Preparation of Nickel Modified Carbon Fibre Electrodes and their Application for Methanol Oxidation

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Abstract: Nickel modified carbon fibre electrodes were prepared by electrochemical oxidation and partial reduction of a graphite fibre electrode with a slow linear potential sweep in 97% H_2SO_4 solution followed by impregnation & ion-exchange with Ni^{+2} species. The cyclic voltammetry of the modified electrode in an alkaline medium showed electrocatalytic activity towards methanol oxidation which is consistent with the behaviour of a polycrystalline nickel electrode in the same media. The electrode fabricated through the ion exchange with 0.1 M Ni solution provided the most significant response for solutions with lower methanol concentrations up to 0.5 M methanol while at higher concentrations of methanol, a poisoning effect was observed resulting in lower performance.

Keywords: Alkaline media, graphite fibre, ion exchange, methanol oxidation, nickel, surface modification.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) offer several advantages over their hydrogen counterparts especially for portable applications such as mobile phone chargers, notebook computers etc. Currently used Pt based electrocatalysts which are most widely investigated [1-6] make mass production difficult due to their low availability and expensive electrode costs. Also issues like CO poisoning severely affect the performance [7] of these cells. Alkaline direct methanol fuel cells are now receiving considerable attention because they allow the use of anion exchange membranes that reduce methanol cross-over – a serious problem with cation exchange membrane used in acidic methanol fuels [8]. Another reason for using alkaline medium is because the kinetics for both methanol oxidation and oxygen reduction reactions is found to be more facile in alkaline medium than in acidic one [9-12]. Even in the case of acidic DMFC however, nickel can in fact be used as a co-catalyst along with Pt-Ru in an acidic medium [13] and Pt-Ru-Ni/C shows better catalytic activity and more CO tolerance compared to Pt-Ru/C catalyst [13] The commercialization of these DMFCs is hindered by lower cell performance which can be attributed to slow anode kinetics [14, 15]. In recent years, the focus of research is towards finding cheaper alternative electrocatalysts and improving the overall cell performance. Non noble transition metal electrocatalysts such as copper [16], nickel [17-24] which oxidise methanol and other alcohols, offer good alternative electrocatalysts. The activity of nickel based electrocatalysts depends on the method of preparation of these electrodes. Rahim *et al.,* [24] showed that only nickel dispersed in graphite is catalytically active for methanol oxidation while massive nickel is not. Also this nickel electrocatayst, after continuous cycling looses its performance due to possible loss of activity of nickel oxide [24]. This is believed to be due to increased thickness of NiO(OH) which acts as a barrier inhibiting the charge transfer process for methanol oxidation. Alternative approaches to the preparation of nickel electrocatalysts that can minimise the build up of such a barrier layer, would be of great interest in the development of non-noble metal electrodes for methanol oxidation. Carbon fibre modified electrodes have been shown to form layers of metal ions distributed in the carbon matrix, creating active sites on the carbon surface instead of a continuous layer of deposited metal. The motivation behind this study is to investigate the effect of this carbon fibre modification and electrode preparation method on electrocatalytic activity towards methanol oxidation.

Since the discovery of the "chiral electrode" by Miller and co-workers [25], several reports have been published about the synthesis of chemically modified electrodes using Miller's amidization procedure [26, 27] or organosilane reagents [28-30] on either metal oxide or air oxidized carbon surfaces. In recent years, there has been considerable interest in the electrochemical properties of chemically modified electrodes involving surface oxidation [31-33] and surface functionalization [33-38]. Also the electrodeposition of several metals, such as Ag, Pb, Cu and Au on carbon fibre electrodes, has been investigated in detail. The deposition of these metals on the graphite fibre involved the exchange of their cations with the H^+ ions of the acidic functional groups remaining in the graphite matrix after the incomplete cathodic reduction of the graphite oxide surface [38]. The electrochemical behaviour of platinised graphite fibre electrodes was studied by Jannakoudakis and co-workers [39]. These electrodes were prepared by deposition of platinum after ion exchange of residual graphite oxide fibres with various platinum compounds in aqueous solutions. These modified electrodes behave electrocatalytically just like bulk platinum electrodes [39]. These electrodes can be stored for long periods in distilled water without losing their mechanical stability and electrocatalytic activity. This same

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method has been used in the present study for the modification of graphite fibres *via* an ion exchange reaction with Ni^{+2} ions. The electrochemical behaviour of the chemically modified electrodes was investigated for the methanol oxidation reaction in an alkaline medium for possible applications in direct methanol fuel cells.
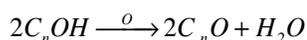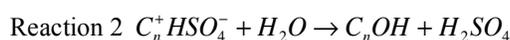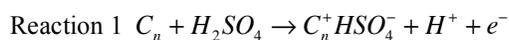
2. EXPERIMENTAL

All chemicals were of analytical grade and used without further purification. All electrolytic solutions were prepared using distilled water and 0.5 M sodium hydroxide was used as a supporting electrolyte unless otherwise stated. All electrochemical studies were carried out in a standard three-electrode glass cell using a Solartron SI 1287 potentiostat.

2.1. Fabrication of Graphite Fibre Electrode

A mechanically stable graphite fibre (Besfight, Toho Rayon Co. Ltd., Grade HTA-7-3000, bundle diameter 1 mm) was used to fabricate the electrode employed in this study. The experimental electrode was prepared by forming a resin case around the carbon fibre placed in plastic holder such as a pipette tip (40 mm in length and 15 mm diameter). The resin mixture used was formed by mixing Epoxy resin (Araldite F) and hardener HY837. After the resin had dried, the electrode was surface polished with 240 grit sand paper to remove the excess epoxy to expose the graphite fibre cross-section that acted as the electrode surface. The electrode surface was finally polished with 1200 grit sand paper and washed repeatedly with distilled water prior to the electrochemical activation and ion exchange.

2.2. Activation of Electrode

The activation of the graphite fibre was achieved by using a slow linear voltage sweep of 2.5 mV s^{-1} in 97% H_2SO_4 electrolyte from an initial potential of 0 V to an upper voltage limit of 2.1 V (Vs SCE) and back [40]. This activation was carried out in the standard three-electrode cell with the graphite fibre electrode as working electrode while a saturated calomel electrode and carbon rod were used as reference and counter electrodes respectively. During the anodic sweep, the graphite fibre is electrochemically oxidised according to the following surface reactions [41]:

Reaction 1 $C_n + H_2SO_4 \rightarrow C_n^+ HSO_4^- + H^+ + e^-$

Reaction 2 $C_n^+ HSO_4^- + H_2O \rightarrow C_nOH + H_2SO_4$

$$2C_nOH \xrightarrow{O} 2C_nO + H_2O$$

This hydroxylated species (C_nOH) undergoes further oxidation readily to produce carbonyl or carboxyl functional groups.

Partial reduction occurs during the cathodic sweep as follows:

Reaction 3 $C_nO \xrightarrow{H^+} C_nO^- H^+$
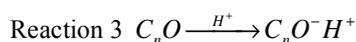
The above surface oxidation and partial reduction enables formation of a high surface concentration of –OH groups that provide the active sites for ion exchange or impregnation by the metal [41]. To investigate the mechanism in detail the activation procedure was also repeated at 1 mV s^{-1} and 5 mV s^{-1}.

The fibre electrode was then washed with distilled water for 10-15 minutes, and vacuum dried at room temperature for 20-25 hours. The vacuum reduction step was used for removal of any oxides formed [40].

2.3. Cation Exchange with Nickel

After the activation, the electrodes were placed in nickel sulphate solutions with different concentrations over a period of 50 hours during which impregnation or ion exchange takes place. The deposition of the nickel takes place through cation exchange with the hydrogen ions of the acidic functional groups left on the carbon surface after partial cathodic reduction of graphite oxide formed during activation [39, 40]. After this procedure, the electrode was again washed thoroughly with distilled water and then vacuum dried at room temperature for 20-25 hours [40]. It was important to ensure that the electrode was left in distilled water between each stage, to reduce any oxide formation due to reaction with oxygen from the air prior to the methanol oxidation study.

2.4. Electrochemical Studies

The electrochemical studies were carried out using Solartron SI 1287 potentiostat in a standard three electrode glass cell where the graphite fibre electrode modified with nickel was employed as a working electrode for the methanol oxidation study, while a saturated calomel electrode (SCE) and graphite rod were used as reference and counter electrodes respectively. Solutions with various concentrations of methanol in 0.5 M NaOH were used as electrolytes. All experiments were carried out at room temperature and all potentials are reported *vs* SCE unless otherwise stated.

3. RESULTS AND DISCUSSION

3.1. Graphite Fibre Activation and Characterisation

Fig. (**1**) represents the cyclic voltammogram for the base graphite fibre electrode before activation and ion exchange. The electrolyte comprised of 0.5 M NaOH (blank) with increasing methanol concentrations from 0 to 0.5 M methanol. As seen from the figure, there is no difference in the electrode response in the methanol solution and in the blank solution which proves that a base graphite fibre electrode does not catalyse the methanol oxidation reaction.

Fig. (**2**) shows the cyclic voltammogram for the activation of the graphite fibre electrode in 97% H_2SO_4, prior to cationic exchange with $NiSO_4$ solutions, as described in the experimental procedure. The aim of this activation step is to promote surface oxidation of the graphite fibres during the anodic scan from 0 V to +2.1 V, and incomplete or partial reduction of the oxide functional groups during the cathodic scan back from +2.1 V to 0 V. Three separate peaks (a_1, a_2 during the anodic sweep and c_1 during the cathodic sweep) are observed. The first peak a_1 at around 0.7 V represents the formation of $C_n^+ HSO_4^-$ (H_2SO_4) salts formed between graphite bulk and the sulphuric acid electrolyte which is then oxidised further to a partly covalent graphite oxide at the second peak a_2 at around 1.4 V according to reaction 1 and 2 above [40]. During the cathodic scan, only partial reduction of the graphite oxide formed during the anodic sweep, occurs at the third peak c_1 at around 0.4 V, resulting in formation of

–OH surface groups [40] on the graphite fibre according to Reaction 3, which will allow for subsequent cationic exchange with nickel ions to form graphite-nickel electrodes according to reaction 4 [41]:
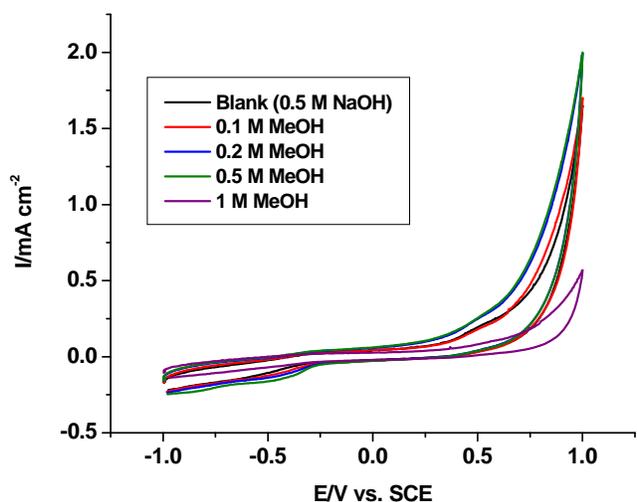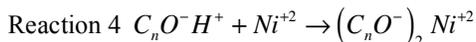
Reaction 4 $C_nO^-H^+ + Ni^{+2} \rightarrow \left(C_nO^-\right)_2 Ni^{+2}$

Fig. (1). Methanol oxidation at base graphite electrode (no modification) in 0.5 M NaOH solutions, 25 mV s^{-1} scan rate.
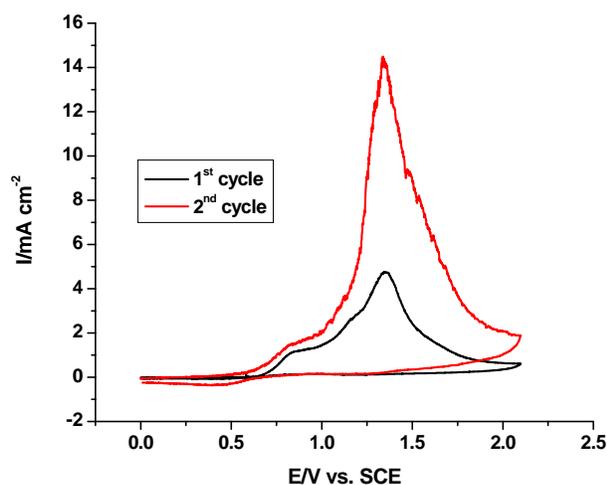

Fig. (2). Activation of graphite fibre electrode in 97% H$_2$SO$_4$, scan rate 2.5 mV s^{-1}.

Fig. (**3**) shows the activation process at various scan rates. Typical results obtained for methanol oxidation with the 'activated' graphite fibre electrode, prior to any cationic exchange with nickel are presented in Fig. (**4**). The electrolyte solutions comprised a base 0.5 M NaOH with increasing concentration of methanol. As seen in the figure, the current response is quite low, with no significant anodic peak for methanol oxidation observed.

Cyclic voltammograms obtained at the graphite fibre electrodes in 0.5 M NaOH after activation and ion exchange are illustrated in Fig. (**5**). By comparing the response of this electrode with the response for a nickel foil electrode (shown in the inset in Fig. **5**), the nickel modified graphite fibre

electrode is seen to behave like a nickel electrode. Anodic peak at approximately 0.5 V *vs* SCE in both curves (b) and inset of Fig. (**5**) correspond to the oxidation of Ni^{+2} to Ni^{+3} according to [24]:
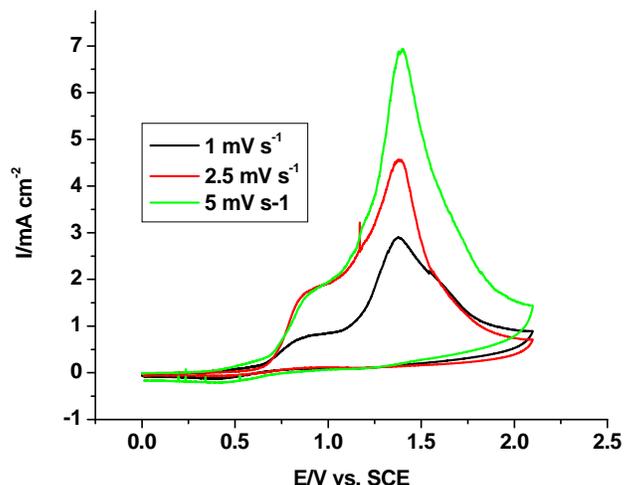

Fig. (3). Activation of Graphite Fibre Bulk in 97% H$_2$SO$_4$ solution, at 1 mV s^{-1}, 2.5 mV s^{-1}, 5 mV s^{-1} scan rate.
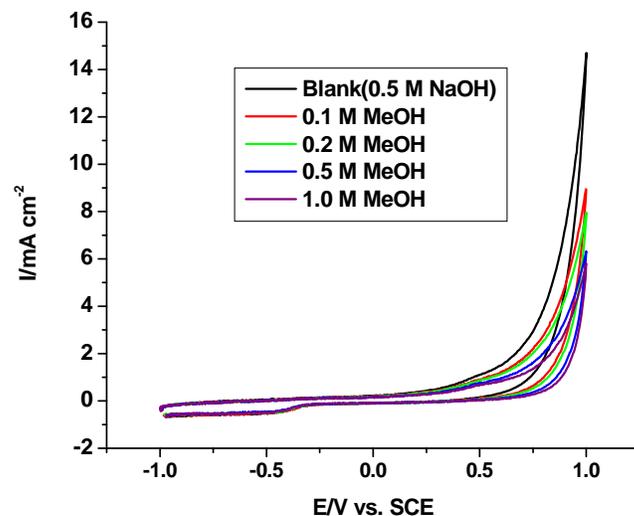

Fig. (4). Methanol oxidation in 0.5 M NaOH solutions, at residual graphite electrode (activation in H$_2$SO$_4$, no Ni ion ex.), at 25 mV s^{-1} scan rate.

Reaction 5 $Ni^{+2} \rightarrow Ni^{+3} + e^-$

During the cathodic sweep, a reduction peak is observed at around 0.3 V corresponding to the reduction of Ni^{+3} to Ni^{+2}.

Reaction 6. $Ni^{+3} + e- \rightarrow Ni^{+2}$

while at -0.6 V, a second cathodic peak is observed corresponding to the reduction of dissolved oxygen from the solution. This peak is absent in case of nickel foil as the strongly adsorbed oxygen on nickel foil is not reduced as easily. This is due to the fact that smooth nickel is very sensitive to dissolved oxygen from solution and it gets strongly adsorbed on the surface [42]. Here in addition to
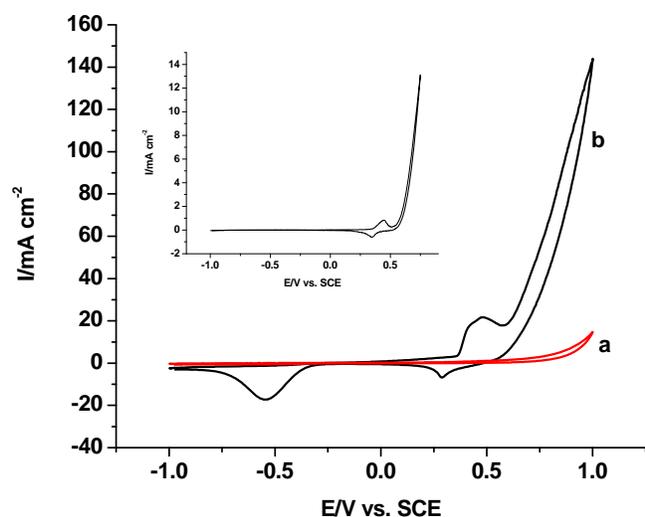
Fig. (5). Cyclic voltammogram for Ni-modified graphite fibre electrode in 0.5M NaOH solution; corresponding response for Nickel foil in inset.

oxygen reduction, there is also possibility of reduction of carboxyl functional groups. Fig. (**2**) indicates even without any activation and modification, the electrode shows reduction peak around -0.5 V (which could only be due to dissolved oxygen) and the same peak area increases after activation and modification which may suggest the possible partial reduction of carboxyl functional groups.

Another observation is while the Ni(OH)$_2$/NiOOH transformation occurs reversibly on bulk nickel (as noted from the potential peak separation), on dispersed nickel, this transformation occurs quasi-reversibly or irreversibly. This could possibly be due to the IR drop across the graphite substrate. Also the shape of the Ni (II) /Ni (III) transition (i.e. peak separation, peak current ratios and peak potentials), is influenced by the thickness of the nickel film [24] and for thicker deposited nickel oxide films, the voltammogram begins to show the typical features of an electrode with higher resistance. In contrast, the activated graphite fibre electrode with no Ni ion exchange (Fig. **4**) shows no anodic or cathodic peaks at 0.5 and 0.3 V respectively, confirming the absence of any Ni on the electrode surface before modification.

The amount of nickel deposited on the surface of graphite fibre was estimated from the calculation of the charge transferred during the nickel oxidation reaction in 0.5 M NaOH in the absence of methanol (peak around 0.5 V in Fig. **5**). The charge was calculated by converting the E axis to time and then integrating the I-t curve. Other analytical

methods like XPS failed to detect any deposited nickel (in case of 0.1M, 0.2M Ni samples); however this may be attributed to difficulties with sample preparation when embedding the electrode in resin, as well as the very small quantity of nickel that may not be detectable using XPS or other analytical techniques. From the charge calculations, the amount of nickel deposited on the carbon fibre electrode during the ion exchange is calculated and shown in Table **1**.

Surprisingly, the amount of Ni on the electrode surface, as calculated from the charge transferred during the oxidation of Ni^{+2} to Ni^{+3} appears to decrease as the Ni^{+2} ion concentration in the ion exchange solution increases from 0.2 to 0.5 M. This effect will be discussed further later.

Assuming an approximate electrode surface area of 0.007855 cm^2 and an atomic radius for Ni of 124 pm, a surface coverage of approximately 3.2×10^5 atoms/layer is calculated for the electrode modified in 0.1 M NiSO$_4$, showing that there are multiple atomic layers of Ni on the electrode surface indicating activation of sites on the surface as well as in the bulk.

3.2. Methanol Oxidation Results

These Ni modified electrodes were tested for their electrocatalytic activity towards methanol oxidation and the results are depicted in Figs. (**6-8**) which represent results for electrodes modified by ion exchange in 0.1 M, 0.2 M and 0.5 M NiSO$_4$ solutions respectively. The electrolytes comprised of varying concentrations of methanol in 0.5 M NaOH. Corresponding voltammograms are also presented for the modified electrodes in 0.5 M NaOH as the blank electrolyte.
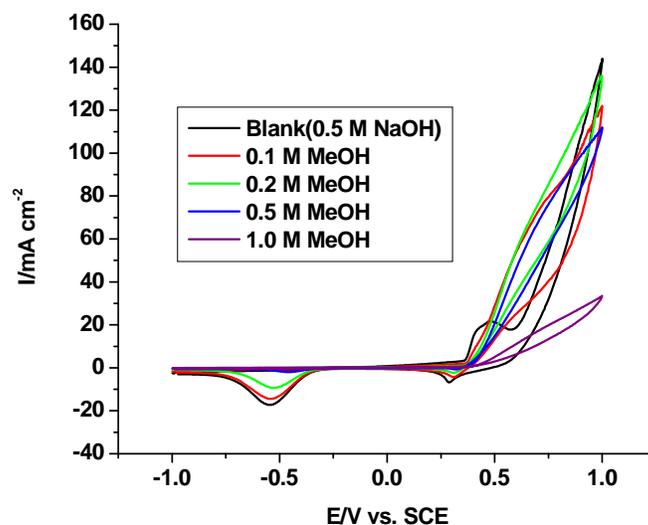

Fig. (6). Methanol oxidation in 0.5M NaOH solution, at graphite-nickel electrode (0.1M Ni ion ex.), at 25mV/s Scan Rate.

Table 1.   Calculation for Amount of Nickel in the Modified Carbon Fibre Electrodes

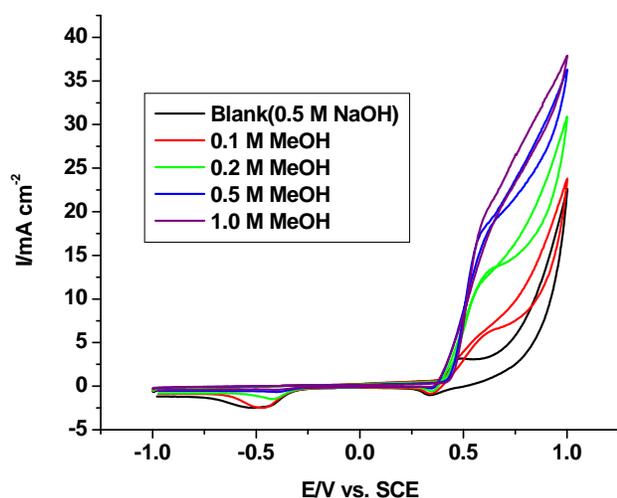| Electrode	Charge (Coulombs)	No. of Moles	No. of Atoms
0.1 M Ni modified	1.21×10^{-6}	1.26×10^{-11}	7.56×10^{12}
0.2 M Ni modified	4.72×10^{-7}	4.90×10^{-12}	2.95×10^{12}
0.5 M Ni modified	1.4×10^{-8}	1.55×10^{-13}	9.36×10^{10}

Fig. (7). Methanol oxidation in 0.5M NaOH solution, at graphite-nickel electrode (0.2M Ni ion ex.), at 25mV/s Scan Rate.
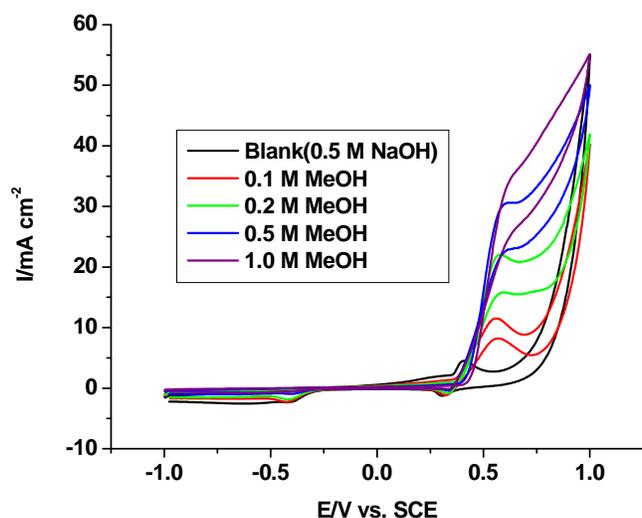

Fig. (8). Methanol oxidation in 0.5M NaOH solution, at graphite-nickel electrode (0.5M Ni ion ex.), at 25mV/s Scan Rate.

Fig. (**6**) shows that in the absence of methanol, an anodic peak appears at around 0.45 V with the corresponding cathodic peak at around 0.3 V, these being attributed to the Ni (II)/ Ni (III) couple [24]. There is also another cathodic peak at around -0.6 V which is attributed to reduction of dissolved oxygen and also partial reduction of carboxyl groups from the carbon matrix. This behaviour is consistent with that of a polycrystalline nickel electrode confirming that the graphite fibre electrode has been successfully modified with nickel. In the presence of methanol, another anodic peak appears at 0.6 V which is consistent with the oxidation potential of methanol at polycrystalline nickel. Increasing the methanol concentration in the electrolyte solution results in an initial increase in the peak response up to a methanol concentration of 0.2 M, followed by a decreasing response with a further increase in methanol concentration. The probable reason for this appears to be a poisoning of the electrode due to accumulation of methanol oxidation products on the surface. Similar results were obtained for the electrodes modified by ion exchange in 0.2 M and 0.5 M

$NiSO_4$ solutions. A comparison of these results with those in Figs. (**7**, **8**) shows that the electrode modified in 0.1 M Nickel gives a higher current response than that for electrodes modified in 0.2 M and 0.5 M $NiSO_4$ solutions. In contrast to the electrode modified in 0.1 M $NiSO_4$ however the graphite fibre electrodes modified in 0.2 M and 0.5 M $NiSO_4$ shows a consistent trend of an increasing anodic current response with increasing methanol concentration.

Fig. (**9**) shows the overlay response for activated graphite fibre electrode (no Ni modification) in 0.1 M MeOH solution and those for the activated electrodes modified with 0.1 M, 0.2 M and 0.5 M $NiSO_4$ solutions. As seen in the figure, the response for the 0.1 M Ni modified electrode is higher than that for higher Ni concentration modified electrodes. Abdel Rahim *et al.,* [41] showed that for Ni electrodeposited on graphite electrode, increasing Ni deposition does not result in a linear increase in current density for methanol oxidation. However there is dramatic increase in current density at low nickel concentration resulting in a maximum followed by a drop in current density at higher concentrations.
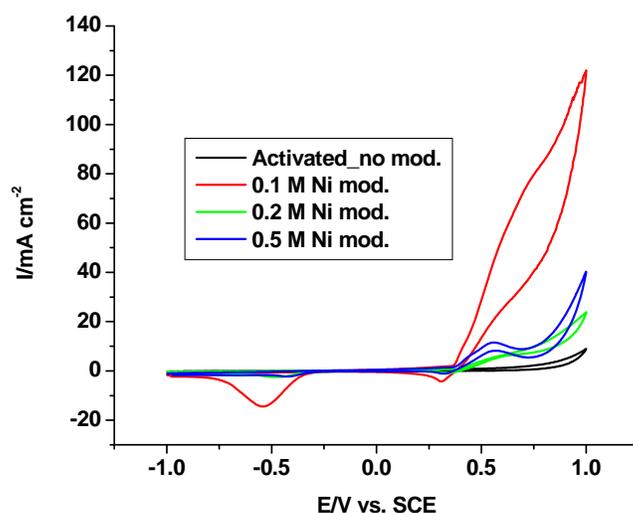

Fig. (9). Methanol oxidation at electrodes with increasing graphite-nickel concentration (0.1M MeOH for 0.1M Ni, "Activated", 0.2M Ni and 0.5M Ni) in 0.5M NaOH solution, at 100mV/s Scan Rate.

This behaviour is shown in Fig. (**10**). The reason for this significant increase in current density for the methanol oxidation on the 0.1 M nickel electrode is not clearly understood. One suggestion is that at lower nickel concentrations the electrode has a higher catalytic surface area available for reaction due to greater dispersion on the surface of the graphite fibres [42]. This is similar to an opinion that with an increase in surface concentration, the layers of nickel become denser on the graphite surface approaching the behaviour of a 'massive nickel electrode' [18]. However, as previously calculated from charge calculations, there was higher surface Ni concentration on the electrode that was modified in 0.1 M $NiSO_4$ solution. On the other hand the Ni modified graphite electrodes formed in 0.2 M and 0.5 M nickel ion exchange solutions showed lower surface Ni concentration and in turn, demonstrate a lower catalytic effect for methanol oxidation. While the explanation for better performance for 0.1 M Ni modified electrode can be given by an increased number of atoms of

nickel deposited on the surface, the exact reason behind the higher deposition of nickel in the case of the 0.1 M Ni modified electrode compared to 0.2 M and 0.5 M Ni electrodes is still not understood.
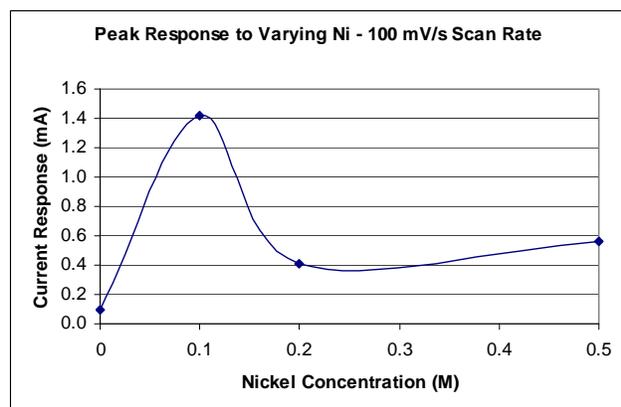

Fig. (10). Average Current Response compared for electrodes with increasing graphite-nickel concentration for methanol oxidation (0.1M MeOH for 0.1M Ni, 'Activated', 0.2M Ni and 0.5M Ni) in 0.5M NaOH solution, at 100mV/s Scan Rate.

Another opinion is that for thin nickel oxides catalysts, the oxidation of methanol proceeds with direct chemical reaction with NiO(OH) produced electrochemically during anodic sweep [18]; while for graphite-nickel electrodes prepared at higher Ni concentrations, oxidation of methanol proceeds by charge transfer, resulting in a decrease in catalytic activity [18]. This is believed to be caused by the increase of NiO(OH) produced at the surface of the electrode inhibiting the effective oxidation of methanol rather than promoting it [18].

However this is not consistent with Fleischmann *et al.,* [17], who suggested a mechanism that methanol oxidation is the result of nickel species changing from one state to the next, and an accumulation of NiO(OH) should in turn lead to an increase in the oxidation of methanol. The mechanism suggested is as follows.

$$Ni(OH)_{2(ads.)} \rightarrow NiOOH^{\cdot} + e^{-} + H^{+}$$

$$NiOOH^{\cdot} + CH_3OH_{(ads.)} \rightarrow Ni(OH)_2 + [CH_2OH]^{\cdot} + H_2O \ [17]$$

It is quite possible that the reality is a combination of these opinions and that the Fleischmann *et al.,* suggested mechanism of the promotion of organic compound oxidation does not follow a linear progression. It is possible that the true mechanism is not a one way reaction but rather approaches equilibrium and that there is a critical methanol concentration at which inhibition of further oxidation takes place. Further experimentation is necessary to confirm these suggestions.

3.3. Deterioration of Nickel Modified Electrode

The Fig. (**11a**, **b**) represent the effect of extended operation of the Ni modified working electrodes under potentiostatic electrolysis in a 0.5 M MeOH solution at 0.6 V and 0.65 V *vs* SCE, the voltage at which NiO(OH) would

begin to form on the surface of the working electrodes. This also correlates to the potential at which methanol oxidation begins to be significantly promoted. The figures show a slight increase in current over the extended period of operation. It is likely that this increase in activity of both electrodes over the extended period was due to an increase in the formation of Ni (III) species thereby allowing more efficient oxidation of the methanol in solution. This is confirmed in Fig. (**12**) where a cyclic voltammogram recorded in 0.5 M methanol in 0.5 M NaOH after polarization shows a significant increase in current density compared to the response before polarization.

It was observed that the nickel electrodes prepared by electrodeposition of nickel on graphite disks lose their electrocatalytic activity due to formation of a thick layer of NiO(OH) which inhibits charge transfer (discussed in detail in section 1) and have to be reduced back to nickel in order to regain their activity [18]. In our studies, a potentiostatic treatment at 0.65 V *vs* SCE, improves the electrocatalytic activity. In previous studies [24], the whole electrode surface is covered by nickel and with continuous cycling, there is increase in the thickness of Ni (III) layer making the electrode to behave very similar to bulk nickel and hence lower catalytic activity. In our studies, nickel is likely to be dispersed in the carbon matrix instead of a continuous layer and during the potentiostatic studies, even though there is a increase in Ni(III) formation, the layer of Ni(III) is not continuous. Electrical conduction to the carbon matrix is therefore facilitated and hence the better activity compared to electrodeposited electrode.

Although these results can not conclude that there is no deterioration of the electrodes after extended electrolysis, a slight increase in activity was observed and this may be due to exposure of a greater surface area of the working electrode or the accumulation of NiO(OH) species in the carbon matrix that may be linked to the increase in oxidation as predicted by Fleischmann *et al.,* (1971) [17]. Further experimentation is required to determine the actual cause of the phenomenon however.

3.4. XPS Studies

Carbon fibre without any resin was used as a substrate for activation in 97 % H_2SO_4 for XPS studies to avoid the interference of resin. Another electrode modified with nickel after activation was also used to study the nature of bonding and presence of nickel and results are presented in this section.

Fig. (**13**) represents wide angle spectra for an activated carbon fibre without any ion exchange (a) and nickel modified electrode (b) while the individual binding energy spectra for carbon, sulphur and oxygen are shown in Fig. (**14**).

In Fig. (**14a**), the peak at around 288.8 eV corresponds to O=C=O group while the peaks at 286.2 and 285.6 eV correspond to C=O and C-O binding energies. The peak at 284.6 eV is due to either C-C or C-H group [43]. In Fig. (**14b**, **c**), the peaks at 532.1 and 533.5 eV are due to S=O and S-O respectively while sulphur shows peak at 169.02 eV corresponding to sulphate ion [43].
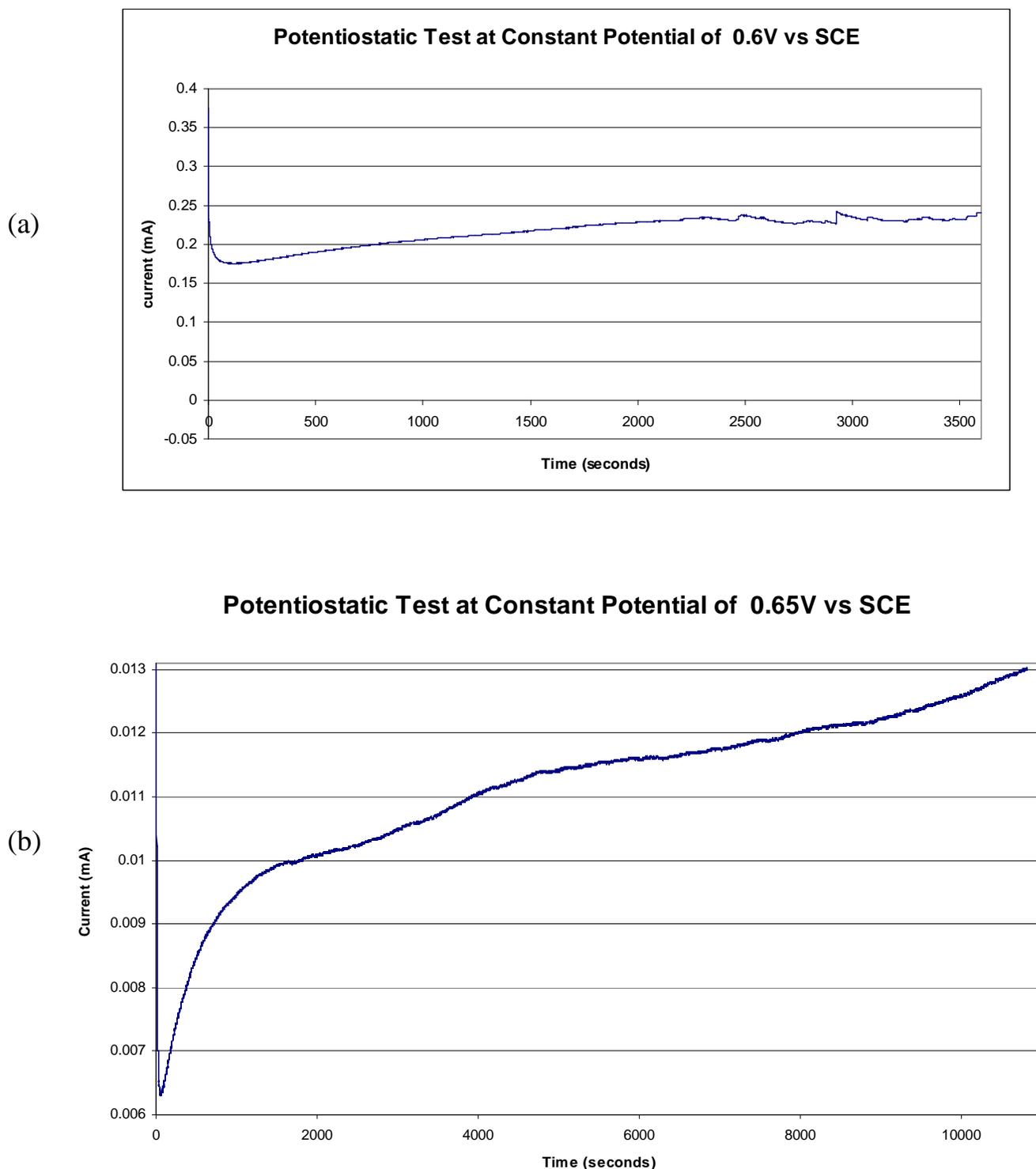
(a)

Potentiostatic Test at Constant Potential of 0.6V vs SCE

current (mA) — Time (seconds)

(b)

Potentiostatic Test at Constant Potential of 0.65V vs SCE

Current (mA) — Time (seconds)

Fig. (11). Extended Activity of graphite-nickel electrode (0.2M Ni ion ex.) in 0.5M MeOH and 0.5M NaOH, (**a**) at a constant potential of 0.6V*vs* SCE over 1 hour, (**b**) at a constant potential of 0.65V *vs* SCE over 3 hours.

Therefore it is confirmed from XPS spectra that there is a presence of sulphate ion in the carbon fibre matrix after the activation process despite thorough washing with distilled water. The S2p3 state of sulphur is due to presence of sulphuric acid in the carbon matrix and hence there is possibility of expansion of carbon fibre matrix during the activation. In that case the active functional groups are also created in the bulk of the expanded matrix where metal modification is possible through ion exchange. This explains the multiple layers of coverage discussed in section 3.1 for nickel.

XPS spectra were also recorded for the Ni modified carbon fibre electrodes (without vacuum drying step after ion
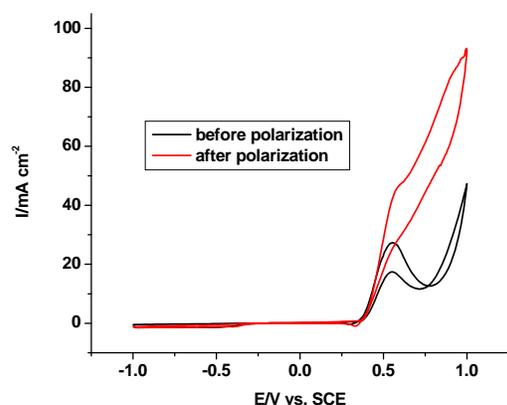
Fig. (12). Cyclic voltammogram obtained in 0.5 M MeOH in 0.5M NaOH for 0.1M Ni modified electrode before and after polarization.

exchange) and the results for wide angle measurements and individual measurements for carbon, oxygen, sulphur are similar to those obtained for carbon fibre without any modification while (d) represents the corresponding measurement for Ni.

In case of Ni spectrum, the peak at binding energy value 856.0 which corresponds to Ni(II) oxidation state and represent bond energy for Ni=O group [43].

Therefore from XPS studies, it is clear that the activation of carbon fibre occurs not only on the surface but also in the bulk of the fibre creating layer like structure with gaps created due to expansion of carbon matrix by H_2SO_4 molecule.

As seen from previous work carried out in our lab, copper displayed increased catalytic activity with increasing
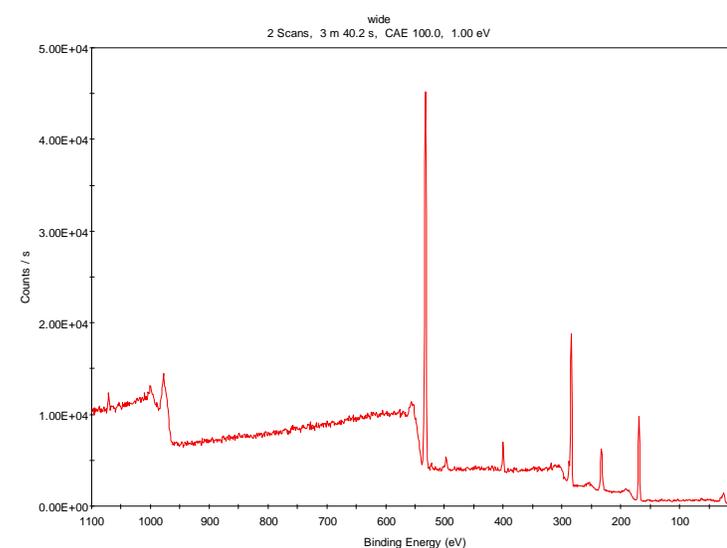
(a)
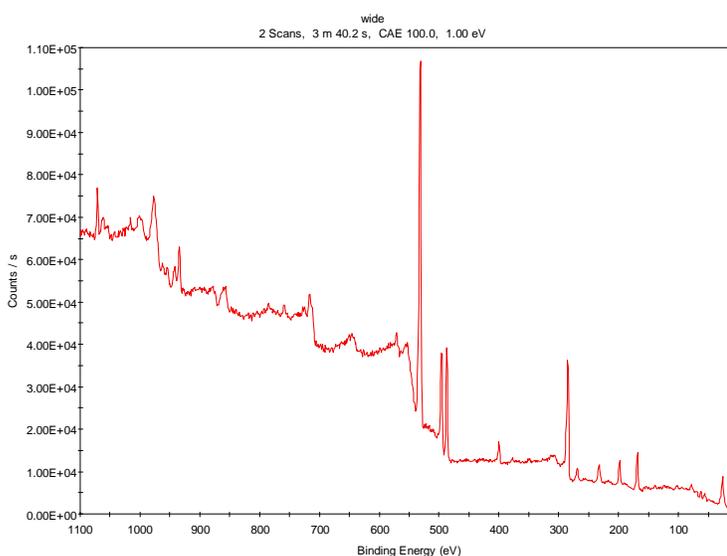
(b)

Fig. (13). Wide angle XPS spectrum for (**a**) activated carbon fibre electrode without any modification and (**b**) Ni modified carbon fibre electrode.

concentration of exchanging solution whereas in case of nickel, the best performance was observed for 0.1 M concentration compared to 0.2 and 0.5 M concentration solutions. This can be explained by differences during the activation step. During the activation of carbon fibre electrode, the sulphate ion from 97% H_2SO_4 causes expansion of the carbon matrix and at the same time corrodes some of the carbon sites creating gaps in the matrix through which metal ions can intercalate to be exchanged with H^+ ions from the bulk. The ionic size of the sulphate ion dictates the amount of metal that can be exchanged during the ion exchange step. The S=O bond length is 149 pm while the diameter of sulphate ion is approx. 160 pm. The ionic diameters of Cu^{+2} and Ni^{+2} are 140 pm and 160 pm respectively. Copper ions due to their smaller ionic size can intercalate easily in and out of the matrix and hence show better electrocatalytic activity compared to metal ions with diameter greater than that of sulphate ion. Therefore nickel and palladium show very small amount of catalyst

exchanged compared to smaller ions like copper on the surface.

3.5. SEM Analysis

Fig. (**15**) represents EDS results for nickel modified electrode which indicates the presence of nickel. SEM image for this electrode is represented in Fig. (**16a**) with the corresponding elemental mapping for nickel and sulphur shown in Fig. (**16b**).

4. CONCLUSIONS

Graphite fibre electrodes were fabricated by encasing a bundle of graphite fibres in resin and polishing the surface to expose their cross-section. These electrodes when modified by ion exchange with nickel behave similar to polycrystalline nickel electrodes and exhibit electrocatalytic activity towards the methanol oxidation reaction. The optimum working conditions for these electrodes were investigated and it was observed that the electrode modified
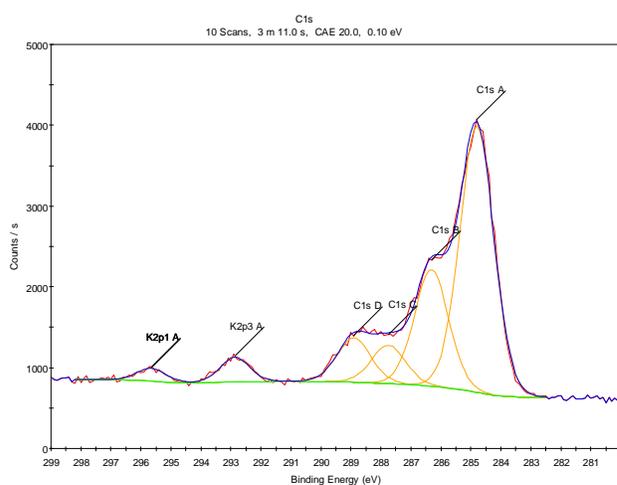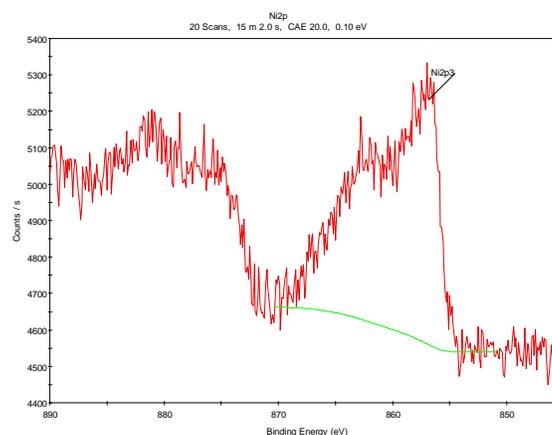
(a)
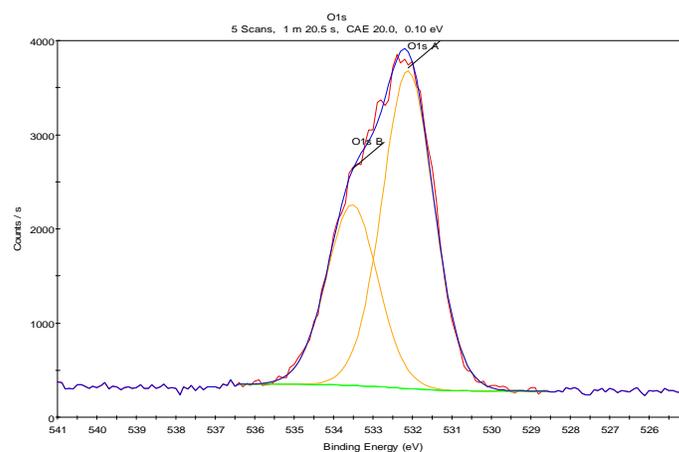
(b)
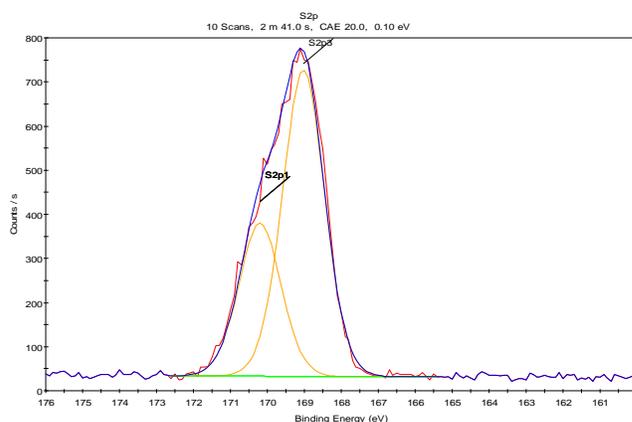
(c)

(d)

Fig. (14). XPS spectrum for carbon (**a**), oxygen (**b**), sulphur (**c**) and nickel (**d**) for Ni modified carbon fibre electrode. Only (**a**), (**b**) and (**c**) are present in case of activated carbon fibre electrode while (**d**) is absent.
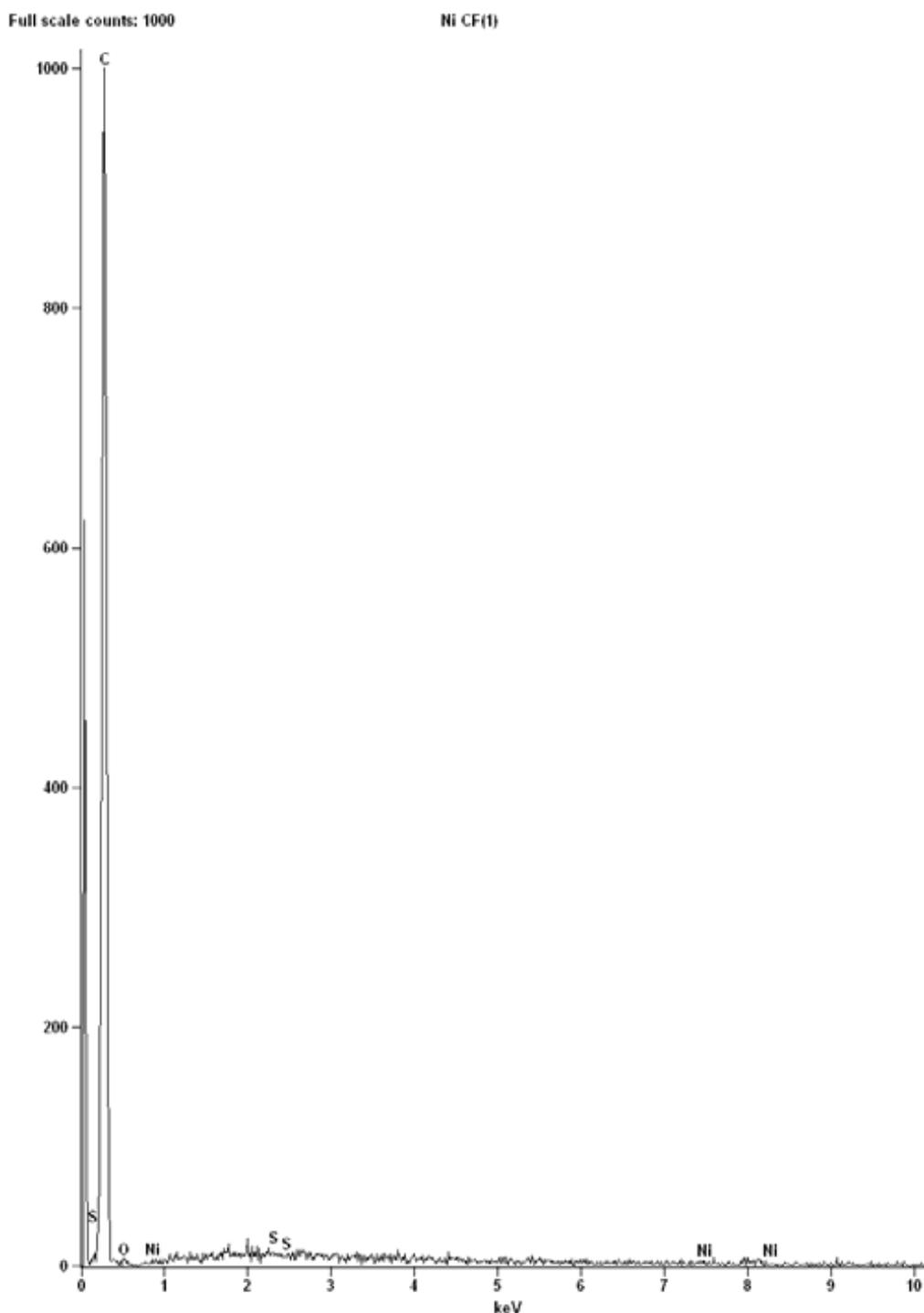
Fig. (15). EDS analysis for Ni modified electrode

by ion exchange in 0.1 M Ni solution provided the highest electrochemical activity with the highest methanol oxidation current observed at lower concentrations in the range of 0.1 M to 0.2 M methanol in 0.5 M NaOH solution. At higher methanol concentrations the anodic peak current at the 0.1 M Ni modified electrode decreased and this is believed to be due to poisoning of the Ni active sites by reaction products. Unlike electrodeposited nickel, the electrode prepared by this process, has nickel distributed in the carbon matrix instead of

as continuous layer that may eventually passivate the surface during extended oxidation. By allowing electrical connectivity with the carbon matrix, the Ni modified graphite fibre electrode retains the electrocatalytic activity and hence shows better performance than nickel foil or electrodeposited Ni.
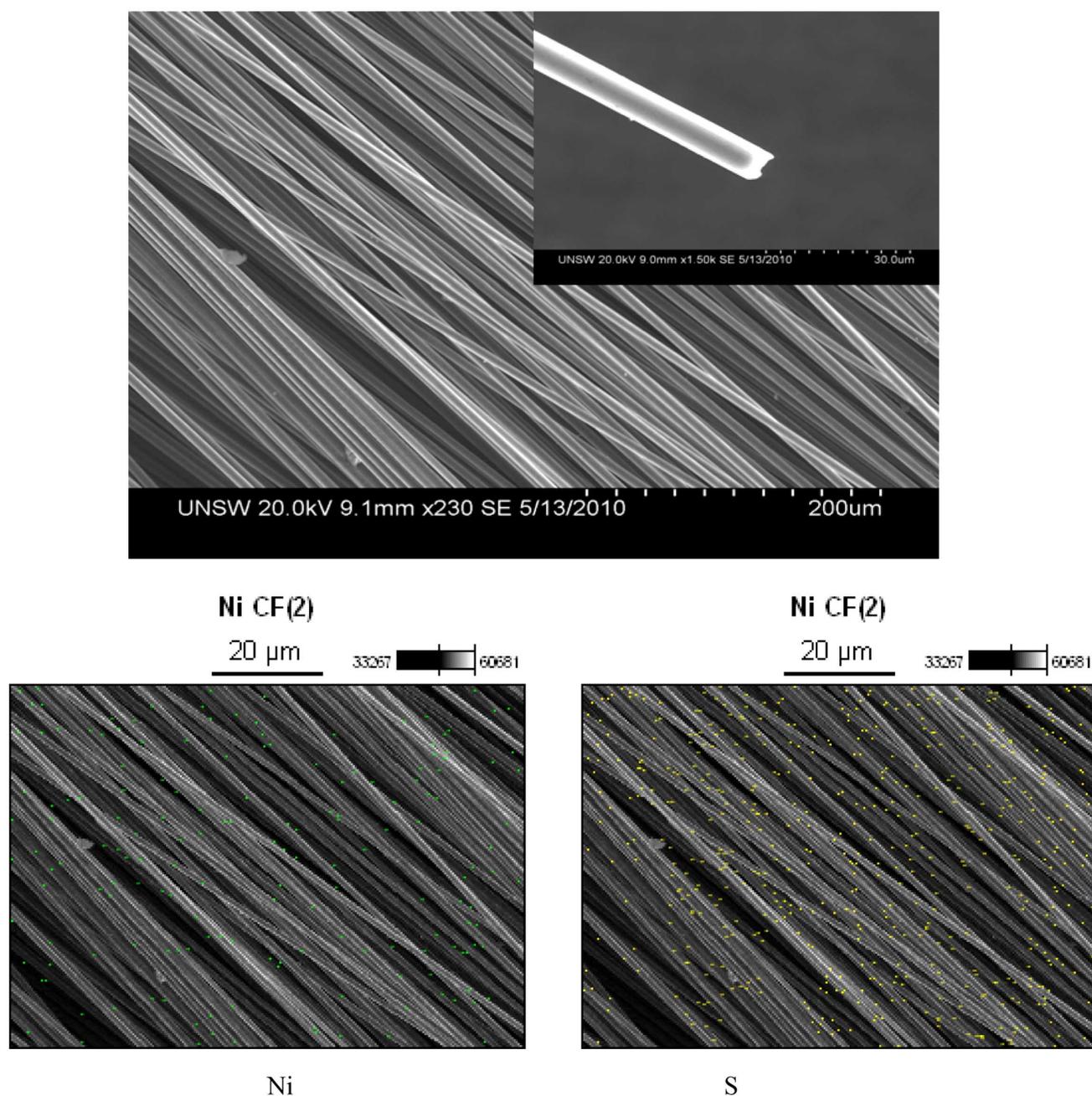
ACKNOWLEDGMENT

Fig. (16). SEM & elemental mapping of Ni and S for nickel modified electrode with inset showing a single fibre.

CONFLICT OF INTEREST

None declared.

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