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Article

Preparation of a novel supported electrode comprising a nickel (II) hydroxide-modified carbon paste electrode (Ni(OH)₂-X/CPE) for the electrocatalytic oxidation of formaldehyde

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ABSTRACT

We prepared a novel nickel (II) hydroxide-modified carbon paste electrode (Ni(OH)₂-X/CPE) for the electrocatalytic oxidation of formaldehyde. The electrode was prepared by a simple method without the use of linking chemicals. The prepared Ni(OH)₂-X/CPE material was characterized by scanning electron microscopy and energy dispersive X-ray spectrometry. The electrochemical performance of the proposed electrode was investigated using cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometry. The results indicate that Ni(OH)₂-X/CPE exhibits good electrocatalytic activity with regards to formaldehyde oxidation owing to its nanoporous structure and the large surface area of zeolite X. The values of the electron transfer coefficient and the catalytic rate constant were 0.7 and $6.1 \times 10^4 \text{ cm}^3/(\text{mol}\cdot\text{s})$, respectively. Therefore, the proposed electrode, which showed remarkable electroactivity with regards to formaldehyde oxidation with long-term stability and good reproducibility, could be useful in fuel cells.

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1. Introduction

Fuel cells are electrochemical devices that have long attracted scientific and technological interest. They facilitate the direct conversion of energy derived from a chemical reaction into electricity [1–5]. Recently, much attention has been paid to the development of formaldehyde fuel cells, which are considered attractive alternatives to proton exchange membrane fuel cells [6]. Despite the toxicity of formaldehyde, investigation of its electrooxidation behavior provides useful insight into the electrochemical oxidation of small organic molecules such as methanol, because formaldehyde is an intermediate in methanol oxidation [7]. Moreover, it can be used in various processes such as electroless copper plating and textile manufacture [8]. Numerous reports have been published on the electrooxidation

of formaldehyde, but most have focused on its electrocatalytic oxidation on nanoparticles (NPs) of noble metals such as Pt and Pd, owing to their superior electrocatalytic properties [9,10]. However, noble metal NPs are expensive [11].

Transition metals such as Ni are attractive alternatives to noble metals in electrocatalytic processes because they are abundant, inexpensive and efficient catalysts. It has been reported that anodic oxidation of transition metals in an alkaline medium forms a metal hydroxide layer, which acts as an efficient catalyst for the oxidation of various substances. In alkaline media, Ni²⁺ species form Ni(OH)₂ followed by NiOOH. The NiOOH species can efficiently oxidize various substances such as glucose, methanol, ethanol, formaldehyde, and ammonia [12–19]. Numerous reports have been published on the electrooxidation of formaldehyde on Ni-containing electrodes such

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as Ni/P(1,5-DAN)/MCPE [20], Ni/P(NMA)/MCPE [21], Ni/POT(TX-100)/MCPE [22], and Ni/IL/CPE [23].

Metal NPs can be dispersed on various support materials to achieve the highest possible surface area and efficiency. It is well known that the use of supports for electrode materials offers some benefits such as stabilizing the NPs against aggregation, and increasing the electrode surface area and catalytic activity [24]. However, the performance of supported electrodes can be strongly influenced by the properties of the supports such as their morphology, nanostructure, and porosity [25]. Zeolites are potential electrode support materials that have been intensively investigated by Murray et al. [26]. They can be used in various fields such as electrocatalysis, amperometric determination, electrochemical synthesis, and the assembly of intrazeolite conductive polymers [27].

Zeolites are crystalline microporous aluminosilicate solids with primary building blocks of SiO_4 and AlO_4 tetrahedra that are strongly bonded with oxygen atoms at their corners. They form three-dimensional anionic networks with uniformly sized and distributed pores, cavities, and channels at the molecular level. The anionic networks of zeolites can be attributed to the presence of aluminum in the framework that is electrically balanced by extra framework cations that act as redox-active guests. Zeolites are molecular sieve crystals, and are capable of physically excluding or including molecules or ions according to their sizes relative to that of the zeolite pores. Zeolites are nanoporous materials with micrometer-scale particles; when their particle size is less than 100 nm (nanazeolite), marked improvements in their properties are observed, such as an increase in the accessible surface area and surface activity, and a decrease in diffusion path lengths. Zeolites are usually synthesized from various compositions with a wide range of pore sizes in the presence of cation-directing agents [28]. However, the cations are expensive and non-biodegradable materials, and their removal leads to irreversible aggregation to form larger crystals [29]. Moreover, the required precursors for the synthesis of zeolites are expensive and their use results in increased synthesis costs. Therefore, the use of low-cost materials containing an appropriate amount of silica as an alternative precursor can considerably reduce costs. The popularity of zeolites for use in supported electrodes can be attributed to their nanoporous nature, large surface area, high size selectivity, and tailored pore-size distribution [30].

Because zeolites are nonconductive in electrocatalytic processes, they should be modified with electroactive species. Various modified zeolites such as Ag-zeolites [31], Ti-zeolites [32], and Pt- and Pt-Ru-zeolites [33] have been reported in the literature. Yasumoto et al. [34] reported that the use of Pt and Pt alloys supported on an A-type zeolite instead of carbon in fuel cell electrodes decreased resistance and ohmic power losses. Moreover, Samant and Fernandes [33] have claimed that Pt/HY and Pt-Ru/HY are significantly better catalysts than the conventional Pt supported on carbon (i.e., Vulcan XC-72) for the electrooxidation of methanol in fuel cells.

Zeolite X contains large-diameter pores. It has a well-defined structure and appropriate ion exchange capability. It can be described as a framework of sodalite cages that are con-

nected through hexagonal prisms with pores formed by 12-membered rings; the unit cell is cubic with centers of inversion at the centers of the 12-membered rings [35].

In this work, we synthesized an NaX nanazeolite from stem sweep ash (SSA) without the use of a cation-directing agent, and modified it with $\text{Ni}(\text{OH})_2$. Stem sweep, an agricultural waste product, is one of the potential alternative precursors for the synthesis of zeolites because its ash contains a large amount of silica. The modified NaX nanazeolite was used as a support for the fabrication of a supported carbon paste electrode (CPE) for the electrooxidation of formaldehyde in an alkaline medium. CPE is a promising material for fuel cell anodes; it has some advantages over other solid electrodes including a simple and rapid preparation process, low residual current, and low cost [36]. To the best of our knowledge, no investigation has been made of the use of synthesized NaX nanazeolite from stem sweep as a support for the electrooxidation of formaldehyde.

2. Experimental

2.1. Reagents and apparatus

Formaldehyde (HCHO), graphite powder, paraffin, and sodium aluminate (NaAlO_2) were purchased from Fluka. Hydrochloric acid (HCl), sodium hydroxide (NaOH), and nickel chloride (NiCl_2) were all purchased from Merck. Nanosilica was extracted from SSA according to the method proposed in our previous work [31]. All other chemicals were of analytical grade and were used without further purification. All solutions were prepared with double-distilled water. The nanazeolite was synthesized according to the method proposed in our previous work [31]. In brief, 1.07 g of extracted nanosilica and 0.6 g of sodium aluminate were separately dissolved in NaOH solution (2.58 mol/L). The silicate solution was then added dropwise to the aluminate solution followed by transfer to a Teflon-lined stainless steel autoclave and heating at 60 °C for 72 h. The total volume of the autoclave was 0.1 L and the volume of the synthesized mixture transferred into the autoclave was approximately 0.03 L. The mixture was then filtered, washed, and dried at 80 °C overnight.

A DropSens bipotentiostat/galvanostat (μSTAT 400) was used for all the electrochemical measurements. A conventional three-electrode system was employed with $\text{Ni}(\text{OH})_2\text{-X/CPE}$ as the working electrode, a platinum wire as the auxiliary electrode, and $\text{Ag}|\text{AgCl}$ (KCl solution, 3 mol/L) as the reference electrode. All measurements were performed at room temperature. The morphology of the prepared electrode was examined using a MIRAS3 TESCAN FE-SEM scanning electron microscope (SEM) followed by determination of the elemental composition by energy dispersive X-ray spectrometry (EDS). The X-ray diffraction (XRD) patterns of the nanosilica and nanazeolite were recorded on an advanced Bruker D8 X-ray diffractometer using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of 4°–70°. To obtain the zeolite NP surface texture data, nitrogen adsorption and desorption studies were carried out at the temperature of liquid nitrogen (–196 °C) using a

Quantachrome instrument. The morphologies of the silica and zeolite NPs were examined by scanning electron microscopy (SEM; EM-3200, KYKY).

2.2. Working electrode preparation

A 3:7 (w/w) mixture of NaX nanozeolite (X) and graphite powder, and two drops of paraffin were blended by hand mixing with a mortar and pestle to prepare the X/CPE. The resulting paste was then packed into the bottom of a glass tube with an internal radius of 1.5 mm, and the electrical connection was implemented using a copper wire fitted into the other end of the glass tube. The modification of the prepared X/CPE was performed in two steps.

(1) The X/CPE was soaked in NiCl_2 solution (0.1 mol/L) for 3 min and the prepared Ni-X/CPE was rinsed with water to remove surface-adsorbed species.

(2) The Ni-X/CPE was then conditioned in NaOH solution (0.1 mol/L) by potential cycling between 0.0 and 1 V for about 10 cycles at a scan rate of 0.05 V/s for preparation of the $\text{Ni}(\text{OH})_2$ -X/CPE.

To determine the roles of the nanozeolite and $\text{Ni}(\text{OH})_2$ in the electrooxidation process, the $\text{Ni}(\text{OH})_2$ /CPE and X/CPE were fabricated in the same way without adding nanozeolite and immersing in NiCl_2 solution, respectively.

3. Results and discussion

3.1. Characterization of extracted nanosilica and synthesized NaX nanozeolite

The XRD patterns of the extracted nanosilica and SSA-synthesized nanozeolite are shown in Fig. 1. The inset of

Fig. 1. XRD pattern of synthesized nanoparticles. Inset: XRD pattern of extracted silica.

Fig. 1 exhibits only a broad diffraction peak at a 2θ of about 22° corresponding to the amorphous nanosilica without any detectable impurities. For the synthesized nanozeolite, main peaks at $2\theta = 6.12^\circ$, 10° , and 11.73° can be observed, which confirm the synthesis of pure phase NaX nanozeolite. All the peaks matched very well with the XRD powder patterns of the NaX zeolites (JCPDS 39-0218) [37]. The SEM images of the extracted NaX nanozeolite and nanosilica are shown in Fig. 2(a) and (b), respectively. As can be seen in Fig. 2(b), the extracted silica NPs appeared as spherical shapes and their average particle size was under 100 nm. The SEM image of the synthesized zeolite NPs clearly shows formation of spherical crystallites. The size distribution of the NPs can be estimated to be in the range of 40–80 nm. Therefore, the differences in the XRD patterns and surface morphologies of the silica and zeolite NPs confirm successful synthesis of the nanozeolite.

Figure 3 shows the pore size distribution of the zeolite NPs.

Fig. 2. SEM micrographs of (a) synthesized nanoparticles, (b) extracted nanosilica, and (c) $\text{Ni}(\text{OH})_2$ -X/CPE, and EDS spectra of (d) X/CPE and (e) $\text{Ni}(\text{OH})_2$ -X/CPE.

Fig. 3. Pore size distribution of synthesized nanozeolite.

The narrow peak at about 1.9 nm and a broad distribution of larger pores of 8–10 nm can be observed for the synthesized NPs. The surface texture data are summarized in Table 1.

3.2. Characterization of Ni(OH)₂-X/CPE electrode surface

EDS was used to investigate the elemental composition of the electrode surface. Typical EDS spectra of the X/CPE and Ni(OH)₂-X/CPE are shown in Fig. 2(d) and (e), respectively. The EDS spectrum of X/CPE provides evidence of the presence of C, O, Na, Al, and Si on the X/CPE surface. For Ni(OH)₂-X/CPE, in addition to the aforementioned elements, Ni was also present. As expected, after soaking the X/CPE in NiCl₂ solution, the Ni²⁺

Table 1

Surface texturing data of synthesized nanozeolite.

BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Micropore volume (cm ³ /g)	Specific surface area (m ² /g)	External surface area (m ² /g)
478	0.36	3	0.19	410	69

was replaced by Na⁺. These results prove that the ion exchange process was successfully performed and Ni species were present at the electrode surface. The SEM image of Ni(OH)₂-X/CPE in NaOH solution is shown in Fig. 2(c). The white spots in the image can be attributed to the formation of Ni(OH)₂ precipitates in the alkaline medium produced by the reaction between the Ni²⁺ NPs and the OH⁻ ions in the NaOH solution. The layers of irregular flakes are assigned to graphite powder.

3.3. Electrochemical behavior of Ni(OH)₂-X/CPE

To investigate the electrochemical behavior of the Ni(OH)₂-X/CPE electrode in alkaline solution, cyclic voltammograms (CVs) of the proposed electrode were recorded in NaOH solution (0.1 mol/L) at different scan rates, as shown in Fig. 4(a). Two peaks were observed in the CVs: one in the anodic sweep and the other in the cathodic sweep. A probable mechanism is that at the X/electrolyte interface, the ion exchange process occurs in accordance with the following extrazeolite electron-transfer mechanism expressed by Bessel and Rolison [38]:

Fig. 4. (a) CVs of Ni(OH)₂-X/CPE in NaOH solution (0.1 mol/L) at different scan rates. (1) 0.005; (2) 0.01; (3) 0.015; (4) 0.04; (5) 0.075; (6) 0.09; (7) 0.1; (8) 0.2; (9) 0.3 V/s. (b) Plot of peak potential vs. $\log v$ at the scan rates in the range 0.005–0.3 V/s for both anodic and cathodic peaks. (c) Plot of peak current vs. v at the scan rates in the range 0.005–0.075 V/s for both anodic and cathodic peaks. (d) Plot of peak current vs. $v^{1/2}$ at $v > 0.075$ V/s for both anodic and cathodic peaks.

where E^+ is an electrolyte cation and the descriptors z , s , and int stand for zeolite, solution, and zeolite-solution interface, respectively. This ion exchange process results in the transport of Ni^{2+} ions to the electrode surface where they react with OH^- to produce $Ni(OH)_2$. During the anodic reaction, $Ni(OH)_2$ at the surface of the electrode is oxidized to nickel oxy-hydroxide ($NiOOH$), and during the cathodic reaction, $NiOOH$ is reduced to $Ni(OH)_2$. Therefore, the observed redox peaks of $Ni(OH)_2$ -X/CPE in NaOH solution (0.1 mol/L) can be attributed to the Ni^{3+}/Ni^{2+} redox couple according to the following mechanism [39]:

At the scan rate of 0.01 V/s, a pair of well-defined redox peaks with $E_{1/2} = 0.5$ V and a peak-to-peak potential separation (ΔE_p) of 0.22 V vs. Ag|AgCl appeared. As can be seen in Fig. 4(a), the ΔE_p increased with increasing scan rate, which demonstrates that the interaction between the electrolyte ions and the modified film leads to limitation of the charge transfer kinetics. This behavior can be interpreted with the theory described by Laviron for the linear potential sweep voltammetric response in the case of surface-confined electroactive species at low concentrations [40].

The expressions for $\Delta E_p > \frac{0.2}{n} mV$, where n is the number of exchanged electrons, can be written as follows:

$$E_{pc} = E^0 + \left(\frac{RT}{\alpha nF} \right) \ln \left[\frac{\alpha}{m} \right] \quad (3)$$

$$E_{pa} = E^0 + \left(\frac{RT}{(1-\alpha)nF} \right) \ln \left[\frac{1-\alpha}{m} \right] \quad (4)$$

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha) - \log \left(\frac{RT}{nFv} \right) - \frac{\alpha(1-\alpha)nF\Delta E_p}{2.303RT} \quad (5)$$

where $m = \left(\frac{RT}{F} \right) \left(\frac{k_s}{nv} \right)$, and E_{pc} , E_{pa} , α , k_s , and v are the cathodic and anodic peak potentials, the electron-transfer coefficient, the apparent charge-transfer rate constant, and the scan rate, respectively. These expressions can be used to determine α by measuring the variation of the E_p with respect to the scan rate, and k_s for electron transfer between the electrode and the surface-deposited layer by measuring the E_p values. Also, Fig. 4(b)

shows the plot of E_p versus logarithm v at the scan rates in the range 0.005–0.3 V/s for both anodic and cathodic peaks. As can be seen, the E_p is proportional to $\log v$ at scan rates higher than 0.075 V/s, which was demonstrated by Laviron. Therefore, from Fig. 4(b) and the equations given above, the value of the anodic electron transfer coefficient (α) and the cathodic electron transfer coefficient (β) are estimated to be 0.76 and 0.24, respectively, which indicates the difference between the rate limiting steps for anodic and cathodic directions [41]. Furthermore, the mean value of k_s is estimated to be 0.014 s⁻¹. The linear dependence of anodic and cathodic peak currents over a scan rate range of 0.005–0.075 V/s is shown in Fig. 4(c). This linear dependence can probably be attributed to the electrochemical activity of immobilized redox species at the modified electrode surface.

Figure 4(d) shows the linear dependence of anodic and cathodic peak currents versus $v^{1/2}$ at $v > 0.075$ V/s. This dependence indicates the presence of a diffusion-controlled process in the total redox behavior of $Ni(OH)_2$ -X/CPE, which arises from the charge neutralization of the film during the oxidation-reduction process [42].

To clarify the electrochemical response of $Ni(OH)_2$ -X/CPE to formaldehyde oxidation, its CVs were recorded in NaOH solution (0.1 mol/L) in the absence and presence of 0.022 mol formaldehyde at a scan rate of 0.05 V/s. As shown in Fig. 5(a), in the presence of formaldehyde, the oxidation and reduction peaks of Ni^{3+}/Ni^{2+} were increased and decreased, respectively. The increase in the oxidation peak is due to coincidence of the formaldehyde oxidation current with the oxidation of Ni^{2+} to Ni^{3+} . Moreover, the decrease in the reduction peak can be attributed to the partial consumption of Ni^{3+} species for the oxidation of formaldehyde. As can be seen in Fig. 5(a)(2), the onset of the formaldehyde oxidation is at about 0.43 V and a large oxidation peak of formaldehyde is observed at 0.67 V. Therefore, according to these observations and those reported previously in the literature [43,44], the following mechanism can be proposed for the electrocatalytic oxidation of formaldehyde on the surface of $Ni(OH)_2$ -X/CPE:

Fig. 5. (a) CVs of $Ni(OH)_2$ -X/CPE in NaOH solution (0.1 mol/L) in the (1) absence and (2) presence of 0.022 mol/L formaldehyde at a scan rate of 0.05 V/s; (b) CVs of $Ni(OH)_2$ -X/CPE at concentrations of (1) 0.002, (2) 0.009, (3) 0.016, and (4) 0.027 mol/L in NaOH solution (0.1 mol/L).

This mechanism can be interpreted as follows: formaldehyde is converted to methylene glycol ($\text{CH}_2(\text{OH})_2$) in aqueous solution. Because the pK_a of methylene glycol is 12.8, it can exist in its ionized form ($\text{CH}_2(\text{OH})\text{O}^-$) in NaOH (0.1 mol/L). Hence, $\text{CH}_2(\text{OH})\text{O}^-$ is oxidized to $\text{CH}_2(\text{O})\text{O}^-$ by the Ni(III) species on the electrode surface. The voltammetric responses of $\text{Ni}(\text{OH})_2\text{-X/CPE}$ were recorded for formaldehyde at levels of 0.002, 0.009, 0.016, and 0.027 mol in NaOH solution (0.1 mol/L), as represented in Fig. 5(b). It can be seen that an increase of formaldehyde concentration leads to an increase in the oxidation current and a decrease in the reduction current. These results clearly demonstrate the electrocatalytic activity of this electrode during formaldehyde oxidation, and corroborate the mechanism proposed above. The electrocatalytic process is summarized in Scheme 1.

Cyclic voltammetric investigation of formaldehyde oxidation on different electrodes is a useful tool for monitoring the modification process. Fig. 6(a) displays the voltammetric responses of CPE, X/CPE, $\text{Ni}(\text{OH})_2\text{/CPE}$ and $\text{Ni}(\text{OH})_2\text{-X/CPE}$ to formaldehyde in NaOH solution (0.1 mol/L). As can be seen, neither oxidation nor reduction took place on the CPE or X/CPE. However, a well-defined oxidation peak was observed on the $\text{Ni}(\text{OH})_2\text{-X/CPE}$ while a small oxidation peak appeared on the $\text{Ni}(\text{OH})_2\text{/CPE}$ due to the oxidation of formaldehyde. It can be concluded that Ni(II) ions in the nanozeolite framework play a significant role and act as active sites during the conversion to NiOOH in the formaldehyde oxidation process. Furthermore, to determine the role of nanozeolites in the modification process, the electrochemical response studies of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as a well-known redox couple can be used to characterize the properties of the electrode surface. Therefore, the CVs of $\text{K}_4[\text{Fe}(\text{CN})_6]$ in the KCl solution (0.1 mol/L) were recorded for the CPE and X/CPE. As shown in Fig. 6(b), the peak current of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple for X/CPE was about twofold greater than that for CPE. The typical Nyquist plots for CPE and X/CPE are shown in Fig. 6(c). As can be seen, X/CPE had a smaller

Scheme 1. Representative schematic describing the mechanism of formaldehyde electrooxidation on the surface of $\text{Ni}(\text{OH})_2\text{-X/CPE}$.

semicircular diameter and electron transfer resistance (R_{et}) than CPE. This can be attributed to the presence of nanozeolite on the X/CPE. Since nanozeolites have a well-defined porous structure, and good thermal stability and ion-exchange ability, their presence on the electrode leads to improvements in the properties of the electrode surface. Therefore, the number of $\text{Ni}(\text{OH})_2$ ions at the $\text{Ni}(\text{OH})_2\text{-X/CPE}$ active site of formaldehyde oxidation was higher than at the $\text{Ni}(\text{OH})_2\text{/CPE}$ site owing to the presence of nanozeolite on the $\text{Ni}(\text{OH})_2\text{-X/CPE}$.

In comparison with other supported electrodes, the proposed electrode demonstrated good electrocatalytic activity with regards to formaldehyde oxidation (Table 2).

3.4. Effect of scan rate on electrocatalytic oxidation of formaldehyde

The effect of the scan rate on the electrocatalytic oxidation of formaldehyde using $\text{Ni}(\text{OH})_2\text{-X/CPE}$ was also investigated. As can be seen in Fig. 7(a), the anodic peak currents (I_{pa}) increased and the anodic peak potentials shifted to more positive potentials with increasing scan rates, which reveals a kinetic limitation in the oxidation reaction. The plot of anodic peak currents versus scan rate in the range 0.005–0.3 V/s is displayed in Fig. 7(b), and Fig. 7(c) shows the linear relationship between the

Fig. 6. CVs recorded on (a) CPE, X/CPE, $\text{Ni}(\text{OH})_2\text{/CPE}$, and $\text{Ni}(\text{OH})_2\text{-X/CPE}$ in the presence of formaldehyde in NaOH (0.1 mol/L) at a scan rate of 0.05 V/s; (b) CPE and X/CPE in $\text{K}_4[\text{Fe}(\text{CN})_6]$ and KCl solutions (0.1 mol/L); (c) Nyquist plot of the impedance measurements performed on the surface of CPE and X/CPE in $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1.0 mmol/L) containing 0.1 mol KCl.

Table 2

Comparison of supported electrodes used in the electrocatalytic oxidation of formaldehyde.

Modified electrode	Onset potential of formaldehyde oxidation vs. Ag AgCl	E_p (V vs. Ag AgCl)	Saturation limit of formaldehyde for current (mol)	Scan rate (V/s)	Ref.
Ni/POT(TX-100)/MCPE	0.44	0.7	0.048	0.02	[20]
Ni/P(NMA)/MCPE	0.44	0.74	0.07	0.02	[21]
Ni/P(1,5-DAN)/MCPE	0.47	0.8	0.17	0.01	[22]
Ni/IL/CPE	0.45	0.71	0.1	0.02	[23]
Ni/CTAB-PMT/MCP	0.4	0.7	0.054	0.02	[44]
Ni(OH) ₂ -X/CPE	0.43	0.67	0.04	0.05	This work

anodic peak current and the square root of the scan rate in the range 0.005–0.3 V/s. This dependence confirms that the electrocatalytic process is diffusion controlled. Moreover, slopes of 1.0 or 0.5 for the $\log I_{pa}$ versus $\log v$ plots can be theoretically attributed to the adsorption- or diffusion-controlled current, respectively [45]. As shown in Fig. 7(d), the plot of $\log I_{pa}$ versus $\log v$ was linear and had a slope of 0.48, which is approximately equal to the theoretically expected value of 0.5 for a diffusion-controlled current. Furthermore, the linear relationship between E_{pa} and $\log v$ can be attributed to the irreversible electrocatalytic oxidation of formaldehyde on the Ni(OH)₂-X/CPE, which is shown in Fig. 7(f). E_{pa} can be represented by the following equation [46]:

$$E_p = \left[\frac{2.303RT}{(1-\alpha)n_a F} \right] \log v + k \quad (8)$$

where α is the electron transfer coefficient, n_a is the number of electrons transferred, and k is the constant. The constants R , T , and F have their usual meanings. Using the slope of the corre-

sponding linear regression equation in Fig. 7(f), the value of α was calculated to be 0.7.

3.5. Effect of formaldehyde concentration

Figure 8(a) exhibits the voltammetric responses of Ni(OH)₂-X/CPE in the presence of various concentrations of formaldehyde at the scan rate of 0.05 V/s. It can be seen that addition of excessive concentrations of formaldehyde leads to an increase in the oxidation peak currents and potentials. In fact, increasing concentration leads to contamination of the electrode surface with oxidation products, which limits the charge transfer kinetics and increases overpotential. This can shift the peak potential to more positive potentials. Fig. 8(b) shows the linear relationship between oxidation currents and formaldehyde concentrations up to 0.04 mol/L. However, the oxidation current levels off at concentrations higher than 0.04 mol/L (inset of Fig. 8(b)) owing to saturation of the active sites

Fig. 7. (a) CVs of Ni(OH)₂-X/CPE oxidizing formaldehyde in NaOH solution (0.1 mol/L) at different scan rates. (1) 0.005; (2) 0.01; (3) 0.015; (4) 0.025; (5) 0.05; (6) 0.06; (7) 0.07; (8) 0.09; (9) 0.1; (10) 0.2; (11) 0.3 V/s; (b) Plot of anodic peak current vs. v ; (c) Plot of current vs. $v^{1/2}$; (d) Plot of $\log I_{pa}$ vs. $\log v$; and (e) Plot of E_{pa} vs. $\log v$.

Fig. 8. (a) CVs of Ni(OH)₂-X/CPE in the presence of various concentrations of formaldehyde up to 0.04 mol/L at the scan rate of 0.05 V/s; (b) Plot showing the dependency of oxidation peak current on formaldehyde concentration with standard deviations of slope (S_m) and intercept (S_b) of 0.2 and 4.37, respectively.

at the electrode surface.

3.6. Chronoamperometric study

Chronoamperometry was used for further investigation of formaldehyde oxidation on Ni(OH)₂-X/CPE. This technique was used to evaluate the catalytic rate constant of the formaldehyde oxidation [45]. The double-step chronoamperograms of Ni(OH)₂-X/CPE were recorded by setting the potential of the proposed electrode at 0.7 V (first step) and 0.35 V (second step) vs. Ag|AgCl in the absence and presence of formaldehyde. According to the Cottrell equation [39], the exponential I - t curves (Fig. 9) can be attributed to a diffusion-controlled process. Inset (a) of Fig. 9 shows a linear relationship between I and $t^{-1/2}$ in the absence of formaldehyde. The rate constant of the electrocatalytic formaldehyde oxidation at the active sites of Ni(OH)₂-X/CPE was also calculated using the obtained chronoamperograms and the following equation [45]:

$$\frac{I_c}{I_L} = \gamma^{1/2} \left[\pi^{1/2} \operatorname{erf}(\gamma^{1/2}) + \exp(-\gamma) \gamma^{1/2} \right] \quad (9)$$

where, I_L and I_c are the currents in the absence and presence of formaldehyde, respectively, and $\gamma = kC_0t$ is the argument of error function. C_0 , k , and t are the concentration of formaldehyde in the bulk solution, the catalytic rate constant, and the elapsed time, respectively. When γ exceeds 2, the error function is almost equal to 1 and the equation can be shortened to:

$$\frac{I_c}{I_L} = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (k C_0 t)^{1/2} \quad (10)$$

Therefore, from the slope of the I_c/I_L versus $t^{1/2}$ plot (inset (b) of Fig. 9) and from the above equation, the mean value of k was found to be approximately $6.1 \times 10^4 \text{ cm}^3/(\text{mol}\cdot\text{s})$. These results demonstrate good electrocatalytic oxidation of formaldehyde on the Ni(OH)₂-X/CPE surface.

3.7. Stability, repeatability, and reproducibility

As another attractive feature of the modified electrodes is their long-term stability, the stability of Ni(OH)₂-X/CPE was examined using chronoamperometry in NaOH (0.1 mol/L) and formaldehyde solution (0.005 mol/L) at a constant potential of

Fig. 9. (a) Chronoamperometric curves obtained with Ni(OH)₂-X/CPE in the absence (1) and presence (2) of formaldehyde (0.016 mol/L) in NaOH solution (0.1 mol/L). First and second potential steps were 0.7 and 0.35 V vs. Ag|AgCl (KCl 3M), respectively. (b) Dependence of current on $t^{-1/2}$, derived from the chronoamperogram data (a) in the main panel. (c) Dependence of I_c/I_L on $t^{1/2}$, derived from the chronoamperogram data.

Fig. 10. Chronoamperogram obtained using Ni(OH)₂-X/CPE in formaldehyde (0.005 mol/L) and NaOH solutions (0.1 mol/L) at a constant potential of 0.7 V vs. Ag|AgCl for 2000 s.

0.7 V vs. Ag|AgCl for 2000 s, as shown in Fig. 10. As can be seen, the current remained relatively stable after the given time. Moreover, the relative standard deviation (RSD) for 10 successive measurements using the same Ni(OH)₂-X/CPE electrode during formaldehyde oxidation was calculated to be approximately 3.2%. Also, three freshly prepared Ni(OH)₂-X/CPE electrodes were used for formaldehyde oxidation and an RSD of 6.3% was obtained. These results suggest that the proposed electrode has long-term stability and acceptable repeatability and reproducibility.

4. Conclusions

A novel Ni(OH)₂-X/CPE electrode was fabricated by a low-cost, facile, and simple method without using linking chemicals. The electrode exhibited very efficient electrocatalytic activity with regards to formaldehyde oxidation. The values of the electron transfer coefficient (α) and the catalytic rate constant were 0.7 and $6.1 \times 10^4 \text{ cm}^3/(\text{mol}\cdot\text{s})$, respectively. These results indicate that the proposed electrode can overcome the kinetic limitations presented by formaldehyde oxida-

tion because the presence of nanozeolite on the electrode leads to enlargement of the Ni(OH)₂ active sites on the electrode surface. Furthermore, the proposed electrode showed satisfactory stability and reproducibility, which make it attractive for application in formaldehyde fuel cells.

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Graphical Abstract

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Preparation of a novel supported electrode comprising a nickel (II) hydroxide-modified carbon paste electrode (Ni(OH)₂-X/CPE) for the electrocatalytic oxidation of formaldehyde

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A novel Ni(OH)₂-X/CPE was first prepared and used for the electrocatalytic oxidation of formaldehyde. This electrode exhibited good electrocatalytic activity with regards to formaldehyde oxidation owing to its nanoporous structure and the large surface area of zeolite X.

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用于电催化氧化甲醛的新型Ni(OH)₂-X/CPE负载电极的制备

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摘要: 采用一种简易的方法制备了新型Ni(OH)₂-X/CPE电极, 并将其用于电催化氧化甲醛反应. 采用扫描电镜和能量散射谱对所制Ni(OH)₂-X/CPE电极进行了表征, 并运用循环伏安法、电化学阻抗谱和计时电流法考察了该电极的电化学性能. 结果表明, 该Ni(OH)₂-X/CPE电极对甲醛氧化表现出高电催化活性, 这归功于X具有纳米孔结构和大的比表面积. 电子传递系数和催化反应速率常数分别为0.7和 $6.1 \times 10^4 \text{ cm}^3/(\text{mol} \cdot \text{s})$. 该电极对甲醛氧化具有高而稳定的电催化活性, 且制备重复性高, 有望应用于燃料电池中.

关键词: 燃料电池; 电催化剂; 多孔NaX纳米分子筛; 甲醛; 计时电流法

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