

A study of the electrocatalytic oxidation of methanol on a nickel–salophen-modified glassy carbon electrode

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Abstract Nickel–salophen-modified glassy carbon electrodes prepared by transferring one drop of Ni–salophen complex solution on the electrode surface. This modified electrode has been used for the electrocatalytic oxidation of methanol in alkaline solutions with various methods such as cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. The electrooxidation was observed as large anodic peaks, and early stages of the cathodic direction of potential sweep around 20 mV vs. Ag|AgCl|KCl_{sat}. A mechanism based on the electrochemical generation of Ni (III) active sites and their subsequent consumptions by methanol have been discussed. EIS studies were employed to unveil the charge transfer rate as well as the electrical characteristics of the catalytic surface. For the electrochemical oxidation of methanol at 5.0 M concentration, charge transfer resistance of nearly 0.936 kΩ was obtained, while the resistance of the electrocatalyst layer was about 111.6 Ω.

Keywords Electrocatalysis · Modified electrode · Glassy carbon · Salophen · Methanol electrooxidation

Introduction

Fuel cells are devices in which an electrochemical reaction is used to generate electricity. A variety of materials may

be suitable for use as a fuel, depending on the materials chosen for the components of the cell. Organic materials, such as methanol, are attractive choices for fuels due to their high specific energies [1]. In the electrochemical oxidation of methanol, the electrode material is clearly an important parameter where a high efficient electrocatalyst is needed [2]. One of the impeding problems in the commercialization is perhaps the high overpotential associated with the direct electrooxidation of methanol [3]. In this area, some papers have been reported in the literatures [4–6]. Therefore, a considerable increase in power density and fuel utilization was obtained by optimizing the different components of fuel cells [7–9].

Although electrocatalysts based on Pt [10] and Pt-Ru alloys [11] have been developed and indeed exhibit good activities, high costs of these materials are often very prohibitive. A great deal of interest has recently been centered on the materials immobilized onto the electrode surface and capable of mediating fast electron transfer from methanol, namely its electrooxidation [12, 13]. Because catalysis is a surface effect and the catalyst needs to have the highest possible surface area, carbon-supported electrodes are generally used as catalyst [14]. It is well established that nickel can be used as a catalyst due to its surface-oxidation properties. Many electrodes involving nickel as a component in their manufacture can be used as catalyst in fuel cells [15, 16]. It is commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [17, 18]. One of the very important uses of nickel as a catalyst is its application in the oxidation of alcohols. Therefore, several studies on the electrooxidation of alcohols at the Ni have been reported [1, 19].

The purpose of the present work is to study electrochemically the methanol oxidation on a nickel–salophen-modified glassy carbon electrode (NiS/MGC) in alkaline

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solutions and bring it to the attention of workers in the field of direct methanol fuel cell development.

Experimental

The chemicals

Sodium hydroxide and methanol (from Merck) used in this work were analytical grade and were used without further purifications. Doubly distilled water was used throughout. The synthesis of salophen ligand by the following procedure was adopted. Briefly, 1.0 mol of 1,2-diamminobenzene, 2.0 mol of salicylaldehyde was dissolved in pure ethanol, and the mixture was refluxed for 1 h. Then, the product was recrystallized in ethanol and washed with distilled water. The procedure of NiS complex synthesis was shown in Scheme 1.

Apparatus

The cyclic voltammetric experiments were carried out using a Radiometer Model DEA 322 digital electrochemical analyzer equipped with an IMT electrochemical interface, and a personal computer was used for data storage and recording. Cyclic voltammograms were done in a conventional three-electrode cell using a GC disc electrode (from Radiometer) as working electrode (with 2 mm in diameter). Auxiliary electrode and reference electrode were a platinum wire and saturated calomel electrode (from Radiometer), respectively.

Electrochemical impedance spectroscopy (EIS) studies were carried out in a conventional three-electrode cell powered by an electrochemical system comprising of Auto Lab model 100 potentiostat/galvanostat. The frequency range of 100 kHz to 1 MHz and the modulation amplitude

of 10 mV were employed for impedance studies. A dual Ag|AgCl|KCl_{sat}, a Pt wire and a GC disk (modified or bare) electrode with 2 mm diameter were used as the reference, counter, and working electrodes, respectively. All studies were carried out at 298±2 K.

The preparation of working electrode

The GC disc electrode (supplied from Auto Lab) was mechanically polished with 600 grit sand paper and then with 0.05 μm α-alumina powder. The polished surface was rinsed with acetone and then with doubly distilled water prior to modification. The preparation of modified electrode consists of the following steps: 75 μL (two droplets) of a 1.0×10⁻³ M solution of nickel–salophen complex in acetone was gradually deposited on the surface of working electrode. The electrode was dried every time in an air medium at 298±2 K for 15 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 100 cycles of potential scans. These parameters were obtained experimentally as optimum values for complete maximum activation of electrode surface towards electrocatalytic oxidation of methanol.

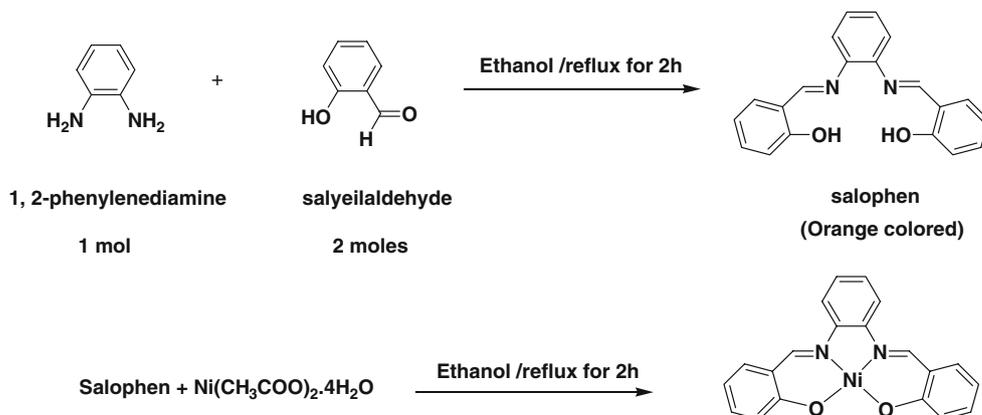
Results and discussion

Parameters affecting the electrode modification

Effect of complex concentration

The effect of the NiS complex concentration on the oxidation peak height of methanol in a solution containing 0.10 M NaOH and 0.10 M methanol in the various

Scheme 1 The synthesis of NiS complex



concentration of NiS complex (1.0×10^{-4} – 3.0×10^{-2} M) was investigated (Fig. 1). As can be seen, at 1.0×10^{-3} M of complex concentration, the electrocatalytic oxidation of methanol increases and shows a maximum peak current. Surface-bonded hydroxyl radicals play a fundamental role in the catalysis oxidation of methanol in NaOH solution [1]. When the entire electrode surface is covered by NiS 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 complex concentration of 1.0×10^{-3} M is proposed for the methanol oxidation at the surface of this modified electrode (as shown in Fig. 1).

Electrocatalytic oxidation of methanol

The NiS complex layer at the electrode surface acts as a catalyst for the oxidation of methanol in 0.10 M NaOH solution. Figure 2 shows the behavior of this electrode in absence and presence of 0.1 M methanol. This figure indicates clearly that the applied modifier on the surface of this electrode participates directly in the electrocatalytic oxidation of methanol. In the over region of potential, where only Ni (III) species exists at the electrode surface, an anodic peak (b) appears with a large current with respect to that of the former one. The height of this peak increases linearly with methanol concentration in solution,

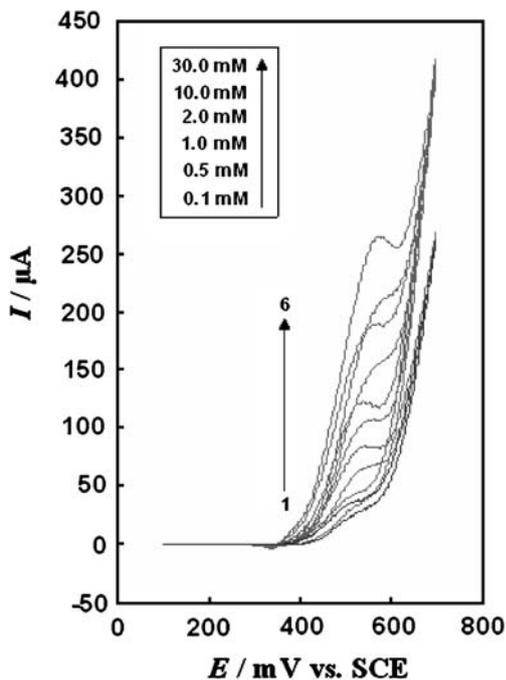


Fig. 1 Cyclic voltammograms of modified electrode in 0.1 M NaOH and 0.1 M methanol at different concentrations: the numbers 1–6 correspond to 0.1, 0.5, 1.0, 2.0, 10.0, and 30.0 mM of modifier. Potential sweep rate is 20 mV s^{-1}

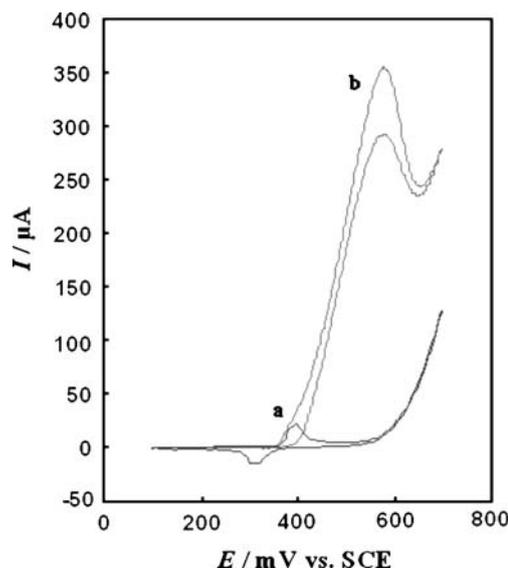


Fig. 2 Cyclic voltammograms of bare GC electrode (a) and NiS/MGC electrode (b) in 0.1 M NaOH and 0.1 M methanol. Potential sweep rate is 20 mV s^{-1}

indicating that it pertains to the process in which methanol is involved.

At this potential (potential of methanol oxidation), the composition of surface layer of nickel is NiO–salphen. It was suggested that methanol is oxidized and NiOOH transformed to $\text{Ni}(\text{OH})_2$ [1, 20]. Therefore, the oxidation of methanol reduces the amount of NiOOH on the surface of electrode. This transformation could be explained by the formation of nickel oxides with different morphologies in the presence of methanol. In the oxidation of alcohols at the nickel electrode in alkaline solution, different hypotheses are given in the literatures. El-Shafei [2] studied the oxidation of methanol on the glassy carbon electrode modified by nickel hydroxide in alkaline medium and found that methanol oxidation occurred via Ni (III). Fleischmann et al. [1, 21] proposed a mechanism for alcohol oxidation and suggested that the NiOOH acts as an electrocatalyst. According to this mechanism, there is an accumulation of $\text{Ni}(\text{OH})_2$ species in the presence of methanol. This hydroxide necessarily evolves towards more stable species, and its oxidation is attained at more positive potentials. For this reason, the quantity of NiOOH species necessary for methanol oxidation begins to decrease in the current density of methanol oxidation.

On the basis of the above literature, we proposed the following mechanism for the mediated electrooxidation of methanol on Ni/NiO–salphen electrode. This mechanism may be written as follows, taking into account that the mechanism of electrooxidation does not change with temperature variation within the explored temperature range:

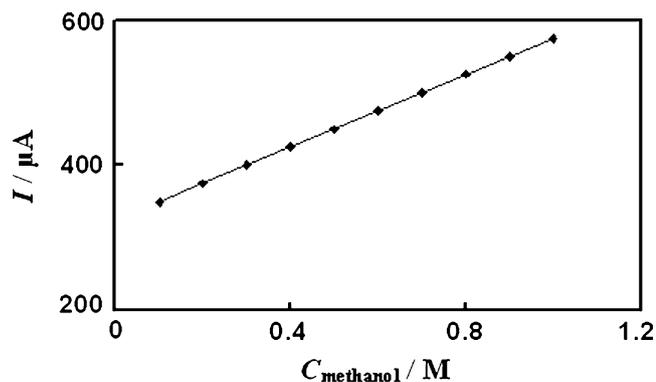


Fig. 3 Variation of anodic peak current of methanol oxidation at surface of modified electrode in 0.1 M NaOH at different concentrations: 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 M of methanol. Potential sweep rate is 20 mV s^{-1}

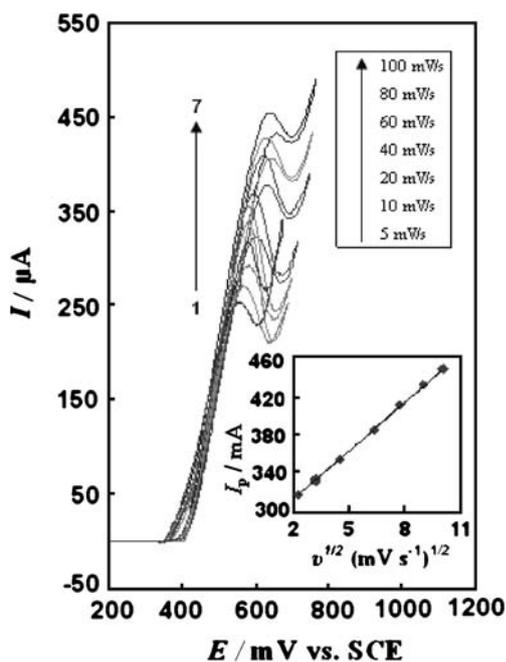
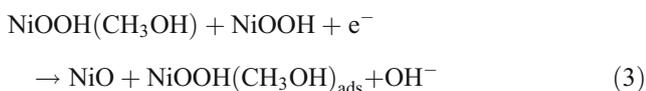
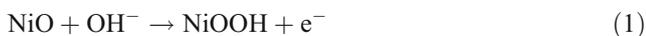


Fig. 4 Typical cyclic voltammograms of methanol oxidation at NiS/MGC electrode in 0.1 M methanol and 0.1 M NaOH at different sweep rates: the numbers 1–7 correspond to 5, 10, 20, 40, 60, 80, and 100 mV s^{-1} of potential. Inset: variation of the anodic current with the square root of sweep rate

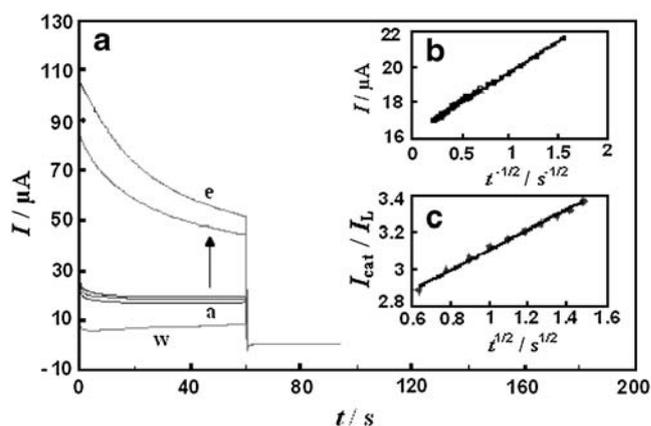
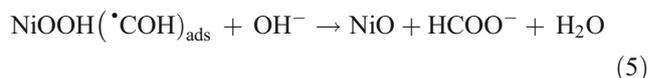
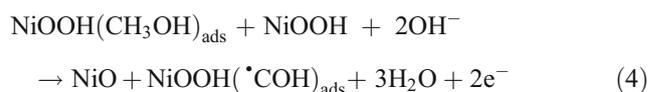


Fig. 5 **a** Double-step chronoamperograms of NiS/MGC electrode in 0.1 M NaOH solution containing methanol with different concentrations of 0.0 (w), 0.1 (a), 0.2 (b), 0.3 (c), 0.4 (d), and 0.5 (e), respectively. **b** Plot of I_{cat} versus $t^{1/2}$ obtained from chronoamperograms of (a). **c** Dependence of I_{cat}/I_L on the $t^{1/2}$ driven from the chronoamperograms data of (a). Potential steps were 600 mV vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ for oxidation and 300 mV vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ for reduction



Moreover, the efficiency of the prepared NiS for methanol oxidation, characterized by anodic peak current density, is significantly high in comparison with other modified electrodes reported in the literatures [16, 19, 21].

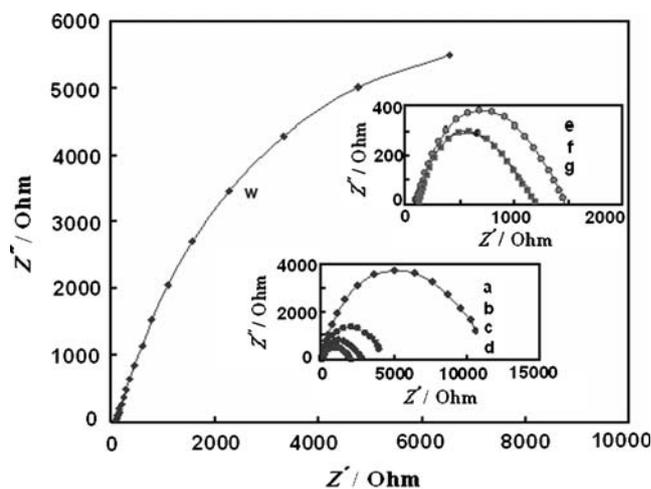
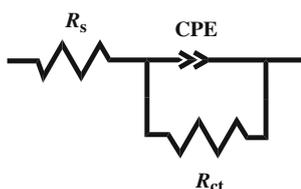


Fig. 6 Nyquist diagrams of NiS/MGC electrode in the absence (w) and 0.1 (a), 0.2 (b), 0.5 (c), 2.0 (d), 3.0 (e), 4.0 M (f), 5.0 M (g) methanol in 0.1 M NaOH solution and corresponding fitted curves. DC potential is 600 mV vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$



Scheme 2 The proposed equivalent circuit

Effect of methanol concentration

Figure 3 shows the effect of methanol concentration on the anodic peak current of methanol at NiS/MGC electrode in 0.10 M NaOH solution. It is clearly observed that as the methanol concentration increases, the anodic peak height increases linearly with methanol concentration up to 1.0 M. It can be assumed that this 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 rate depends on the reaction between methanol and Ni (III) species, which is present in the film.

Also, the cathodic peak is dramatically diminished at the low methanol concentration and disappears entirely as its concentration is raised. These observations, along with the fact that methanol is not electroactive in the potential window under consideration, point to the electrocatalytic nature of phenomenon.

Effect of scan rate on the anodic peak heights

The effect of scan rate on the anodic peak current ratio at modified (NiS/MGC) electrode in the presence of 0.10 M methanol in 0.10 M NaOH is shown in Fig. 4. This curve shows that the anodic current for methanol oxidation at NiS/MGC electrode increases rapidly with increasing the potential scan rate. Indeed, the time window for methanol oxidation process at higher scan rates

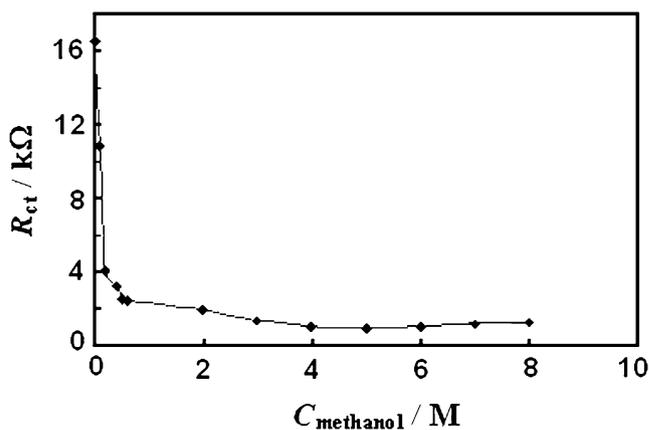


Fig. 7 Dependence of R_{ct} on methanol concentration derived from the data of Nyquist diagrams in Fig. 6

becomes very narrow avoiding the facile electron transfer between substrate and catalytic sites. Although the slow removal of adsorbed intermediates may contribute to the anodic peak, the origin of the anodic peak is still diffusion as clearly indicated in the linear dependency of the anodic peak current on the square root of potential sweep rate (Fig. 4).

Chronoamperometry

Figure 5a presents the current–time behavior in the absence (w) and in the presence of various concentration of methanol (a–e) in 0.1 M NaOH solution at the potential steps of 600 mV vs. Ag|AgCl|KCl_{sat} for oxidation and 300 mV vs. Ag|AgCl|KCl_{sat} for reduction at NiS/MGC electrode. The net current (background subtracted) vs. $t^{1/2}$ has linear dependency up to the current density of 22 μA (Fig. 5b). The dominance of a diffusion-controlled process is indicated. The transition current is obviously due to the mediated oxidation of methanol by NiOOH species and is substantiated upon increasing the concentration of methanol. Also, as the electrolysis potential is stepped down to 300 mV vs. Ag|AgCl|KCl_{sat}, no significant current is obtained indicating the irreversibility of the process.

Table 1 The values of the elements in equivalent circuit fitted in the Nyquist plots of Fig. 6 and the corresponding relative errors

| CPE | | | | |
|----------------|---|--------------------|----------------------------------|------------------|
| $R_s \ \Omega$ | $T_0 \times 10^{-4} \Omega^{-1} \text{ s}^{-1}$ | Parameters (n) | $R_{\text{ct}} \ \text{k}\Omega$ | $C_m \ \text{M}$ |
| 96 (0.47%) | 0.1154 (0.40%) | 0.7580 (0.11%) | 16.51 (0.95%) | 0.0 |
| 93.6 (0.46%) | 0.2352 (0.60%) | 0.8037 (0.18%) | 4.04 (0.58%) | 0.1 |
| 92.8 (0.35%) | 0.2859 (0.45%) | 0.8245 (0.13%) | 3.18 (0.41%) | 0.2 |
| 95.6 (0.38%) | 0.3383 (0.88%) | 0.8533 (0.23%) | 2.47 (0.51%) | 0.5 |
| 99 (0.3%) | 0.4780 (1.1%) | 0.8085 (0.25%) | 1.49 (0.51%) | 2.0 |
| 94.9 (0.42%) | 0.5965 (1.86%) | 0.8108 (0.43%) | 1.22 (0.81%) | 3.0 |
| 109.1 (0.45%) | 0.2334 (2.71%) | 0.6635 (0.59%) | 1.01 (0.94%) | 4.0 |
| 111.6 (0.34%) | 0.2109 (2.83%) | 0.6774 (0.62%) | 0.936 (0.80%) | 5.0 |

For an electroactive material, the current corresponding to the electrochemical reaction (under diffusion controlled) is described by Cottrell's equation [22]:

$$I = nFAgD_{\text{app}}^{1/2}C_0\pi^{1/2}t^{-1/2} \quad (6)$$

where, D_{app} and C_0 are the apparent diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. The plot of I versus $t^{1/2}$ would be linear, and from its slope (Fig. 5b), the mean value of D_{app} of methanol was calculated $2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The ratio of the transient current in the presence of methanol (I_{cat}) to the limiting current in its absence (I_L) follows [23]:

$$I_{\text{cat}}/I_L = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (7)$$

where the argument of the error function (γ) equals $k'C_m t$ with k' , C_m , and t are the apparent rate constant of methanol consumption, the bulk concentration of methanol and the time of measuring I_{cat} . For $\gamma > 1.5$, $\text{erf}(\gamma^{1/2})$ almost equals unity and Eq. 7 reduces to:

$$I_{\text{cat}}/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(k'C_m t)^{1/2} \quad (8)$$

From the slope of I_{cat}/I_L vs. $t^{1/2}$ plot, the value of k' was calculated to be $7.95 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Fig. 5c).

Electrochemical impedance spectroscopy

Figure 6 presents the Nyquist diagrams of NiS/MGC electrodes recorded at 530 mV vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ dc-offset both in the absence (w) and presence of methanol in various concentrations (a–g) in 0.1 M NaOH solution. In the absence of methanol, a slightly depressed semicircle was observed. A steady decrease was seen in the diameter of semicircle in the methanol concentration ranges from 0.1 to 5.0 M.

The equivalent circuit compatible with the results of EIS study is presented in Scheme 2. In this circuit, R_s , CPE, and R_{ct} represent solution resistance, a constant phase element corresponding to the double-layer capacitance, and the charge-transfer resistance associated with the oxidation of methanol, respectively.

Table 1 shows the values of the equivalent circuit elements obtained by fitting the experimental results. The goodness of this fitting can be judged by the estimated relative errors as presented in the parentheses. In Table 1, T_0 and n are the CPE impedance coefficient and exponent, respectively.

The methanol concentrations dependency of R_{ct} is studied (Fig. 7). As can be seen, an initial sharp drop is terminated to a very slow change with the increase of methanol concentration to above 0.5 M.

Conclusion

This work presents the electrooxidation of methanol on NiS/MGC electrode in alkaline solutions. It is concluded that the electrooxidation of methanol starts around 400 mV vs. SCE, occurs through a mediated electron transfer mechanism catalyzed by Ni (III) species, which forms in the same potential region. The optimum complex concentration for modification, optimum methanol concentration, and optimum potential scan rate have been obtained.

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