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A cheap and an efficient electrode for electrocatalytic oxidation of methanol with nickel particles dispersed into sodium dodecyl sulfate modified carbon paste electrode

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Abstract

A sodium dodecyl sulfate modified carbon paste electrode (SDS/CPE) was developed in this work based on the surface modification method. The modified electrode was prepared by immersing SDS/CPE in a nickel nitrate solution. This electrode showed strong accumulation ability toward nickel ions. Then modified electrode was conditioned by potential recycling in a potential range of 0.2–0.8 V (vs. Ag/AgCl/KCl) by cyclic voltammetry in alkaline medium. The results showed that the Ni/SDS on the electrode behaves as an efficient catalyst for the electrooxidation of methanol in alkaline medium *via* Ni (III) species formed on the electrode. Moreover, the effects of various parameters such as SDS concentration, methanol concentration, NaOH concentration and nickel nitrate concentration on the electrooxidation of methanol have also been investigated.

Keywords: Electrocatalytic oxidation; methanol; nickel; modified electrode; SDS.

Introduction

Carbon paste electrodes (CPEs) are widely used in electrochemical investigations due to their unique characteristics such as renewability of the electrode surface, versatility of chemical modification and compatibility with various electron mediators [1, 2]. The CPEs are cheaper and are suitable for preparing the electrode material with desired composition and pre-determined properties [3, 4].

Surfactants, a kind of amphiphilic molecules with a hydrophilic head on the one side and a long hydrophobic tail on the other, have been widely used in electroanalytical chemistry [5-7] and electrochemistry [8-10] because of the enhancement effect and the ability to improve the property of the electrode/solution interface. The using of surfactants as modifiers to improve the electrode quality has been reported previously. Digua et al. [11, 12] mixed the amphiphile hexadecyl sulfonic acid into carbon paste to produce a surfactant modified carbon paste electrode. This electrode exhibited strong cation exchange property and the improved electron transfer rate between the substrates and the electrode. Zheng and Zhou [13] prepared surface modification of CPE by SDS. The

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modified electrode had a regular surface covered by a compact monolayer of SDS with a high density of negative charges directed outside. This electrode exhibited strong enrichment ability towards dopamine and discrimination against ascorbic acid. This is attributed to the cation preconcentration ability and anionic repellency of SDS film. Hu [14] studied electrochemical characterization of cetyltrimethyl ammonium bromide (CTAB) modified carbon paste electrode and its application in the immobilization of DNA. The results showed that the electrode had a regulated surface covered by a compact monolayer of CTAB with a high density of positive charges directed outside created a new approach for the preparation of DNA modified electrode.

On the other hand, nickel hydroxide was studied for decades and has attracted considerable attention due to its diverse applications, such as precursors for nickel catalysts and nickel oxides, active electrode materials for alcohols and some organic and biologically important compounds [15-19], its use in electrochromic devices [20], electrochemical capacitors [21] and alkaline batteries [22]. It has also moderately low cost, has low toxicity, and is an alternative to high-cost noble metals.

For the last decade, methanol has been considered to be a liquid fuel of relatively high activity in fuel cell systems. Considerable efforts have been directed towards the study of methanol electrooxidation in solutions of a high pH. The use of alkaline solutions in a fuel cell has many advantages such as increasing its efficiency, a wider selection of possible electrode materials and a better efficiency of oxygen cathode; besides, oxidation reactions of organic fuels exhibit almost no sensitivity to the surface structure [23, 24].

In our previous work, we used to modify carbon paste electrodes with poly (isonicotinic acid) (SDS) /Ni-Co (with different percentages) for electrocatalytic oxidation of glucose and methanol [25, 26]. Also, we prepared a sensor for the analytical determination of hydrogen peroxide by modifying carbon paste electrodes with nickel hexacyanoferrate in alkaline medium [27].

In the present work, we have attempted to design a simple, low cost and an efficient electrode for methanol oxidation by incorporating nickel at the surface of modified carbon paste electrode with SDS. The electrochemical response characteristics of the modified electrode were investigated in optimal conditions.

Experimental

Chemical reagents

SDS was purchased from Merck. Sodium hydroxide, nickel nitrate and methanol obtained in analytical grade from Merck and used without further purification. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was utilized as the pasting liquid for CPE. Graphite powder (particle diameter = 0.1 mm) from Merck was employed as the working electrode substrate.

Apparatus

Electrochemical experiments were performed with a computer controlled potentiostat/galvanostat µ-Auto lab type III modular electrochemical system (Eco Chemie BV, Netherlands), driven with a general purpose electrochemical system (GPES) software (Nova). Voltammetry was done in a three-electrode cell using the modified CPE (MCPE) as working electrode, an Ag/AgCl, KCl (3 M) from the Azar electrode (Urmia, Iran) as reference electrode and a platinum rod from the Azar electrode (Urmia, Iran) as counter-electrode. All experiments were carried out at ambient temperature. No action was taken to remove oxygen from solutions.

Preparation of working electrode

The working electrode was prepared as follows: A mixture (70:30% w/w) of graphite powder and paraffin was blended by hand to produce a homogenous carbon paste. The carbon paste was packed into the cave of a home-made carbon paste electrode (3 mm in diameter) and then smoothed on a weighing paper. Subsequently, 10 µL of 1 mM SDS was dipped onto the surface of the bare electrode. Two minutes later, the electrode was completely rinsed with water to remove unabsorbed modifier and air-dried. Incorporation of Ni (II) ions (as inexpensive metallic ions) on the surface of SDS/CPE by immersing in a well-stirred aqueous 0.75 M Ni $(NO_3)_2$ solution for accumulated time of 10 min has been done. After nickel ions incorporation, the electrode was rinsed with twice distilled water. At the beginning of the experiment, the Ni/SDS/CPE was immersed in 0.1 M NaOH solution and the potentials were cycled between 0.2 and 0.8 V vs. Ag/AgCl/KCl (3 M) at v = 50 mV s^{-1} until a reproducible cyclic voltammogram (CV) was attained.

Results and discussion

Based on some advantages of CPE such as wide potential window, low background current, easy fabrication and low price of electrode, we used a modified CPE. Figure 1 shows the electrochemical behavior of CPE and SDS/CPE in 0.1 M NaOH at v = 50 mV s^{-1}. It can be seen that anodic discharge of H_2O with concomitant production of O_2 is observed to occur for $E > 1.2$ V and $E > 0.8$ V at the surface of CPE and SDS/CPE, respectively. In the present case, significant influence upon the presence of SDS alters the overvoltage of the electrode, influences the rate of electron transfer and increases the observed background current. They confirm the surface of the electrode is changed and covered with SDS. Also, it is well established that surfactants can be adsorbed on solid surfaces to form surfactant films [13].

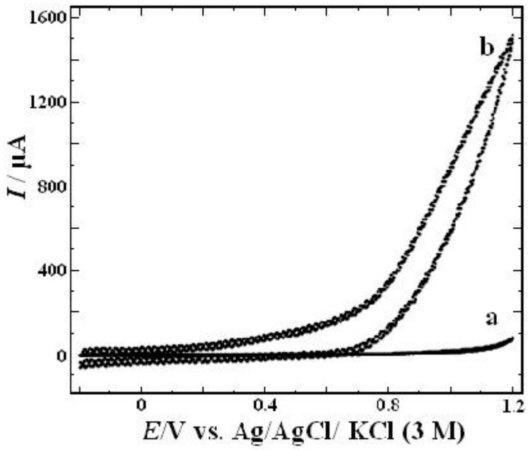


Figure 1. CVs of (a) CPE and (b) SDS/CPE in 0.1 M NaOH solution, v = 50 mV s^{-1}

Figure 2 shows the CVs of Ni/CPE and Ni/SDS/CPE in 0.1 M NaOH solution. As can be seen, a well-developed redox wave was observed on the Ni/CPE and Ni/SDS/CPE. This was related to the oxidation of $Ni(OH)_2$ to NiOOH and the reduction of NiOOH to $Ni(OH)_2$ [28-30]. In contrast to the poor response at bare CPE, the electrochemical signal of Ni (II) /Ni (III) is enhanced at SDS/CPE which is reflected by the magnification of peak currents that it may increase nickel ions at the surface of this electrode. This observation could confirm the presence of SDS films with the negative charges on the surface of modified electrode. Figure 3 represents the schematic description of the modified electrode. The SDS/CPE is covered with high density of negative charges oriented outside and nickel ions accumulated by electrostatic interaction similar to the structure expressed in Figure 3.

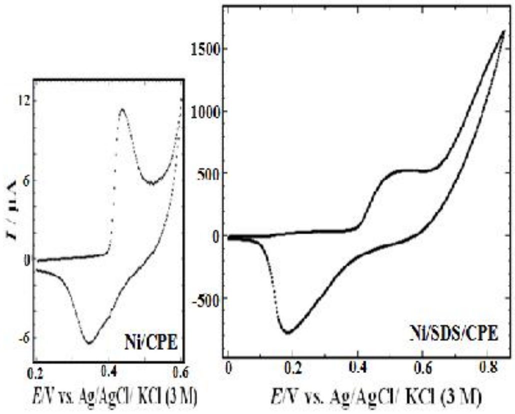


Figure 2. CVs of Ni/CPE and Ni/SDS/CPE in 0.1 M NaOH solution, v = 20 mV s^{-1}

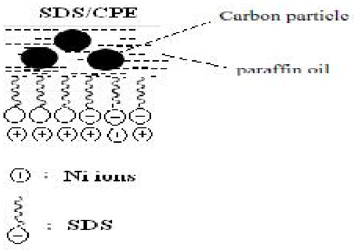


Figure 3. Schematic representation for the Ni/SDS/CPE

Electrochemical behavior of modified electrodes in the presence of methanol

In this work, the electrochemical behavior of methanol was studied at the surface of different electrodes by cyclic voltammetric experiments in 0.1 M NaOH. The results are shown in Figure 4. The addition of 0.1 M methanol to the alkaline solution causes no effect on the electrochemical response of the CPE and SDS/CPE. As can be seen, upon methanol addition (0.1 M), there is an increase in the anodic peak current and a decrease in the cathodic peak current for both of Ni/CPE and Ni/SDS/CPE. This behavior is typical of that expected for mediated oxidation as follows:

$$Ni(OH)_2 + OH^- \rightleftarrows NiOOH + H_2Oe^-$$

$$NiOOH + \text{methanol} \longrightarrow Ni(OH)_2 + \text{products}$$

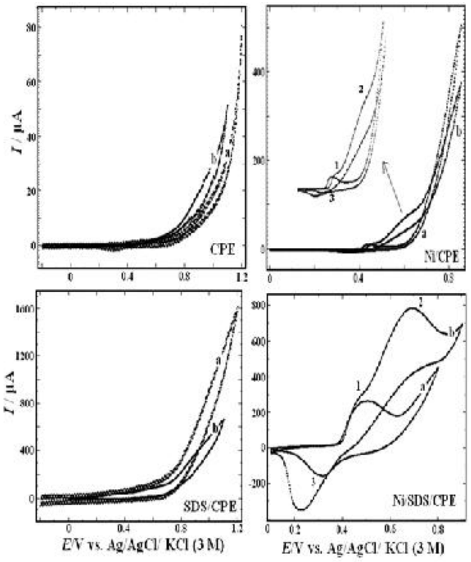


Figure 4. Voltammetric responses for methanol obtained at the surface of different electrodes, solutions: *a* 0.1 M NaOH and *b* 0.1 M methanol in 0.1 M NaOH, $v = 20$ mV s^{-1}

There are two anodic peak; 1 (assigned to the couple α-Ni $(OH)_2$/NiOOH) and 2 (assigned to β-Ni $(OH)_2$/ NiOOH). The corresponding electrode reaction involved in the anodic peak 2 might be:

$\beta\text{-Ni(OH)}_2\text{+OH}^- \rightleftarrows \text{NiOOH+H}_2\text{O + e}^-$

Therefore, the Ni $(OH)_2$ produced in reaction 2 might be β-Ni $(OH)_2$ [31]. β-Ni $(OH)_2$, is different from that of the α-Ni (OH). This is consistent with different redox potentials of α-Ni $(OH)_2$/ NiOOH and β-Ni $(OH)_2$/NiOOH [32, 33], i.e., α-Ni $(OH)_2$ is converted to NiOOH at a lower potential than β-Ni $(OH)_2$ to NiOOH.

The anodic currents for methanol electrooxidation under the same conditions at the surface of different electrodes are given in Figure 5. As can be seen, CPE and SDS/CPE have not shown any catalytic effect of methanol and also the amount of accumulated Ni; therefore, its catalytic effect for methanol oxidation is very low in the absence of SDS. At the surface of Ni/SDS/CPE, methanol oxidation current is improved. As can be seen in this electrode, the amount of accumulated Ni and catalytic current for methanol oxidation is significantly higher.

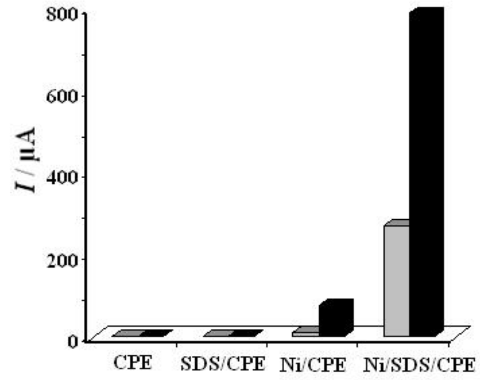
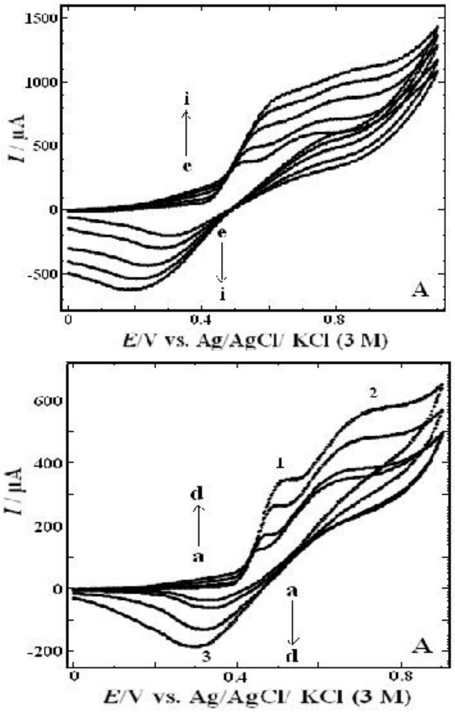
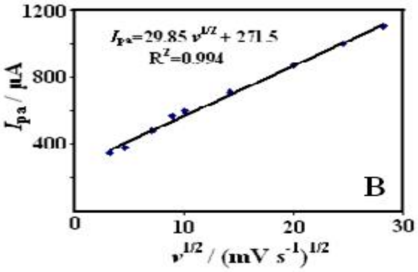


Figure 5. Comparison of anodic currents for various electrodes: in 0.1 M NaOH solution in the absence (gray bar), and presence (black bar) of 0.1 M methanol. Scan rate: 20 mV s^{-1}

CVs for methanol electro-oxidation on Ni/SDS/CPE at different scan rates are depicted in Figure 6a, from which the relationship between peak current versus the square root of the scan rate can be drawn (Figure 6b). The anodic peak currents increase with increasing scan rate ranging from 10 mV s^{-1} to 800 mV s^{-1} in the presence of 0.1 M methanol.





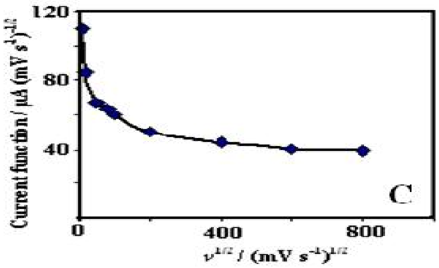


Figure 6 a. CVs of the Ni/SDS/CPE in the presence of 0.1 M methanol at different scan rates: *a* 10, *b* 20, *c* 50, *d* 80, *e* 100, *f* 200, *g* 400, *h* 600 and *i* 800 mV s^{-1}, respectively, b The dependency of I_p on $v^{1/2}$ and c variations of an anodic current function vs. *v*

The linear growth of the anodic current with the square root of the scan rate indicates that the electro-chemical behavior of Ni/SDS/CPE for methanol oxidation is a diffusion-controlled process [34–36]. The positive shift in the peak potential is also observed that may be due to the IR drop generated at high current density values. Figure 6c shows the variations of current function vs $v^{1/2}$. It shows that the oxidation of methanol follows a catalytic mechanism.

Optimization of electrode variables for efficient performance of Ni/SDS/CPE towards methanol oxidation

SDS concentration effect

The effect of SDS loading on the electrocatalytic activity of modified electrode towards methanol oxidation was evaluated. Figure 7a shows the relevant results. As can be seen, the oxidation current shows a maximum value for the SDS concentration of about 8 mM, while for SDS loading higher than 8 mM, a drastic attenuation of the oxidation current was observed. In accordance with this result, the optimum concentration of SDS to obtain a higher current density may be considered as about 8 mM.

Nickel concentration effect

The electrocatalytic oxidation peak currents increased gradually with increasing of concentration of nickel solution. The maximum value was getting at 0.75 M then leveled off, so 0.75 M was chosen as the optimum concentration of nickel, which indicated that the saturated accumulation on Ni/SDS/CPE had been achieved (Figure 7b).

Sodium hydroxide concentration effect

Figure 7c shows the CVs recorded on a Ni/SDS/CPE at various concentrations of sodium hydroxide containing 0.1 M methanol. It is observed that as the concentration of NaOH is increased from 0.1 to 1 M, the methanol oxidation currents increase. It is evident that up to 0.5 M, peak current increases and drops afterwards. Therefore, we used a concentration of 0.5 M sodium hydroxide to investigate the electrochemical behavior of Ni/SDS/CPE in the presence of methanol afterward.

Methanol concentration

In order to evaluate the capacity of Ni/SDS/CPE for electrooxidation of methanol, the effect of its concentration on the corresponding anodic peak currents was investigated by CV. The concentration of methanol in 0.5 M NaOH solution is changed from 0 to 0.6 M. According to the experimental data, the peak current was increased by methanol concentration, and reached a nearly constant value for concentrations higher than 0.5 M for methanol (Figure 8). We assume this effect caused by saturation of active sites on the surface of the electrode.

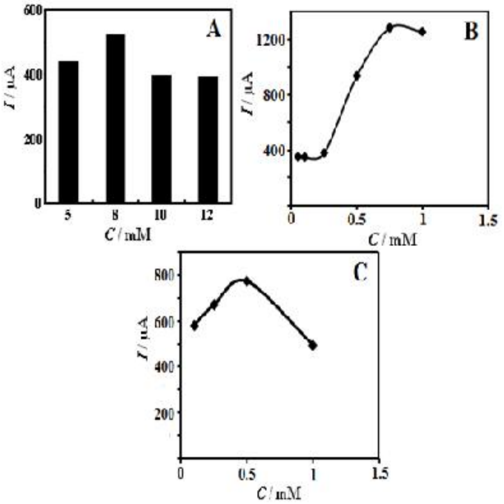


Figure 7. Effect of a SDS concentration, b nickel concentration and c sodium hydroxide concentration on oxidation currents of 0.1 M methanol at the surface of Ni/SDS/CPE, $v = 20$ mV s^{-1}

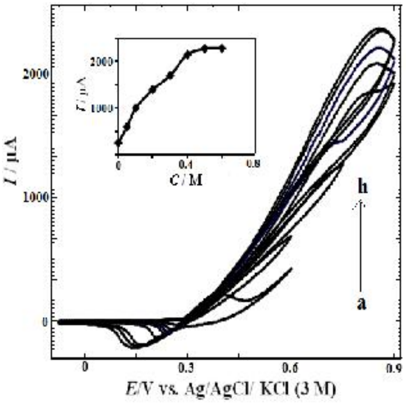


Figure 8. CVs of the Ni/SDS/CPE in 0.5 M NaOH solution with different concentrations of methanol *a* 0, *b* 0.05, *c* 0.1, *d* 0.2, *e* 0.3, *f* 0.4, *g* 0.5, and *h* 0.6 M, $v = 20$ mV s^{-1}, Inset: Plot of I_{pa} vs. methanol concentration

Stability of Ni/SDS/CPE

The stability of Ni/SDS/CPE is checked by measuring its responses for methanol oxidation after three weeks of storage under dry conditions. The electrodes retain about 85% of its initial responses. Such stabilities seem to be acceptable for most practical applications.

Table 1. Comparison of performances of some electrodes in electrocatalysis of methanol oxidation

Electrode	E_{pa}/V	J/mA cm^{-2}	[Methanol]	Reference
NiDMG/Ni[a]	0.65	15.9	0.1	[37]
NiPO-2/GCE[b]	0.66	1.7	1.0	[38]
Ni/AlLDH/NMCC[c]	0.78	31.8	1.2	[39]
Poly(Ni-curcumin)/GC	0.7	17.14	0.1	[40]
Ni/1,5-diaminonaphthalene/CPE	0.64	1.6	0.8	[41]
Ni/P(o aminophenol) SDS/CPE	0.65	16.7	0.37	[42]
$Ni_{80}Co_{20}$/PINA(SDS)/CPE	0.59	27.8	0.6	[26]
$Ni_{50}Co_{50}$/PINA(SDS)/CPE	0.55	3.33	0.3	[26]
Pt/GC	0.8	1.9	0.5	[43]
Pt-C/GC	0.9	7.5	0.5	[43]
Ni/SDS/CPE	0.55	32.57	0.5	Present work

[a]Nickel-dimethylglyoxime complex modified nickel electrode
[b]Mesoporous nickel phosphate modified glassy carbon electrode
[CNi]/Al layered double hydroxide nanoparticle modified carbon ceramic electrode

Conclusion

In this work, we have successfully constructed a novel electrode. The nickel ions incorporated at the surface of SDS/CPE to prepare Ni/SDS/CPE. It has been verified that Ni-SDS/CPE exhibits an excellent electrocatalytic activity in the presence of methanol. This modified electrode is very simple and cheap for electrooxidation of methanol. The cyclic voltammograms showed that Ni/SDS/CPE increased the oxidation current of methanol as compared to other electrodes and anodic peak currents increased by adding methanol. The values of current density and anodic peak potential of methanol at the surface of modified electrode are comparable with those obtained by using another modified electrodes (Table 1).

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