M NaOH at a scan rate of 10 mV s⁻¹. (The inset represents the logarithmic plot)

The relative standard deviation (R.S.D.) value measured for the results of the three prepared electrodes was 3.5%, confirming that the preparation method was reproducible. Additionally, in order to investigate the performance and stability of Ni–MCM-41 electrodes in both the 1:1 and 1:3 ratios towards electrooxidation of methanol, the chronoamperometric experiments were performed at a potential value of +800 mV (MMO) in 1.0 M NaOH in presence of 2.0 M methanol. The results are compared to the same experiment performed at electrodeposited Ni on carbon electrode (Ni/C) and are presented in Fig. 11. The reason for choosing Ni/C electrode is to clarify the role of MCM-41 powder with its porous structure as a host in the catalyst system. It is clear from Fig. 11 that, for all the studied electrodes, the current density values decrease with time because of the partial poisoning of the catalysts, i.e. the applied potential is not positive enough to completely oxidize the reaction intermediates. On the other hand, it was observed that both the initial and steady current densities of

1:1 and 1:3 Ni–MCM-41 electrodes are much higher than that obtained at Ni/C electrode in the entire time range used. However, values of the current density inherent with the 1:1 electrode are much higher than that inherent with the 1:3 electrode. Based on the these results, it can be concluded that the presence of MCM-41 as a catalyst support for Ni can improve the resistance to deactivation caused by the poisoning species.



Figure 11. Chronoamperometric measurements of Ni–MCM-41 electrodes and Ni/C in 1.0 M NaOH in presence of 2.0 M MeOH at a potential step of +800 mV (MMO). (Ni/C is prepared by electrodeposition of Ni for 30 min.)

To increase the oxidation current density and enhance the catalytic activity of the prepared Ni–MCM-41 catalyst, an attempt was made to increase the Ni content in the prepared electrodes. For 1:3 Ni–MCM-41 electrode, it was immersed in 1.0 M NiSO₄ solution for different time intervals. The cyclic voltammetric response of the electrode after each immersion was recorded in 1.0 M NaOH solution in absence of methanol [Fig. 12(a)] and in presence of 2.0 M methanol [Fig. 12(b)] at a scan rate of 10 mV s⁻¹. It is clear from Fig. 12(a) that as the time of immersion in 1.0 M NiSO₄ increases, the first peak (I) at about 0 mV (MMO) corresponding to Ni(OH)₂ formation is slightly decreases, while the height of the peak current of Ni redox species (IIa, IIc) increases. Moreover, the anodic peak of the redox species (IIa) shows a potential shift in the higher potential values with increasing the immersion time. However, a potential shift to less potential values is observed for the cathodic peak (IIc). All of the previous experiments show that immersing the catalyst in NiSO₄ solution can actually increase the Ni contents at the surface of the catalyst. The results of Fig. 12(c) show that the height of

the oxidation peak current density of methanol increases with increasing immersion time up to 20 seconds after which it attains almost constant values.



Figure 12. Effect of immersion time in 1.0 M NiSO₄ solution on: the electrochemical behavior of Ni–MCM-41 in 1.0 M NaOH in absence of methanol (a), in presence of 2.0 M methanol (b) at 10 mV s⁻¹, and on the height of methanol oxidation peak current density (c).

Accordingly, 20 seconds immersion is a quite enough time to saturate the electrode surface with Ni ions. The increase in the height of the oxidation peak current density of methanol at the Ni(II) modified Ni–MCM-41 electrode compared with the unmodified Ni–MCM-41 electrode could be due to the increase of the amount of Ni²⁺ incorporated inside the pores of the catalyst matrix that generate more amount of NiOOH species. The NiOOH species acts as the start material for oxidation of methanol. Based on this result, it was found that the modification of Ni–MCM-41 electrode by immersion in Ni²⁺ solution enhances its catalytic activity towards methanol electrooxidation by 2.7 times greater than that of the unmodified electrode.



Figure 13. The catalytic activity of Ni(II) modified Ni–MCM-41, NiS-1 and TS-1 catalysts towards MeOH electrooxidation as a function of channel pore size.

In our previous studies [28] porous silicalite powders were used to prepare electrodes namely nickel silicalite (NiS-1) and titanium silicalite (TS-1). Those were used as catalysts for the electrooxidation of methanol in alkaline medium. The catalytic performance of the present Ni–MCM-41 electrode is compared to these silicalites (NiS-1 and TS-1) electrodes as a function of channel pore size. All the three electrodes, Ni–MCM-41, NiS-1 and TS-1 are prepared by the same procedure and modified by immersion in Ni ions solution for 20 seconds. The catalytic activity of these electrodes is evaluated towards methanol electrooxidation in NaOH solution. Figure 13 represents a histogram that summarizes the catalytic activity of the three electrodes in terms of the peak current density values of methanol oxidation as a function of channel pore size. It was found that the Ni(II) modified Ni–MCM-41 electrode displayed the highest catalytic activity towards electrooxidation of methanol. Its catalytic

activity is about 1.4 times greater than that of the Ni(II) modified NiS-1 and about 3 times greater than that of the Ni(II) modified TS-1. The results of characterizing the three electrodes revealed that the channel pore size of Ni–MCM-41 is in the range of 2–50 nm, and that of NiS-1 is about 0.74 nm, while TS-1 is about 0.63 nm. Comparing the channel pore size of the studied electrodes, it was observed that as the channel pore size increases the amount of Ni(II) ions incorporated inside the channels increases and the oxidation peak current density of methanol increases. Moreover, these wide pore channels in case of Ni–MCM-41 catalyst may facilitate the removal of oxidation products and increases the stability of the electrodes by decreasing the poisoning effect caused by intermediates generated during methanol oxidation.

4. CONCLUSIONS

• Ni–MCM-41 modified electrodes were successfully prepared by mixing the Ni–MCM-41 powder catalyst with carbon black in adequate ratios.

• The fabricated electrodes displayed a considerable electrocatalytic activity towards electrooxidation of methanol in 1.0 M NaOH solution.

• The catalytic activity was found to depend on the carbon content in the prepared electrode as well as the nickel content.

• A reaction order of 0.6 was estimated with respect to methanol oxidation in NaOH solution.

• An improved stability of the fabricated electrode towards the electrooxidation process of methanol was observed compared to that of Ni/C electrode.

• The catalytic activity of the catalyst was found to increase by modifying the electrode by Ni(II) ions.

• The catalytic activity of the Ni(II) ions modified Ni–MCM-41 electrode was found to be greater than that of Ni(II) modified silicalite based electrodes depending on the channel pore size.

ACKNOWLEDGMENTS

The support of both the Alexander Von Humboldt Stiftung and the Technische Universitat Dresden (Prof. W. Reschetilowski) is greatly appreciated.

References

- 1. M. W. Khalil, M. A Abdel Rahim, A. Zimmer, H. B. Hassan, R. M. Abdel Hameed, J. Power Sources, 144 (2005) 35.
- 2. M. A. Abdel Rahim, H. B. Hassan, R. M. Abdel Hamid, J. Power Sources, 154 (2006) 59.
- 3. R. Zhang, J. Ma, W. Wang, B. Wang, R. Li, J. Electroanal. Chem., 643 (2010) 31.
- 4. D. Gligor, A. Maicaneanu, A. Walcarius, *Electrochim. Acta*, 55 (2010) 4050.
- 5. X. Li, B. Li, J. Xu, Colloids and Surfaces A: Physicochem. Eng. Aspects, 434 (2013) 287.
- 6. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, S. Beck, Nature, 359 (1992) 710.

- 7. K. Roos, A. Liepold, W. Reschetilowski, R. Schmidt, A. Karlsson, M. Stocker, *Stud. Surf. Sci. Catal.*, 94 (1995) 389.
- 8. A. Corma, A. Martinez, V. Matinez-Soria, J. B. Monton, J. Catal., 153 (1995) 25.
- 9. A. Taouli, W. Reschetilowski, Stud. Surf. Sci. Catal., 142 (2002) 1315.
- T. Lehmann, T. Wolff, C. Hamel, P. Veit, B. Garke, A. Seidel-Morgenstern, *Microporous Meters*, 151 (2012) 113.
- 11. Z. Sun, X. Li, A. Wang, Y. Wang, Y. Chen, Y. Hu, Catal. Today, 211 (2013) 126.
- 12. U. Junges, W. Jacobs, I. Voigt-Martin, B. Krutzsch, F. J. Schuth, J. Chem. Soc., Chem. Commun., 22 (1995) 2283.
- 13. C. Cooper, R. Burch, Water Res., 33 (1999) 3689.
- 14. S-J. Park, S-Y. Lee, J. Colloid Interface Sci., 346 (2010) 194.
- 15. C. Wu, L. Wang, P. T. Williams, J. Shi, J. Huang, Appl. Catal.B, 108-109 (2011) 6.
- 16. U. Chaliha, K. G. Bhattacharyya, Catal. Today, 141 (2009) 225.
- 17. C. G. Sonwane, C.W. Jones, and P.J. Ludovice, J. Phys. Chem. B, 109 (2005) 23395.
- 18. M. Pourbais, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd edition Houston, Texas, (1974), pp. 333.
- 19. M. Vukovic, J. Appl. Electrochem., 24 (1994) 878.
- 20. M. A. Abdel Rahim, R. M. A. Hameed, M. W. Khalil, J. Power Sources, 134 (2004) 160.
- 21. R. Ortiz, O. P. Márquez, J. Márquez, C. Gutiérrez, J. Phys. Chem., 100 (1996) 8389.
- 22. M. Fleischmann, K. Korinek, D. Pletcher, J. Chem. Soc., Perkin II, 2 (1972) 1396.
- 23. H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta*, 11 (1966) 1079.
- 24. R. S. Schrebler Guzman, J. R. Vilche, A. J. Arvia, J. Electrochem. Soc., 125 (1978) 1578.
- 25. D. J. Singh, J. Electrochem. Soc., 145 (1998) 116.
- 26. C. Zhang, S-M. Park, J. Electrochem. Soc., 134 (1987) 2966.
- 27. C. Zhang, S-M. Park, J. Electrochem. Soc., 136 (1989) 3333.
- 28. R. M. Abdel Hameed, Ph. D Thesis, Faculty of science, Cairo University, Giza, Egypt (2005).

© 2014 by ESG (<u>www.electrochemsci.org</u>)