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Highly improved electrocatalytic oxidation of methanol on poly(1,5-diaminonaphthalene)/ nickel nanoparticles film modified carbon nanofiber

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Abstract

A nanocomposite based on a carbon nanofiber/conducting polymers and nickel nanoparticles was developed using cyclic voltammetry. The dispersion, morphology, conductivity and structure of the modified electrode are characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and chronoamperometry (CA). It has been demonstrated that the nanocomposite improves efficiency towards electrocatalytic oxidation of methanol. The saturation limits concentration of methanol to obtain a higher current density is about 0.6 M with a current's stability for more than 2h.

1. Introduction

The combination of the conducting polymers and metallic nanoparticles has attracted considerable attention in the last years, due to their high potential application in different fields such as sensors, biosensors and catalysis [1-4]. In particular, the use of polymers/metals nanoparticles/carbon nanomaterials has attracted increasing interest in electrocalytic oxidation of methanol **[5-9].** Methanol oxidation is of great importance in fuel cell technology, namely in the direct methanol fuel cell (DMFC) aimed to power electric vehicles. However, direct electrooxidation is a very complex reaction because many intermediate species are involved. In order to overcome this problem, different supports have been used for methanol oxidation such as graphite, carbon blacks, glassy carbon, graphene, carbon nanotubes and carbon nanofibers. Al-Enizi et al have synthesized the nickel oxide at the doped nitrogen carbon nanofibers on glassy carbon electrode for methanol oxidation **[7]**. The electrocatalytic efficiency for the Pt-modified poly(pyrogallol)/graphene electrode toward methanol oxidation was investigated by Qiaofang et al **[10**]. Raoof et al have prepared poly(2-Methoxyaniline) on the multi-walled carbon nanotube, using platinum nanoparticles modified poly(2-Methoxyaniline)/carbon nanotube for the electrocatalytic oxidation of methanol and formaldehyde **[11]**. For the same purpose, nanocomposites based on graphene-supported Pd_1Pt_3 or platinum nanoparticles supported on the surface of poly(N-acetylaniline) functionalized graphene nanosheets have been used **[12-14]**.

Compared to other carbon materials, carbon nanofiber exhibits unique characteristics in terms of high surface area and electrical conductivity. Carbon nanofibers were considered an ideal material for various promising applications in direct methanol fuel cells (DMFCs), due to their extraordinary electronic, thermal, mechanical and chemical properties. Wang et al. have prepared Pt/carbon nanofiber nanocomposites by the reduction of hexachloroplatinic acid, using formic acid (HCOOH) in an aqueous solution containing electrospun carbon nanofibers for electrochemical capacitance application **[15]**. Moreover, Ojani et al have incorporated the nickel particles in poly(1,5-diaminonaphthalene) at the surface of carbon paste electrode for electrocatalytic oxidation of methanol [**16**].

At our best knowledge, there is no paper devoted to carbon nanofiber (CNF) combined with conducting polymers and metals nanoparticles for catalytic oxidation of methanol. In this work, The nanocomposite CNF/Poly(1,5-DAN) modified electrode was prepared by electropolymerization of 1,5-diaminonaphthalene on carbon nanofiber. The obtained CNF/Poly(1,5-DAN) electrode was combined with nanoparticles of nickel to fabricate the modified electrode (CNF/Poly(1,5-DAN)/NiNPs). Then, this nanocomposite was applied for electrocatalytic oxidation of methanol.

2. **Experimental**

2.1. *Materials*

Graphite (powder, <20µm, synthetic 100%), 1,5-diaminonaphthalene (1,5-DAN 97%), mineral oil heavy (CAS: 8042-47-5), Carbon Nanofiber (PR-25-XT-PS, powder), methanol (99,8%), were purchased from Sigma–Aldrich (USA). All other reagents were analytical reagent grade and used as received. All solutions were prepared with distilled water.

2.2. *Apparatus and Equipment*

Electrochemical experiments were carried out with an Autolab (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N potentiostat/galvanostat controlled by GPES 4.9 software. The spectroscopy experiments (EIS) was performed by FRA software version 4.9, the treatment of data was performed using Origin 6.0 software. The carbon paste electrode was used as working electrodes, saturated calomel electrode was used as the reference electrode, and platinum as the counter electrode.

2.3. *Preparation of modified electrodes*

2.3.1. *Preparation of carbon paste electrode*

The carbon paste electrode (CPE) was obtained by homogeneous mixing of graphite powder (1g) and mineral oil (300 µl) in a mortar and pester. The paste was then inserted into the electrode cavity (3mm) and electrical contact was made by means of a stainless steel wire.

2.3.2. *Preparation of carbon nanofiber modified carbon paste electrode*

The CNF solution was prepared by using 10 mg of carbon nanofiber dispersed in 2 mL of isopropanol then ultrasonicated for 20 min to obtain a black suspension (5 mg/mL). The suspension was sonicated for 5 min before each film preparation. Dispersion of CNF on carbon paste electrode was obtained after dispersing about 5µL of carbon nanofiber solution on the CPE surface **[17, 18].** After the evaporation of isopropanol in air, the resulting carbon nanofiber modified carbon paste electrode (CPE/CNF) was obtained.

2.3.4. *Polymerization of 1,5-diaminonaphthalene*

The electrode was immersed in the cell containing 5 mM of 1,5-diaminonaphthalene. The polymerization of 1,5-DAN was carried out using cyclic voltammetry (for 40 cycles) between −0.2 V and +1.0V at 50mVs−1 in 1M HCL solution to obtained modified electrode.

2.3.5. *Preparation of nickel nanoparticles*

The nickel nanoparticles were prepared by applying a potential of -0.3V for the 30s in a solution containing $NiCl_2$. So, the modified electrode was prepared by electropolymerization of 1,5-DAN on carbon nanofiber which was dispersed on the carbon paste electrode surface. Then the NiNPs was incorporated into polymer film to prepare the nanocomposite. The figure 1 summarizes all procedures used for fabrication of the modified electrode.

3. Results and discussion

3.1. *Electrochemical characterization of the polymer modified electrode*

3.1.1. *1,5-diaminonaphthalene modified electrodes*

In order to compare the electropolymerization of the polymer on the bare an modified electrode by Carbon nanofiber, the first step consists on electropolymerization of 1,5-diaminonaphthalene at the surface of carbon paste electrode. Both the anodic and cathodic peaks of the polymer increased in the subsequent polymerization scans. The anodic was observed at a potential of 0.51V with a current density about 3.3mA/cm^2

and 11 mA/cm^2 for 15th and 40th scan respectively as shown in figure 2. The same results were obtained by other authors by using glassy carbon electrode or carbone paste electrode [**16,19**]

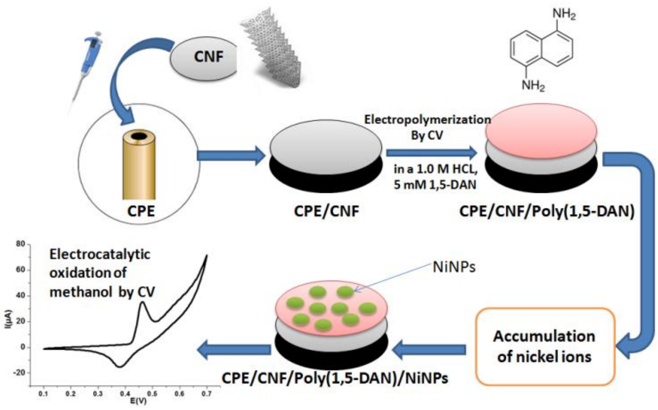

Figure 1: Schematic illustration of the whole steps of fabrication of modified electrode Schematic illustration of the whole steps of fabrication of modified electrode

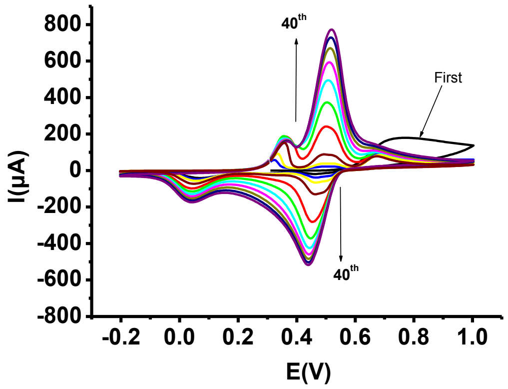

Figure 2: Cyclic voltammograms of electropolymerization of 1,5-DAN at the surface of CPE during 40 consecutive potential cycles between −0.2 and 1.0 V in a 1.0 mol/L HCL at 5 mmol/L 1,5-DAN, 50mV.s^{-1}

In the second step, the polymerization of 1,5-DAN was conducted on the CPE modified by CNF. Figure 3.A shows the cyclic voltammograms of the electropolymerization of 1,5-DAN. The value of anodic current recorded at 40th scan was 34.5 mA/cm^2 (About 3 fold higher than that obtained using only CPE (figure 3.B)) indicating that the film is more conducting. This result confirmed the good dispersion and distribution of nanofibres in the polymer.

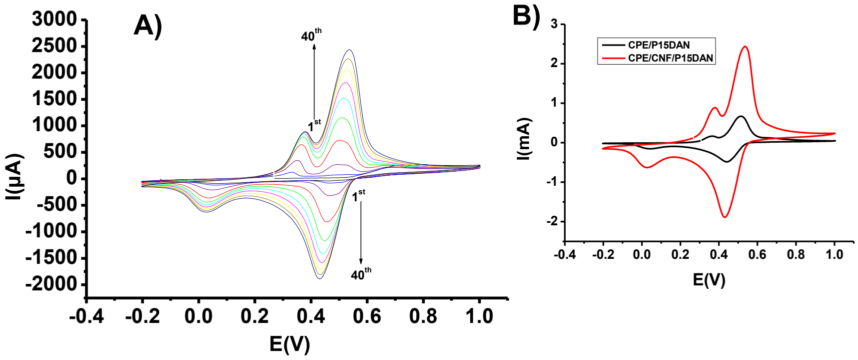

Figure 3: A) Cyclic voltammograms of electropolymerization of 1,5-DAN at the surface of CPE/CNF during 40 consecutive potential cycles between −0.2 and 1.0 V in a 1.0 mol/L HCL at 5 mmol/L 1,5-DAN, 50mV.s^{-1}, B) the compared voltammograms between CPE/Poly(1,5-DAN) and CPE/CNF/Poly(1,5-DAN) at 40th cycle.

The large current obtained during the electropolymerization of monomer in solution on CNF dispersed on CPE surface was attributed to the good electrical conductivity of the electrode. These materials have been recognized as ideal material support in terms of their large surface area, and excellent physical and chemical properties. Table 1 gives the compared study between CPE/Poly(1,5-DAN) and modified carbon paste electrode with CNF/Poly(1,5-DAN). It seems, the immobilization of carbon nanofiber accelerates the electrochemical response when using poly(1,5-DAN) composite in acidic solution. These results are in agreement with the reported by Barakat et al., when using multiwalled carbon nanotube (MWCNT) **[17]**. The same behavior was observed with poly(N-acetylaniline) functionalized graphene nanosheets **[13]**.

Table 1: Comparison of cyclic voltammograms parameters of CPE/CNF/Poly(1,5-DAN) at 40th scan of modified electrodes.

Modified electrode	$\mathbf{I_{pic}}$(µA)	I_{pic} of ME1/ME2
CPE/Poly(1,5-DAN)	774.97	**3.1**
CPE/CNF/Poly(1,5-DAN)	2416.33	

3.1.2. *CPE/CNF/Poly(1,5-DAN) behavior in acid and basic media*

Since, our work concern alkaline fuel cell, the response of the synthesized polymer film was studied in alkaline solution (0.1 mol/L NaOH). The choice of alkaline medium is due to its advantage in electrochemical modified electrodes based on Nickel particles, which have demonstrated a long-term stability in alkaline solutions and excellent capability to catalyze the oxidation of methanol [20, 21]. The redox behavior of the polymer is strongly dependent on the pH of the electrolyte solution **[16,22].** Then, the obtained CPE/CNF/Poly(1,5-DAN) was taken from the polymerization medium, rinsed with distilled water to remove any traces of 1,5-DAN monomer. The electrode was then immerged in solution of 1 mol/L HCl and 0.1 mol/L NaOH respectively. Figure 4 shows a cyclic voltammetry in acidic and basic medium, while the peaks are well defined in 1 mol/L HCl, a complete loss of activity is observed in 0.1 mol/L NaOH. The modified electrode by CNF and Poly(1,5-DAN) did not show any redox behavior, indicating that the film was isolating and act as a membrane. Similar results are obtained for the combination of nanomaterials with other polymers such as polyaniline and polypyrrole **[15,23,24].** However, the film was not degraded under these experimental conditions and its response was recovered when the electrode was immersed in an acidic supporting electrolyte solution.

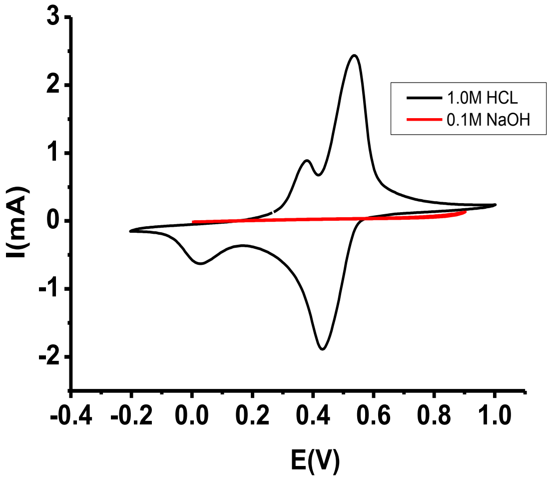

Figure 4: Electrochemical responses of CPE/CNF/Poly(1,5-DAN): in 1 mol/L HCL solution and in 0.1 mol/L NaOH solution, 50mV.s^{-1}

3.1.3. *Incorporation of Ni(II) ions into CNF/Poly(1,5-DAN) film*

Nickel nanoparticles were prepared generally by emerging electrode in a solution of 1 mol/L $NiCl_2$ at open circuit for 30min. Accumulation of nickel ions was carried out by complex formation between Ni(II) and amine sites in the polymer backbone **[16,19,25]**. The polarization behavior was examined in 0.1 mol/L NaOH. In our work, and with the aim of reducing the time of analysis, the nickel nanoparticles was prepared by applying a potential of -0.3V for the 30s in 0.6 mol/L of Ni(II) to obtained CPE/CNF/Poly(1,5-DAN)/NiNPs. Then the modified electrode was polarized in the alkaline medium by cyclic voltammetry in the potential range of 0.1V to 0.7V with a potential sweep rate of 50 mV.s^{-1} for ten scans. The obtained NiNPs is completely comparable with those prepared at the surface of other electrodes in previous studies **[16, 19, 25, 26].**

3.1.4. *Electrochemical impedance study*

The electrochemical impedance spectroscopy (EIS) technique is as powerful technique to characterize the electrochemical process that occur at the electrode/solution interface. Therefore, the electrochemical properties of bare and modified electrode were evaluated using EIS techniques. The impedance measurements were performed in the presence of 0.1 mol/L NaOH solution with an applied potential of 0.6 V and 5 mV as an amplitude at scanning frequency from 10 mHz to 50 kHz. Figure 5 shows the EIS diagrams of the CPE/Poly(1,5-DAN), CPE/CNF/Poly(1,5-DAN) and CPE/CNF/Poly(1,5-DAN)/NiNPs. The Nyquist plots for CPE and all modified electrodes in 0.1 mol/L NaOH (figure 4), The EIS of CNF/Poly(1,5-DAN) modified carbon paste electrode consisted of a semicircle section corresponding to charge transfer resistance (R_{CT}). Comparing with the all bare modified electrodes, the electron transfer resistance reduced distinctly. The EIS results have confirmed the conclusions deduced from the above cyclic voltammetry experiments.

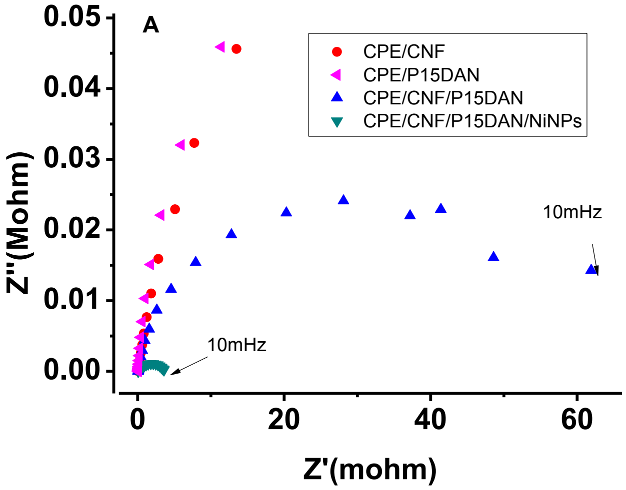

Figure 5: Electrochemical impedance spectra of the modified electrodes in 0.1 mol/L NaOH. The frequency range was 10 mHz - 50 kHz, at E=0.6V and the amplitude was 5 mV.

Table 2 shows significant different parameters in responses for electrodes by EIS of bare and modified electrodes respectively. The transfer resistance (Rct) of CNF/Poly(1,5-DAN)/NiNPs nanocomposite (3.7 mΩ) modified electrode was lower than that of CNF/Poly(1,5-DAN) (52.72 mΩ), but more lower than that of CNF (296.4 kΩ) and Poly(1,5-DAN) (295.8 kΩ) modified carbon paste electrode, which was attributed to improved conductivity of the nanocomposite.

Table 2: Electrochemical parameters extracted from the EIS data (figure 4) obtained from all modified electrodes in 0.1 mol/L NaOH.

L'électrode modifiée	R_c (ohm)	R_{ct} (Ω)	CPE (µF/cm²)
CPE	138.3	3402.7 K	11
CPE/Poly(1,5-DAN)	17.06	295.8 K	45
CPE/CNF	125.5	296.4 K	96.7
CPE/CNF/Poly(1,5-DAN)	65.60	0.053	252
CPE/CNF/Poly(1,5-DAN)/NiNPs	**62.75**	**0.004**	**1506**

3.1.5. *Characterization by scanning electron microscopy*

Scanning electron microscopy (SEM) technique is very useful to evaluate the dispersion of the carbon nanofibers. Also, the metallic nanoparticles can be observed by this technique. To investigate the morphology of the fabricated CPE/CNF/Poly(1,5-DAN)/NiNPs, scanning electron microscopy was carried out and the results are shown in figure 6. The images of CNF modified carbon paste electrode show a well dispersed CNF and a typically smooth surface in figure 5.A. by contrast, the surface of CNF in figure 5.B is rougher after the decoration of Poly(1,5-DAN), and the nanofibers diameter increases because of the thickness of the polymer shell. We can also observe in SEM images the presence of crystals of Ni nanoparticles due to the incorporation of Ni(II) ions into poly(1,5 diaminonaphthalene) film.

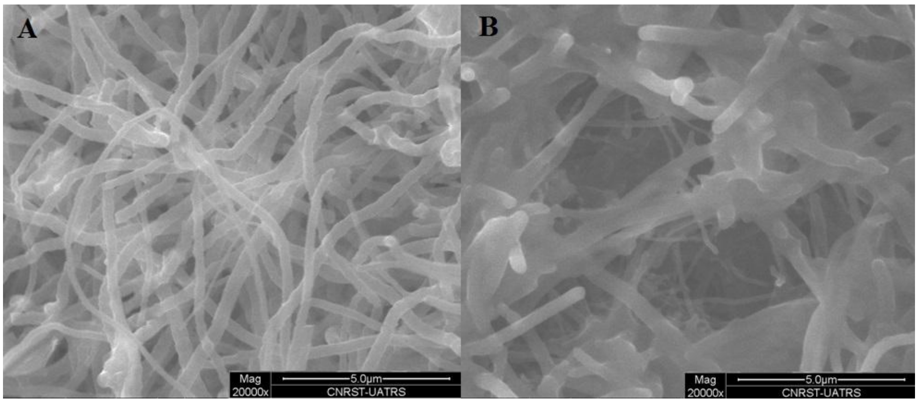

Figure 6: Scanning electron microscopy (SEM) of modified electrodes of A) CPE/CNF and B) CPE/CNF/P15DAN/NiNPS.

3.2. *Application of modified electrode for electrocatalytic oxidation of methanol*

The oxidation of methanol was studied at a CPE/CNF/Poly(1,5-DAN)/NiNPs electrode by cyclic voltammetric experiments, in presence and absence of 0.1 mol/L of methanol. The electrocatalytic activity was carried out in 0.1 mol/L NaOH using scan rate of 10 mV.s^{-1}. The typical results obtained for a potential scan from 0.1V to 0.7 V are shown in figure 7.

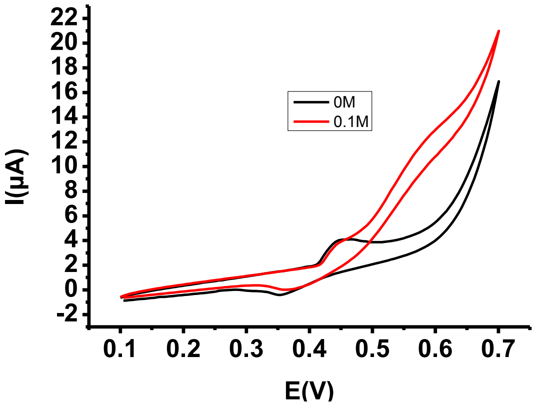

Figure 7: Electrochemical responses CPE/CNF/Poly(1,5-DAN)/NiNPs in 0.1 mol/L NaOH solution at 10 mV.s−1 to: 0.0 and 0.10 mol/L methanol.

For all bare electrodes, no electrochemical response was observed for 0.1 mol/L methanol. Upon using CPE/CNF/Poly(1,5-DAN)/NiNPs polarized modified electrode, an anodic peak around 0,6 V was detected which evidenced that the CPE/CNF/Poly(1,5-DAN)/NiNPs polarized modified electrode could considerably catalyze the electrooxidation of methanol. The electrooxidation process of methanol could be illustrated as follow: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

In the next part, different parameters of electrodeposition of nickel nanoparticles such as nickel concentration, potential and time of accumulation will be investigated.

3.2.1. *Effect of nickel concentration*

The effect of the nickel concentration on the response of methanol oxidation was investigated by using cyclic voltammetry. The deposition of Nickel nanoparticles on the polymer film was carried out by using a fixed potential of -0.3 V for 30 s and by varying the concentration of nickel between 0.6 and 2 mol/L. The response of modified electrode with nickel oxide was then studied in 0.1 mol/L methanol. The oxidation potential of methanol is around 0.66V and the peak oxidation increased when increasing the concentration of Nickel showing a maximum response at 1.5 mol/L. Therefore, this concentration was selected for the following experiments.

3.2.2. Accumulation potential

The effect of the accumulation potential of nickel was studied in the range of potential between -1.0 and -0.1V. The modified electrode was prepared at the different potential for accumulation time of the 30s by using CPE/CNF/P15DAN electrode. Table 3 shows the effect of the accumulation potential (E_{accu}) of nickel on the ox/red peak current of nickel and on the peak current of 0.1 mol/L methanol in the potential range of -1.0 to -0.1V. The stripping peak current of methanol was found to increase with the potential of the accumulation solution up to -0.9V. Above -0.9V it became practically constant due to the surface saturation. The maximum stripping peak current was obtained at accumulation potential of -0.9V. Thus, −0.9V was chosen as the accumulation potential in further studies.

Table 3: The results by CV for the ox/red peak current of nickel and 0.1M oxidation of methanol in 0.1 mol/L NaOH

	E_{accu} (V)	**-0.1**	**-0.3**	**-0.6**	**-0.8**	**-0.9**	**-1**
Nickel pics	**ΔE(V)**	0.21	0.13	0.099	0.107	0.094	0.185
Methanol oxydation	**I(µA)**	9.9	44.3	80	123	568	570

3.2.3. Optimization of accumulation time

The dependence of anodic peak currents with an accumulation time for 0.1 mol/L methanol oxidation by CV at the scan rate of 10 mV.s^{-1}, was also investigated in alkaline medium at accumulation potential of -0.9V in 1.5 mol/L nickel solution (Figure 8). The anodic peak current increased with the increasing the accumulation time from 10 to 45 s. After that, the anodic peak current decreased. Hence, for all subsequent measurements, pre-concentration time of 45 s was adopted.

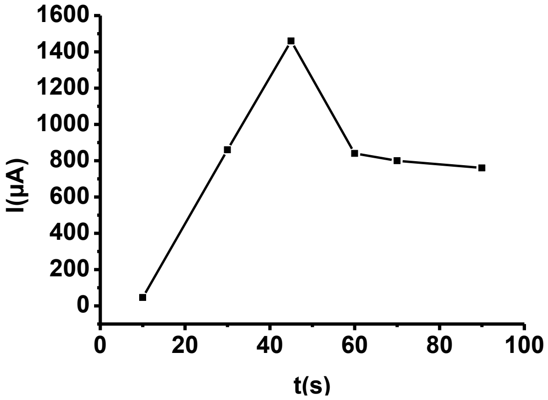

Figure 8: The plot of peak current versus accumulation potential value with a methanol concentration of 0.1 mol/L.

3.3. *Effect of methanol concentration*

After the optimization of all parameters, the modified electrode was used to study the effect of methanol concentration for fuel cells application. The oxidation of methanol in the range 0.05 to 1 mol/L was studied on this electrode. Figure 9 shows the behavior of this modified electrode in the presence of different methanol concentrations from 0.05 to 1 mol/L by CV at the scan rate of 50 mV.s^{-1}. The oxidation potential appears at 0.7

V with a peak current of 1.8 mA for a concentration of 0.05 mol/L. The methanol oxidation curves reveal that methanol oxidation peaks increase with increasing methanol concentration.

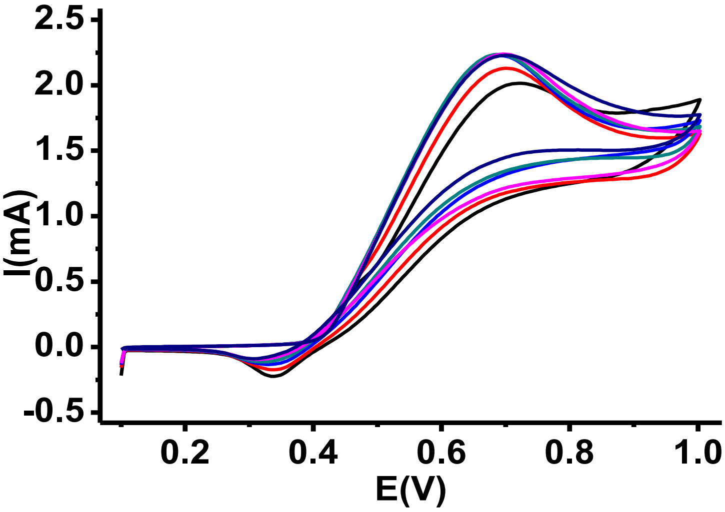

Figure 9: Current–potential curves of the CPE/CNF/Poly(1,5-DAN)/NiNPs for electrocatalytic oxidation of methanol at the scan rate of 50 mV.s^{-1} in 0.1 mol/L NaOH solution with different concentrations of methanol: 0.05 to 1 mol/L.

The current curves obtained at different methanol concentrations are much higher even with low concentration. This indicates clearly that our composite modified electrode CPE/CNF/Poly(1,5-DAN)/NiNPs acts as an effective catalyst for the oxidation of methanol in 0.1 mol/L NaOH solution. This is explained by the unique characteristics of the carbon nanofibers. Table 4 showed that with increasing the methanol concentration, the current peak height increase with methanol concentration up to 0.6 mol/L. While the methanol concentration exceeds this limit, the rate of the whole oxidation process seems to be limited by the fact that the catalytic process in origin and its rate depends on the reaction between methanol and Ni(III) species **[16,19].**

Table 4: The results extracted from the CV data (figure 9) obtained with CPE/CNF/Poly(1,5-DAN)/NiNPs for electrocatalytic oxidation of methanol at the scan rate of 50 mV.s^{-1} in 0.1 mol/L NaOH solution.

Methanol concentration (mol/L)	0.05	0.1	0.2	0.4	0.6	0.8	1
I (mA)	1.8	2	2.13	2.23	2.24	2.24	2.243

The comparison of CPE/CNF/P15DAN/NiNPs with other modified electrodes for oxidation of methanol was listed in table 5. It could be seen that this proposed catalysis was comparable and even better to the previous reports. These results indicated that CPE/CNF/P15DAN/NiNPs modified electrode is an appropriate platform for the electrocatalytic oxidation of methanol for fuel cells.

The operation stability and power of CPE/CNF/Poly(1,5-DAN)/NiNPs catalyst toward methanol oxidation reaction was evaluated under the same optimum conditions. The chronoamperometric curves were obtained in the solution of 0.1 mol/L NaOH containing 0.6 mol/L methanol for 120 minutes at 0.7 V. Figure 10.A shows a highest initial current density and retain 16.4 mA/cm², indicating that the catalyst has much better stability during operation. Figure 10.B gives results of the power test with modified electrode in 0.1 M NaOH solution containing 0.6 mol/L methanol. The maximum power density of the electrocatalyst was 12 mW/cm² at 0.7 V. However, the catalyst with the CNF/Poly(1,5-DAN)/NiNPs modified electrode had good performance as electrocatalyst. The power of catalysis was calculated by the following relationship:

$$P = \frac{E \times I}{S}$$

With: P (Power density), E (Potential), I (current) and S (electrode surface).

Table 5: Comparison of the electrodes modified with nanocomposite for oxidation of methanol.

Electrodes	**Modified**	**Saturation limits of methanol** (mol/L)	**Technique**	**References**
GCE	Pt/NCL-RGO	0.5	CV, CA	**[5]**
GCE	Pt-NG	1	CV, CA	**[6]**
GCE	NiO/N-CNFs	1.5	CV, CA	**[7]**
GCE	Pt/NCQDs-MWCNT	0.5	CV, EIS, CA	**[8]**
GCE	Pt/P2MA/MWCNT	1.36	CV, EIS	**[11]**
GCE	Pt/HNPHCS	1	CV, CA	**[27]**
GCE	Ni/N-CNFs	3	CV, CA, EIS	**[28]**
MWCNTs	Pt-RuO_2/DAAQ-MWCNTs	0.5	CV	**[29]**
Cu	PTCOxNMC	0.1	CV, EIS	**[30]**
CPE	Cu/P(2ADPA) Copper-poly(2-aminodiphenylamine)	0.5	CV, CA, EIS	**[31]**
GCE	Au@PtCu NPs	0.5	CV, LSV, CA, CP	**[32]**
CPE	CNF/P15DAN/NiNPs	0.6	CV, CA, EIS	**This work**

Glassy carbon electrode (GCE); carbon paste electrode (CPE); multi-walled carbon nanotubes (MWCNT) ; Nitrogen-doped carbon layer (NCL); Reduced graphene oxide (RGO); nitrogen-doped graphene (NG); Hierarchical nitrogen-doped porous hollow carbon spheres (HNPHCS), doped nitrogen carbon nanofibers (N-CNFs); N-doped carbon quantum dots (NCQDs), carbon nanfibres (CNF) ; 1,4-diaminoanthraquinone (DAAQ) ; poly(2-Methoxyaniline) (P2MA) ; poly(2-aminodiphenylamine) (P(2ADPA)); polytyramine-copper oxalate nanocomposite modifie copper (PTCOxNMC), Cyclic voltammograms (CV); Electrochemical impedance spectroscopy (EIS); Chronoamperometry (CA) ; linear sweep voltammogram (LSV), Chronopotentiometry (CP)

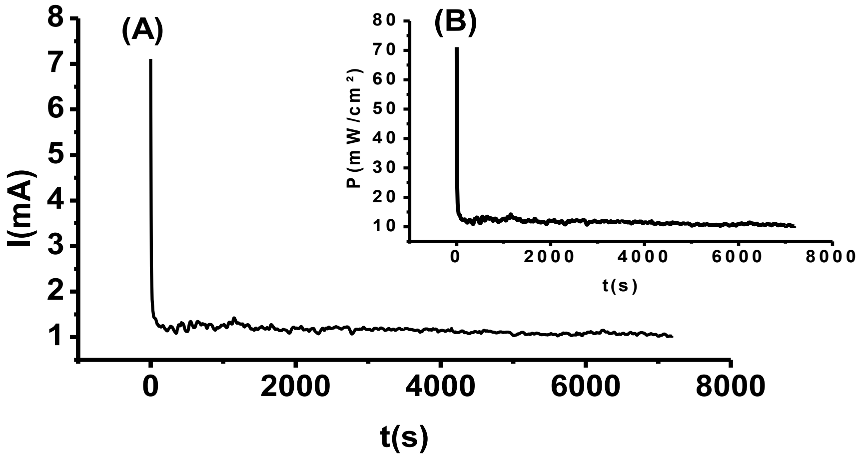

Figure 10: A) Chronoamperometric curves of CPE/CNF/Poly(1,5-DAN)/NiNPs modified electrode in 0.1 M NaOH at 0.6 mol/L methanol **B)** Power density of modified electrode with 0.6 mol/L of methanol.

Conclusion

A new modified electrode was successfully prepared by electropolymerization of 1,5-DAN on carbon nanofibers dispersed on carbon paste electrode surface, followed by the incorporation of nickel nanoparticles by electrodeposition method. The characterization of the electrode by voltammetric techniques, EIS and SEM shows that a well dispersed CNF with the presence of nickel nanoparticles on the electrode surface was observed and a low charge transfer resistance was obtained. The modified electrode was applied to methanol oxidation. The electrocatalytic activity study of the modified electrode on methanol show a catalyst saturation limits of methanol oxidation was up to 0,6 mol/L. The current density of the catalyst has much better stability during more than 2h of methanol electro-oxidation. Beyond this concentration, the oxidation process seems to be limited by the catalytic process between methanol and Ni nanoparticles.

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