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Article

Encapsulation of a nickel Salen complex in nanozeolite LTA as a carbon paste electrode modifier for electrocatalytic oxidation of hydrazine

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ABSTRACT

A nickel salen complex was encapsulated in the supercages of nanozeolite NaA, LTA (linde type A) structure, using the flexible ligand method. The electrochemical behavior and electrocatalytic activity of a carbon paste electrode (CPE) modified with Ni(II)-Salen-A (Ni(II)-SalenA/CPE) for hydrazine oxidation in 0.1 mol/L NaOH solution were investigated by cyclic voltammetry, chronoamperometry, and chronocoulometry. First, organic-template-free synthesis of nanozeolite LTA was performed and the obtained material was characterized by various techniques. The average particle size of the LTA crystals was estimated to be 56.1 and 72 nm by X-ray diffraction and particle size analysis, respectively. The electron transfer coefficient was found to be 0.64 and the catalytic rate constant for oxidation of hydrazine at the redox sites of Ni(II)-SalenA/CPE was found to be $1.03 \times 10^5 \text{ cm}^3/(\text{mol}\cdot\text{s})$. Investigation of the electrocatalytic mechanism suggested that oxidation of hydrazine occurred through reaction with $\text{Ni}^{3+}(\text{Salen})\text{O}(\text{OH})$ and also direct electrooxidation. The anodic peak currents revealed a linear dependence on the square root of the scan rate, indicating a diffusion-controlled process, and the diffusion coefficient of hydrazine was found to be $1.18 \times 10^{-7} \text{ cm}^2/\text{s}$. The results indicated that Ni(II)-SalenA/CPE displays good electrocatalytic activity toward hydrazine oxidation owing to the porous structure of nanozeolite LTA and the Ni(II)-Salen complex. Finally, the general reaction mechanism for the electrooxidation of hydrazine on Ni(II)-SalenA/CPE in alkaline solution involves the transfer of four electrons, in which the first electron transfer reaction acts as the rate-limiting step followed by a three-electron process to generate environmentally friendly nitrogen and water as final products.

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1. Introduction

Hydrazine (N_2H_4) is a small and reactive molecule with powerful reducing capabilities that can undergo diverse reactions in numerous applications. In addition, it is widely used in various fields, including fuel cells, catalysts, and industrial, agricultural, military, pharmacological, and aerospace applications [1,2]. Further, N_2H_4 is an important chemical of environmental and pharmaceutical interest, and reported to be a neu-

rotoxin that produces carcinogenic and mutagenic effects [3]. Despite the wide application of N_2H_4 in various fields, it has been recognized to be unsafe for humans and therefore, sensitive and fast methods for the detection and determination of N_2H_4 in low concentrations in various media are becoming more significant [2,4]. N_2H_4 is an important high-performance fuel in aerospace propulsion applications, and also has promising potential applications in fuel cells. In fact, N_2H_4 may be an ideal fuel for direct fuel cell systems because the absence of

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carbon atoms in N_2H_4 leads to zero production of species that may poison the electrocatalyst and reduces the overall emission of CO_2 as a greenhouse gas [2]. The direct hydrazine fuel cell (DHFC) exhibits an electromotive force of 1.56 V vs. standard hydrogen electrode (SHE), which is higher than that for other fuel cells using hydrogen (1.24 V) or methanol (1.19 V) as a fuel [5]. In addition, the decomposition products of N_2H_4 , nitrogen and water, are ecologically friendly.

The electrooxidation of N_2H_4 is connected with the technological development of DHFCs. Various materials have been investigated for the electrooxidation of N_2H_4 , including Pt nanoparticles [1], Au-SH-SiO₂/MOF [2], Au electrodes [6], CuNPs-PANI-Nano-ZSM-5 [7], Pd modified multi-walled carbon nanotubes (MWCNTs) [8], nano-Ni-MWNTs-textile electrodes [9], nickel ternary alloys at graphite electrodes [10], nanoporous NiCuP amorphous alloys [11], NiO_x-Pt/C [12], CuO/NiO composite nanofibers [13], modified MWCNTs [14], and modified carbon paste electrodes (CPEs) [15–17].

Zeolites are crystalline aluminosilicate composites of Si, Al, and O with a structure of linked tetrahedra, each consisting of four O atoms surrounding a cation; the structure contains a network of channels and cages [18]. One of the most representative artificial aluminosilicate zeolites, zeolite NaA (LTA), was first synthesized by a hydrothermal crystallization method and has been utilized industrially in catalysts, adsorbents, ion exchangers, and zeolite membranes [19,20]. This material is a microporous crystalline aluminosilicate zeolite that has a channel opening size of 0.4 nm and a cubic structure of three-dimensional pores [19,21]. The preparation of zeolite-modified electrodes (ZMEs) is fast, easy, and cheap [22]. The next challenge is to prepare ZMEs on a carbon substrate for cyclic voltammetry (CV) because the prepared catalysts have to be loaded on a substrate to act as a stable solid electrode [22].

It is important to develop a novel electrode that has high sensitivity and stability for the electrooxidation of N_2H_4 . Some studies have been performed on the synthesis of metal Salen (*N,N'*-bis(salicylidene)ethylenediamine) complexes immobilized on zeolites as active catalysts for organic reactions [23,24]. Most studies have focused on the encapsulation of metal salen complexes in zeolitic hosts for the electrocatalytic oxidation of methanol in alkaline solution [25–28]. There are no literature reports on the application of CPEs modified with nickel(II) salen complexes encapsulated in nanozeolite LTA for the electrocatalytic oxidation of N_2H_4 . Hence, the synthesis of nanozeolite LTA without an organic template was performed and the obtained material was characterized by various techniques. Then, a CPE was modified with a nanozeolite LTA-encapsulated Ni(II)Salen complex (Ni(II)-SalenA/CPE) and its electrocatalytic performance for N_2H_4 oxidation was evaluated in alkaline solution. The reaction mechanism of N_2H_4 oxidation on the modified electrode was further considered using CV, chronoamperometry, and chronocoulometry.

2. Experimental

2.1. Reagents and materials

All chemicals were analytical grade and used without any further purification. NaOH, tetraethyl orthosilicate (TEOS), N_2H_4 , $\text{Ni}(\text{CH}_3\text{COO})_2$, ethylenediamine, salicylaldehyde, KCl, $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_4\text{Fe}(\text{CN})_6$ were purchased from Merck. Diethyl ether (99 wt%) and sodium aluminate were purchased from Daejung Company. Graphite powder and paraffin oil ($d = 0.88 \text{ g/cm}^3$) as the binding agent (both from Daejung Company) were used for preparing the pastes. Deionized water was used throughout the experiments.

2.2. Synthesis of organic-template-free nanozeolite NaA

The synthesis procedure for nanometer-sized zeolite NaA has been described elsewhere [29]. Aluminosilicate gel was prepared by mixing a freshly prepared aluminate solution with a silicate solution at a molar ratio of 1.0 Al_2O_3 :4.0 SiO_2 :5.5 Na_2O :190 H_2O . First, a 300 mL plastic bottle containing a freshly prepared sodium aluminate solution (17.46 g of NaOH, 180 mL of H_2O , and 10.52 g of NaAlO_2) and a stirring bar was immersed in an ice-water bath. The mixture was cooled for 1 h with stirring and then 47.13 mL of TEOS was added. The hydrolysis of TEOS was controlled at 0 °C in order to obtain a nanometer-sized aluminosilicate gel. Stirring was continued at 0 °C for 6 h and then at room temperature for another 24 h. Hydrothermal crystallization was performed at 60 °C for 48 h in a shaker with a rotation rate of 250 r/min. The powdered products were recovered by repeated high-speed centrifugation at 12000 r/min and washing with deionized water until pH < 8, followed by drying at room temperature for 24 h.

2.3. Preparation and characterization of the Ni(II)-SalenA

To prepare Ni(II)A using the ion-exchange method, 2 g of nanozeolite NaA was suspended in 50 mL of $\text{Ni}(\text{CH}_3\text{COO})_2$ aqueous solution (0.01 mol/L), and the mixture was stirred for 24 h at ambient temperature. Then, the solid fraction was filtered, washed three times with deionized water, and dried at 100 °C for 12 h to obtain Ni(II)A [30]. The metal complex was encapsulated in the structure of nanozeolite NaA by using the flexible ligand method [31]. First, Ni(II)A was mixed with excessive amounts of H_2Salen ($n_{\text{ligand}}/n_{\text{metal}} = 3$) in a crucible with a cover. The complexation was performed at 170 °C for 24 h under high vacuum conditions. The molten slurry was cooled to room temperature and extracted with acetone by Soxhlet extraction until the solvent was colorless in order to remove uncomplexed ligands and complex molecules adsorbed on the exterior surface. The extracted sample was then ion-exchanged with a NaCl aqueous solution (0.1 mol/L) to remove uncoordinated Ni^{2+} , followed by washing with deionized water until no chloride ions were detected with a AgNO_3 aqueous solution to obtain Ni(II)-SalenA.

2.4. Apparatus and characterization

Powder X-ray diffraction (XRD) patterns were recorded using a X-ray diffractometer (MPD 3000 Instrument) with Be-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 35.4 kV

and 28 mA. A Perkin Elmer Fourier transform infrared (FT-IR) spectrometer was utilized to record FT-IR spectra at room temperature. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) were performed to determine the crystallite size, morphology, and elemental composition of the synthesized sample using a Mira-3 XMU instrument. The particle size distribution of the synthesized sample was determined using a laser particle sizer (Analysette 22 NanoTec Plus, Fritsch GmbH) to investigate the solid material suspended in distilled water. Measurements of nitrogen adsorption/desorption at the temperature of liquid nitrogen were carried out using volumetric adsorption equipment (Micromeritics ASAP 2020). The specific surface area (S_{BET}) of the samples was estimated by the Brunauer-Emmett-Teller (BET) method [32]. The electrochemical experiments were performed using a potentiostat/galvanostat (SAMA500 electroanalyzer system) with a voltammetry cell in a three-electrode configuration. Ag|AgCl|KCl (3 mol/L) and platinum wire (both from Azar Electrode Company) were used as reference and auxiliary electrodes, respectively. A homemade bare CPE and modified CPEs (Salen/CPE, NaA/CPE, Ni(II)A/CPE, and Ni(II)-SalenA/CPE) were used as working electrodes in the electrochemical experiments.

2.5. Electrode preparation

Typically, to prepare Ni(II)-SalenA/CPE (15 wt%), 30 mg of Ni(II)-SalenA and 170 mg of graphite powder were thoroughly mixed with diethyl ether. After evaporation of the solvent, two drops of paraffin oil (35 wt%) were added and blended in a

mortar by hand mixing for 30 min until a uniformly wetted paste was obtained. The resulting paste was packed into the end of a glass tube (4.0 mm inner diameter and 10 cm length) with a copper wire as an electrical contact. A new surface was obtained by pushing excess paste out of the tube and polishing with weighing paper. For comparison, the bare CPE was prepared in the same way without adding Ni(II)-SalenA, and Salen/CPE, NaA/CPE, and Ni(II)A/CPE were fabricated by adding H₂Salen, NaA, and Ni(II)A, respectively. All currents (I) and charges (Q) were converted to current densities by dividing I or Q by the geometric area (0.12566 cm²).

3. Results and discussion

3.1. Characterization of nanozeolite NaA and Ni(II)-SalenA

XRD pattern of the synthesized nanozeolite is presented in Fig. 1(a). The crystallization products matched the characteristic peaks of zeolite NaA with good crystallinity [27,29]. The main peaks are observed at $2\theta = 7.2^\circ, 10.3^\circ, 12.6^\circ, 16.2^\circ, 21.8^\circ, 24.0^\circ, 26.2^\circ, 27.2^\circ, 30.0^\circ, 30.9^\circ, 31.0^\circ$, and 34.2° , which confirm the synthesis of pure-phase NaA nanozeolite [29,33]. The crystalline size of the synthesized sample was calculated using the Scherrer equation [34]:

$$d = \frac{0.89 \lambda}{\beta \cos \theta} \quad (1)$$

where d is the crystalline size, λ is the wavelength of the X-ray source used in XRD (0.15418 nm), β is the breadth of the observed diffraction line at its half-intensity maximum in radian, and θ is the angle of the main Bragg peak. From the diffraction

Fig. 1. Representative XRD pattern (a), particle size analysis (b), FESEM image (c), and EDS spectrum (d) of nanozeolite NaA.

peaks at $2\theta = 7.2^\circ$, 24° , 27° , 30° , and 34° the average particle size of the synthesized sample obtained using the Scherrer equation was 56.1 nm. It is apparent that the diffraction lines are significantly broadened, which may indicate a smaller crystallite size.

Fig. 1(b) displays a particle size analysis (PSA) graph for nanozeolite NaA according to the Mie theory. The average particle sizes of nanozeolite NaA are between 67 and 78 nm and the mean particle size is about 72 nm, corresponding to a cumulative volume frequency of 78%. Fig. 1(c) shows a FESEM image of the synthesized nanoparticles, which indicates that semispherical nanozeolite NaA particles were formed with an average particle size of less than 100 nm. These results confirmed that the size distribution obtained by PSA is in agreement with the results from XRD analysis and FESEM. In addition, Fig. 1(d) presents an EDS spectrum of the prepared nanozeolite, which confirms the presence of O, Na, Al, and Si in the synthesized sample.

Fig. 2 shows FT-IR spectra of nanozeolite Ni(II)A and Ni(II)SalenA in the wavenumber range of 450–2800 cm^{-1} . A strong wide vibration peak was observed at 830–1300 cm^{-1} (centered at 990 cm^{-1}) for nanozeolite Ni(II)A, which can reasonably be assigned to T–O (T = Si or Al) stretching modes and may overlap with Al–O–Si stretching vibrations [35]. The bands located at 463, 551, and 671 cm^{-1} are ascribed to Si–O–Al bending vibrations, vibrations of external linkages of double six-member rings, and symmetric stretching of internal tetrahedra, respectively [35,36]. The band at about 1660 cm^{-1} is attributed to the bending vibration of water molecules adsorbed on hydroxyl groups [20]. Bands in the range of 1200–1600 cm^{-1} , ascribed to aromatic ring and C=N vibrations of the salen ligand, are clearly observed in the IR spectrum of the Ni(II) SalenA sample [37]. However, these bands of the encapsulated complex were very weak owing to the low concentration in the zeolite cages. In contrast, these bands are absent in the FT-IR spectrum of Ni(II)A. The ligand vibration bands in the other regions are obscured by the presence of zeolitic vibration bands [27]. This observation provides effective evidence for the presence of nickel complexes inside the cavities of nanozeolite NaA in the Ni(II)SalenA sample.

Fig. 2. Representative FT-IR spectra of nanozeolite Ni(II)A and Ni(II)SalenA samples.

Fig. 3 illustrates an FESEM image, EDS spectrum, and elemental mapping for the prepared Ni(II)-SalenA composite. The EDS spectrum confirms the presence of C, O, Na, Al, Si, and Ni in Ni(II)-SalenA, with Ni belonging to SalenA. In addition, the elemental mapping analysis revealed homogeneous distributions of all these elements in the composite material, confirming the uniform distribution of Ni(II)-Salen in the porous NaA nanozeolite framework.

Fig. 4(a) illustrates the nitrogen adsorption-desorption isotherms of NaA, Ni(II)A, and Ni(II)-SalenA at the temperature of liquid nitrogen. The isotherm of NaA nanozeolite was of type II according to Brunauer classification [38]. In addition, the hysteresis loops (type IV isotherm according to IUPAC classification) confirmed the existence of large porosities in nanozeolite NaA, Ni(II)A, and Ni(II)-SalenA [39]. The uptake of nitrogen increased steeply above a relative pressure of about 0.8. Type IV isotherms are observed for many industrial adsorbents [36,39]. Fig. 4(b) shows pore size distribution curves for NaA, Ni(II)A, and Ni(II)-SalenA, which were evaluated from the adsorption branches of the isotherms. This figure shows that the pore diameters do not change with the addition of Ni(II) and Ni(II)-Salen, as all the curves are centered at about 3 nm [40,41]. Table 1 lists the surface areas and pore volumes of NaA, Ni(II)A, and Ni(II)-SalenA calculated by the *t*-plot method. As expected, encapsulation of the Ni(II)-Salen complex in nanozeolite NaA leads to an apparent reduction in the surface area and pore volume of the nanozeolite host. The surface area of NaA (362.4 m^2/g) was significantly reduced to 261.2 and 150.3 m^2/g for Ni(II)A and Ni(II)-SalenA, respectively. A similar trend was also observed for the total pore volume, which decreased from 0.26 cm^3/g for NaA to 0.18 and 0.14 cm^3/g for Ni(II)A and Ni(II)-SalenA, respectively. This drastic reduction in the pore volume might originate from the presence of Ni(II)-Salen in the pores of NaA [38,42]. It can be deduced that

Fig. 3. FESEM-EDS analysis and elemental mapping of Ni(II)-SalenA.

Fig. 4. (a) Nitrogen adsorption-desorption isotherms of nanozeolite NaA, Ni(II)A, and Ni(II)-SalenA at the temperature of liquid nitrogen. (b) Pore size distributions obtained from the adsorption branch of the corresponding isotherm according to the BJH method.

the Ni(II)-Salen complex is present in the cavities of NaA rather than on the external surface [25]. As can be seen in Table 1, the micropore volume is bigger than the mesopore volume and the micropore surface area is greater than the external surface area for all samples. Therefore, the porosities of synthesized nanozeolite NaA, Ni(II)A, and Ni(II)-SalenA mostly consist of micropores.

3.2. Electrochemical investigation of fabricated electrodes

CV was used to investigate the electrochemical properties of the bare CPE and Ni(II)-SalenA/CPE in 5 mmol/L $K_4Fe(CN)_6$ and 5 mmol/L $K_3Fe(CN)_6$ solution containing 0.1 mol/L KCl (Fig. S1). The experimental results showed reproducible anodic and cathodic peaks ascribed to the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple at a scan rate of 20 mV/s on the surface of CPE and Ni(II)-SalenA/CPE. As can be seen in Fig. S1, the anodic and cathodic peak currents for Ni(II)-SalenA/CPE are higher than those for bare CPE. Peak-to-peak separations (ΔE_p) of 210 and 100 mV were observed for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple on the surface of CPE and Ni(II)-SalenA/CPE, respectively, indicating that these systems are quasi-reversible [43]. The value of ΔE_p for Ni(II)-SalenA/CPE was much closer to the expected value (59 mV) for a reversible one-electron process. This finding indicated that the electron-transfer kinetics of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ were facilitated at the

Ni(II)-SalenA/CPE surface in contrast to that of the bare CPE.

FESEM was performed in order to analyze the surface structure of the fabricated CPE and Ni(II)-SalenA/CPE, as illustrated in Fig. 5. As can be seen in Fig. 5(a), the bare CPE consisted of a layer of irregular flakes of graphite powder isolated from each other. After the addition of Ni(II)-SalenA to the graphite powder to fabricate Ni(II)-SalenA/CPE, it can be seen that Ni(II)-SalenA was completely distributed on the surface of the electrode, indicating that Ni(II)-SalenA was irregularly incorporated into the CPE (Fig. 5(b)) [20,44]. In addition, Fig. 5(c) and (d) displays the EDS spectra of CPE and Ni(II)-SalenA/CPE, respectively. The data obtained from these spectra revealed that only carbon existed on the surface of CPE, whereas C, O,

Fig. 5. Representative FESEM images of bare CPE (a) and Ni(II)-SalenA/CPE (b). EDS spectra of (c) bare CPE and (d) Ni(II)-SalenA/CPE.

Table 1

Physical properties of nanozeolite NaA, Ni(II)A, and Ni(II)-SalenA determined from nitrogen adsorption-desorption isotherms.

Sample	S_{BET}^a (m ² /g)	S_{Ext}^b (m ² /g)	S_{mic}^c (m ² /g)	V_{tot}^d (cm ³ /g)	V_{mic}^e (cm ³ /g)	V_{meso}^f (cm ³ /g)
NaA	362.4	21.3	341.1	0.26	0.23	0.03
Ni(II)A	261.2	14.1	247.1	0.18	0.16	0.02
Ni(II)-SalenA	150.3	11.7	138.6	0.14	0.12	0.02

^a BET surface area. ^b The external surface area. ^c The micropore surface area. ^d The total pore volume. ^e The micropore volume; both S_{Ext} and V_{mic} were obtained by the t-plot method. ^f The mesopore volume ($V_{Tot} - V_{mic}$).

Na, Al, Si, and Ni were present on the structure of Ni(II)-SalenA/CPE.

3.3. Electrochemical behavior of Ni(II)-SalenA/CPE in alkaline media

Fig. S2 illustrates consecutive cyclic voltammograms of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution at a scan rate of 50 mV/s. It is worth observing that a pair of redox peaks appears at 495 and 310 mV in the first cycle, which is assigned to the $\text{Ni}^{2+}(\text{Salen})/\text{Ni}^{3+}(\text{Salen})$ redox couple. In the subsequent cycles, the anodic and cathodic peaks are shifted to negative potential values and eventually stabilized at 440 and 305 mV, providing evidence for the alteration of the active composition of Ni complexes as a result of repeated polarization [45]. The current growth with the number of potential cycles can be ascribed to progressive enrichment of the electroactive species $\text{Ni}^{2+}(\text{Salen})(\text{OH})_2$ converted from $\text{Ni}^{2+}(\text{Salen})$ on or near the surface of the modified electrode [43,46,47]. The inset in Fig. S2 depicts the anodic, cathodic, and formal potentials vs. the number of potential cycles. As can be seen, the peak potentials and the formal potential E^0 ($0.5(E_{\text{pa}} + E_{\text{pc}})$) both reach stable values after about 50 cycles. Fig. S3 shows cyclic voltammograms of CPE and Ni(II)-SalenA/CPE in 0.1 mol/L NaOH at a scan rate of 20 mV/s in the absence of N_2H_4 . The onset potentials for oxygen evolution were observed at 0.61 and 0.66 V on the surface of Ni(II)-SalenA/CPE and bare CPE, respectively, and the current for water oxidation was increased on the surface of Ni(II)-SalenA/CPE. This behavior is due to the catalytic effect of Ni(II) on the surface of Ni(II)-SalenA/CPE and is in agreement with previous work for the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple [13,25,27,43,48].

Typical cyclic voltammograms for the electrochemical behavior of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution at various scan rates (0.01–1.0 V/s) are illustrated in Fig. S4. A pair of well-shaped redox peaks with a peak-to-peak potential separation (ΔE_p) of 60 mV was detected at a scan rate of 0.01 V/s. In addition, ΔE_p increased with increasing scan rate, which indicated the presence of a limitation in the charge-transfer kinetics arising from chemical interactions between the electrolyte ions and the modified film [48,49]. According to a theory proposed by Laviron [50], at $\Delta E_p > 200/n$ mV, the electron-transfer coefficient (α) can be calculated by measuring the variation of the peak potential (E_p) with respect to $\log v$ and the apparent charge-transfer rate constant (k_s) for electron transfer between the electrode and the surface layer can be calculated by measuring the E_p values, as given in the following equations [50,51]:

$$E_{\text{pa}} = E^0 + \left[\frac{RT}{(1-\alpha)nF} \right] \quad (2)$$

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

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log \left(\frac{RT}{nFv} \right) - \left(\frac{\alpha(1-\alpha)nF\Delta E_p}{2.303RT} \right) \quad (4)$$

Inset (a) in Fig. S4 displays plots of E_p with respect to $\log v$ in the range of 0.010–1.0 V/s for both the anodic and cathodic peaks on Ni(II)-SalenA/CPE in 0.1 mol/L NaOH. It can be seen

that E_p is proportional to $\log v$ at $v > 0.075$ V/s, as confirmed by Laviron [50]. The value of α was found to be 0.584, which indicated that the rate-limiting steps for the cathodic and anodic reactions might not be the same. In addition, the mean value of the charge-transfer rate constant (k_s) was calculated to be 0.087 s^{-1} .

Inset (b) in Fig. S4 displays plots of the anodic and cathodic peak currents vs. v at low values from 0.010 to 0.075 V/s. According to the slope of these two lines, the surface coverage of redox species (Γ^*) on Ni(II)-SalenA/CPE can be estimated using the following equation [52]:

$$I_p = \frac{n^2 F^2 A \Gamma^* v}{4RT} \quad (5)$$

where I_p , n , and A are the peak current, the number of electrons involved in the reaction ($n = 1$), and the surface area of the electrode (0.12566 cm^2), respectively. Γ^* was calculated to be about $2.75 \times 10^{-8} \text{ mol/cm}^2$, considering the mean of the anodic and cathodic currents. In addition, the mass of nickel loaded on the surface of Ni(II)-SalenA/CPE was obtained as $0.203 \mu\text{g}$. For the higher potential scan rates of 0.1–1.0 V/s, the peak current density values are proportional to the square root of the scan rate, indicating a diffusion-controlled process, which reflects that the charge transfer of the $\text{Ni}(\text{OOH})(\text{Salen})/\text{Ni}(\text{OH})_2(\text{Salen})$ couple is limited by the relatively slow diffusion of OH^- ions toward the film (inset (c) in Fig. S4) [26,53].

3.4. Electrocatalytic activity of Ni(II)-SalenA/CPE for electrooxidation of hydrazine

Fig. 6 illustrates cyclic voltammograms of bare CPE, Salen/CPE, NaA/CPE, Ni(II)A/CPE, and Ni(II)-SalenA/CPE in the absence and presence of 20 mmol/L N_2H_4 in 0.1 mol/L NaOH as a supporting electrolyte at a scan rate of 20 mV/s. It can be seen that there are no electrochemical responses on the bare CPE, Salen/CPE, and NaA/CPE in the absence or presence of N_2H_4 (Fig. 6(a)–(c)). A pair of well-defined redox peaks with a large anodic peak current intensity ($j_{\text{pa}} = 0.8 \text{ mA/cm}^2$) and a small peak-to-peak potential separation ($\Delta E_p = 100 \text{ mV}$) is observed on Ni(II)-SalenA/CPE in the absence of N_2H_4 (Fig. 6(e)). Meanwhile, a small anodic signal ($j_{\text{pa}} = 0.4 \text{ mA/cm}^2$) with $\Delta E_p = 160 \text{ mV}$ is observed on the surface of Ni(II)A/CPE (Fig. 6(d)), suggesting that Ni(II)-SalenA in alkaline solution reacts with OH^- to produce $\text{Ni}(\text{OH})_2\text{-SalenA}$, which acts as an active site for the redox process. In the absence of N_2H_4 in Fig. 6(e), the anodic peak located at 0.440 V corresponds to the oxidation of $\text{Ni}(\text{OH})_2\text{-SalenA/CPE}$ to $\text{Ni}(\text{OOH})\text{-SalenA/CPE}$, and the cathodic peak positioned at 0.305 V is ascribed to the reverse transformation [46,47]. These results confirmed that the presence of Ni(II)-SalenA in the fabricated electrode had a great influence on improving the oxidation currents.

After addition of N_2H_4 to the supporting electrolyte, anodic electrocatalytic peaks were obtained for Ni(II)A/CPE and Ni(II)-SalenA/CPE, and the catalytic current on the surface of Ni(II)-SalenA/CPE was about 3-fold greater than that obtained on Ni(II)A/CPE. Clearly, the larger catalytic current for N_2H_4 oxidation on Ni(II)-SalenA/CPE relative to that on Ni(II)A/CPE results from Ni(Salen), not Ni^{2+} ions. These results revealed

Fig. 6. Cyclic voltammograms of fabricated electrodes in the absence and presence of 20 mmol/L N_2H_4 in 0.1 mol/L NaOH at a scan rate of 20 mV/s. (a) bare CPE, (b) Salen/CPE, (c) NaA/CPE, (d) Ni(II)A/CPE, (e) Ni(II)-SalenA/CPE. (f) Cyclic voltammograms of all fabricated electrodes in the presence of 20 mmol/L N_2H_4 in 0.1 mol/L NaOH at a scan rate of 20 mV/s.

that the Ni(II)-Salen complex as an electron-transfer mediator plays an effective role in the N_2H_4 oxidation process [25–27]. For better comparison, the cyclic voltammograms of bare CPE, Salen/CPE, NaA/CPE, Ni(II)A/CPE, and Ni(II)-SalenA/CPE in the presence of 20 mmol/L N_2H_4 are shown in Fig. 6(f). As can be seen in this figure, no signals for the oxidation of N_2H_4 appear on bare CPE, Salen/CPE, and NaA/CPE. In addition, the catalytic current on Ni(II)-SalenA/CPE is greater than that on Ni(II)A/CPE. Upon complexation with the salen ligand, Ni(II)-SalenA/CPE exhibits a higher activity than Ni(II)A/CPE, which is attributed to an interaction between the central Ni^{2+} ions and the H_2Salen ligand. The partially filled d -orbitals of Ni^{2+} ions interact with the π -electron orbitals of the oxygen and nitrogen atoms in H_2Salen , which accelerates charge transfer between the metal ions and the ligand under an external electric field [27]. In addition, the encapsulated complex molecules in nanozeolite NaA may somewhat inhibit the solvent and electrolyte from approaching bulk redox sites. The ligand-centered process can make more molecules undergo electron transfer than Ni^{2+} , and the adsorbed Ni(II)-Salen complexes can act as mediators for improving the communication between intrazeolite complexes, thereby enhancing the electroactivity for N_2H_4 oxidation [25,27,54]. It can be noted that the synthesized nanozeolite NaA has nanocages of about 3 nm that are interconnected through channels of 0.8–1.2 nm. As a result, salen complexes can be encapsulated successfully in the supercages of the nanozeolite [40]. This arrangement enables interactions between partially coordinated Ni(Salen) molecules in adjacent sites in a nanocage through zeolite lattice oxygens, resulting in a redistribution of d electrons in Ni^{2+} ions, which results in a great improvement in electrocatalytic performance.

As can be seen in Fig. 6(e), the oxidation peak appears at

about 0.57 V for N_2H_4 oxidation on the Ni(II)-SalenA/CPE surface and the cathodic peak current is also decreased. This result indicated that the applied modifier (Ni(II)-SalenA) in this process participates directly in the electrocatalytic oxidation of N_2H_4 . Taking into account all these observations and in agreement with the literature [10–13,55], a mechanism for electrocatalytic oxidation of N_2H_4 at the Ni(II)-SalenA/CPE surface can be suggested. This mechanism corresponds to that typically observed for mediated oxidation (electrocatalytic reaction, EC' mechanism), as illustrated in the following equations. As shown in the chemical reaction (C'), N_2H_4 is oxidized by NiOOH-SalenA, which is produced via an electrochemical reaction (E).

3.5. Effect of hydrazine concentration and scan rate

Fig. 7(a) illustrates the cyclic voltammograms of Ni(II)-SalenA/CPE at various concentration of N_2H_4 (0–80 mmol/L) in 0.1 mol/L NaOH solution at a scan rate of 20 mV/s. In addition, Fig. 7(b) shows zoomed cyclic voltammograms for 0, 3, 20, and 70 mmol/L N_2H_4 . As shown in Fig. 7(b), no reduction peak is observed at N_2H_4 concentrations greater than 20 mmol/L. An obvious gradual enhancement of the anodic peak current is observed with increasing N_2H_4 concentration, suggesting an interaction between N_2H_4 and the redox sites of the film confined at the surface of electrode. At concentrations above 60 mmol/L, no remarkable increase in the anodic peak current is observed (Fig. 7(c)), indicating that upon increasing the concentration of N_2H_4 , the onset potential of Ni(II)SalenA

Fig. 7. (a) Cyclic voltammograms of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution at a scan rate of 20 mV/s with different concentrations of N_2H_4 : 0.0, 3.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, and 80.0 mmol/L. (b) Zoomed cyclic voltammograms for 0.0, 3.0, 20.0, and 70.0 mmol/L N_2H_4 . (c) Plot of j vs. N_2H_4 concentration. (d) Mass activity diagram of Ni(II)-SalenA/CPE in the absence and presence of 20.0 mmol/L N_2H_4 .

oxidation moves to positive values. This behavior is possibly due to the adsorption of intermediates on the remaining active sites, which hinders further oxidation of N_2H_4 as a greater overpotential is necessary for the oxidation of N_2H_4 [26,56]. Thus, 60 mmol/L N_2H_4 represented the optimum concentration, above which the adsorption of oxidation products at the surface of the modified electrode may obstruct further oxidation. In addition, it can be noted that at high concentrations of N_2H_4 , there appears to be an obvious deviation from the linear response, most probably owing to kinetic limitation [48]. The normalized current voltammogram for the N_2H_4 oxidation process at the Ni(II)-SalenA/CPE surface (i.e., current normalized by the mass of loaded Ni^{2+}) is displayed in Fig. 7(d). The mass of loaded Ni^{2+} was determined from the surface coverage [48].

In order to further clarify the electrooxidation mechanism of N_2H_4 on Ni(II)-SalenA/CPE, the effect of the potential scan rate on the cyclic voltammetric response was considered at a constant concentration of N_2H_4 (i.e., 10.0 mmol/L) in 0.1 mol/L NaOH, as depicted in Fig. 8(a). It can be observed that with increasing potential scan rate, the anodic peak potential shifts to more positive values, whereas the cathodic peak potential shifts toward more negative values owing to a kinetic limitation in the reaction between the redox sites of Ni(II)-SalenA/CPE and N_2H_4 . In addition, it can be found that the cathodic peak current increases with the scan rate because there is not enough time at high scan rates for the catalytic reaction be-

tween N_2H_4 and Ni(III)-SalenA, some of which is then reduced during the reverse scan. The increase in the peak current with the scan rate can be considered to indicate adsorption or diffusion control of the process.

A plot of j_{pa} vs. $\nu^{1/2}$ in the range of 0.01–1.0 V/s was found to be linear (Fig. 8(b)); meanwhile, a plot of j_{pa} vs. ν did not show a linear curve (Fig. 8(c)). This observation suggested that this process is a diffusion-controlled process rather than a surface-controlled process [20,48,57]. A slope of 1.0 or 0.5 is expected for $\log j_{\text{pa}}$ vs. $\log \nu$ plots when an adsorption or diffusion process is included, respectively [27,48]. A linear region is observed in the plot of $\log j_{\text{pa}}$ vs. $\log \nu$ for the oxidation of N_2H_4 on Ni(II)-SalenA/CPE with a slope of 0.4118 (Fig. 8(d)), which is close to the theoretically expected value of 0.5 for a purely diffusion-controlled current. The small difference from the theoretical value probably arises from a kinetic limitation in the overall reaction [43]. A plot of the scan-rate-normalized current intensity ($j_{\text{pa}}/\nu^{1/2}$) vs. ν is depicted in Fig. 8(e). The observed polynomial decrease in the plot corresponds to an EC' process, which emphasizes that a subsequent irreversible chemical step is included in the overall process [51,57].

A Tafel plot ($\log I_p$ vs. E_p) was constructed using the data derived from the rising part of the current-voltage curve recorded for 10 mmol/L N_2H_4 on Ni(II)-SalenA/CPE at a scan rate of 10 mV/s (Fig. 8(f)). This rising part of the voltammogram, known as the Tafel region, is affected by the electron transfer kinetics

Fig. 8. (a) Cyclic voltammograms recorded on Ni(II)-SalenA/CPE in the presence of 10 mmol/L N_2H_4 in 0.1 mol/L NaOH at various scan rates; from inner to outer: 0.010, 0.020, 0.035, 0.050, 0.060, 0.075, 0.100, 0.125, 0.150, 0.175, 0.200, 0.250, 0.300, 0.400, 0.500, 0.600, 0.700, 0.800, 0.900, and 1.0 V/s. Plots of j_{pa} vs. ν (b), j_{pa} vs. $\nu^{1/2}$ (c), $\log j_{\text{pa}}$ vs. $\log \nu$ (d), and $j_{\text{pa}}/\nu^{1/2}$ vs. ν (e). (f) Cyclic voltammogram of Ni(II)-SalenA/CPE in the presence of 10 mmol/L N_2H_4 in 0.1 mol/L NaOH at a scan rate of 10 mV/s. The inset in (f) shows the Tafel plot corresponding to this voltammogram.

between N_2H_4 and the modified electrode. The Tafel slope is equal to $n(1-\alpha)F/2.303RT$, where n is the number of electrons in the rate-determining step, α is the electron transfer coefficient, and F , R , and T have their usual meanings. As can be seen in the inset of Fig. 8(f), a slope of 6.07 V/decade was obtained, which indicated that the rate-limiting step was a one-electron-transfer process [2]. In addition, the charge-transfer coefficient, α , was determined to be 0.64.

From the plot of I_p vs. $\nu^{1/2}$, the number of electrons (n) involved in the overall reaction can be obtained according to the following equation for a totally irreversible diffusion-controlled process [52]:

$$I_p = 3.01 \times 10^5 n [(1-\alpha)n_\alpha]^{1/2} ACD^{1/2} \nu^{1/2} \quad (6)$$

The calculated slope of the I_p vs. $\nu^{1/2}$ plot is $3.43 \mu\text{A}/(\text{mV}\cdot\text{s})^{1/2}$, which corresponds to the total number of electrons transferred during the catalytic oxidation of N_2H_4 of 4.0 ($n = 4.4$), considering $(1-\alpha)n_\alpha = 0.36$, $C = 1.0 \times 10^{-5} \text{ mol}/\text{cm}^3$, and $D = 1.18 \times 10^{-7} \text{ cm}^2/\text{s}$, as obtained by chronoamperometry (see below), and $A = 0.12566 \text{ cm}^2$. On the basis of this study and that reported in the literature [58], the following mechanism can be suggested for the oxidation of N_2H_4 on the surface of Ni(II)-SalenA/CPE in alkaline solution, considering that N_2H_4 is in its unprotonated form in 0.1 mol/L NaOH solution:

The rate-determining step involves the transfer of one electron followed by a three-electron process to give N_2 and H_2O as the final products. The overall reaction equation can be expressed by the following reaction, showing that N_2H_4 oxidation on Ni(II)-SalenA/CPE produces nitrogen and water [10].

3.6. Chronoamperometric studies

Chronoamperometry was used to measure the catalytic rate constant and diffusion coefficient of N_2H_4 on the surface of the modified electrode. Fig. 9 exhibits double-step chronoamperograms for the redox process recorded by setting the potential of Ni(II)-SalenA/CPE at 0.65 and 0.30 V vs. Ag|AgCl|KCl (3 mol/L) in the absence and presence of different concentrations of N_2H_4 . Plots of I_{cat}/I_L vs. the square root of time ($t^{1/2}$) exhibited a linear dependency (inset (a) in Fig. 9). The catalytic rate constant (k_{cat}) for the electrocatalytic oxidation of N_2H_4 on the active sites of the modified electrode can be estimated according to the following equation [56, 59]:

$$\frac{I_{\text{cat}}}{I_L} = (\pi k_{\text{cat}} c_0)^{1/2} t^{1/2} \quad (7)$$

where I_{cat} and I_L are the currents in the presence and absence of N_2H_4 , respectively, k_{cat} is the catalytic rate constant ($\text{cm}^3/(\text{mol}\cdot\text{s})$), c_0 is the bulk concentration of N_2H_4 (mol/cm^3), and t is the elapsed time (s). From the slopes of the I_{cat}/I_L vs. $t^{1/2}$ plots for all concentrations, the mean value of k_{cat} was determined to be $1.03 \times 10^5 \text{ cm}^3/(\text{mol}\cdot\text{s})$. Table 2 compares the catalytic rate constant obtained in this work with those reported by others in the literature. As shown in Table 2, the catalytic rate constant for N_2H_4 oxidation on the surface of Ni(II)-SalenA/CPE is larger than those reported in the literature. This is probably because N_2H_4 as the electron transfer media has an inherently higher apparent electron transfer rate constant, showing good electrochemical properties. Therefore, Ni(II)-SalenA/CPE can overcome the kinetic limitation to some extent for N_2H_4 electrooxidation by a catalytic process and can decrease the overpotential for the oxidation of N_2H_4 .

A plot of I vs. $t^{-1/2}$ shows a linear dependence, which indicates diffusion-controlled behavior, and this result is in good agreement with the CV experiments. For an electroactive material, the current response under diffusion control is described by the Cottrell equation [43,48,52]:

Fig. 9. Double-step chronoamperograms of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution in the absence and presence of 5, 10, 15, 20, 30, 40, 50, and 60 mmol/L N_2H_4 . The potential steps were 0.65 and 0.30 V vs. Ag|AgCl|KCl (3 mol/L). Inset (a) shows the dependence of I_{cat}/I_L on $t^{1/2}$ at each concentration of N_2H_4 . Inset (b) shows the dependence of I on $t^{-1/2}$ for 40 mmol/L N_2H_4 . Inset (c) shows a plot of the slopes of the straight lines vs. N_2H_4 concentration.

$$I = nFAcD^{1/2}\pi^{-1/2}t^{-1/2} \quad (8)$$

where c is the bulk concentration of N_2H_4 (mol/cm³), D is the diffusion coefficient (cm²/s), A is the electrode area (0.12566 cm²), and I is the current controlled by the diffusion of N_2H_4 from the bulk solution to the electrode/solution interface. Inset (b) in Fig. 9 displays the experimental plot of I vs. $t^{-1/2}$ for 40 mmol/L N_2H_4 at the surface of Ni(II)-SalenA/CPE. The same curve was plotted for each concentration and then the slopes of the resulting straight lines were plotted vs. N_2H_4 concentration (inset (c) in Fig. 9) [56]. From the slope of the resulting plot and using the Cottrell equation, the mean value of D was determined to be 1.18×10^{-7} cm²/s in the range of 5–60 mmol/L N_2H_4 . A comparison of the obtained D value with other diffusion-coefficient values in the literature was performed, as presented in Table 2.

It should be noted that a comparison with other catalysts reported in the literature is rather difficult owing to various factors, such as concentration of electrolyte, potential sweep rate, and concentration of N_2H_4 , which affect the activity of electrocatalysts toward N_2H_4 oxidation. However, we have endeavored to prepare a rough comparison of the electrocatalytic data with previous research on metal catalysts available in the literature. It seems that Ni(II)-SalenA/CPE can act as a comparable catalyst for hydrazine hydrate oxidation. As can be seen, the modified electrode shows good electrocatalytic activity toward N_2H_4 oxidation in terms of anodic peak potential compared with G/NiCuCo [10], CuO/NiO composite nanofibers [13], Ni(II)-BA-MWCNT-PE [60], RGSS/GCE [61], and

Ni(II)(Salen)Y/GCE [62]. The k_{cat} value on the Ni(II)-SalenA/CPE surface is comparable to k_{cat} values on the surface of various electrodes reported in Table 2. In addition, the data in this table indicate that the Ni(II)-SalenA modified electrode can overcome the kinetic limitation to some extent for N_2H_4 electrooxidation by a catalytic process and can decrease the overpotential for the oxidation reaction of N_2H_4 [27].

3.7. Chronocoulometric studies

The electrocatalytic oxidation of N_2H_4 on Ni(II)-SalenA/CPE was investigated using the chronocoulometry technique. Fig. 10 shows the double-step chronocoulomograms in the absence and presence of different concentrations of N_2H_4 (5–60 mmol/L) with applied potential steps of 0.65 and 0.30 V vs. Ag|AgCl|KCl (3 mol/L). The chronocoulometric curve of Ni(II)-SalenA/CPE in the blank solution (0.1 mol/L NaOH) displayed an almost symmetrical shape, which indicates that almost equivalent charges are consumed for the oxidation and reduction of surface-confined Ni(OH)₂/NiOOH sites. A level line appeared when the potential was stepped down to 0.30 V, implying that the electrooxidation processes are irreversible [27,52]. This result showed similar behavior to that described above using CV and chronoamperometry techniques. The charge value associated with forward chronocoulometry was greater than that observed for backward chronocoulometry in the presence of N_2H_4 .

The chronocoulometry technique was also used to estimate

Table 2Comparison of the electrocatalytic activity of Ni(II)-SalenA/CPE for N₂H₄ oxidation with those of some previously reported catalysts.

Description	Electron transfer rate constant, k_s (s ⁻¹)	Heterogeneous rate constant, k_{cat} (cm ³ /(mol·s))	Diffusion coefficient, D (cm ² /s)	Peak potential (E_p) vs. RHE ^m	Ref.
Au-SH-SiO ₂ @Cu-MOF/GCE ^a	—	1.67×10^3	4.15×10^{-6}	1.14	[2]
CuNPs-PANI-Nano-ZSM-5 ^b	—	9.8×10^4	8.4×10^{-6}	1.30	[7]
G/NiCuCo ^c	—	—	6.28×10^{-6}	1.66	[10]
NPA-NiCuP electrode ^d	—	4.29×10^4	—	1.37	[11]
CuO/NiO composite nanofibers	—	—	—	1.61	[13]
Modified MWCNT paste electrode	—	4.93×10^3	9.5×10^{-4}	0.81	[14]
MBCPE/Fe ₃ O ₄ NPs/DPB ^e	—	5.1×10^3	7.19×10^{-6}	0.76	[17]
Au/titanium dioxide nanotubes	—	—	4.1×10^{-5}	—	[58]
DBC-IL/CNPE ^f	11	3.95×10^4	1.1×10^{-5}	0.78	[63]
Ni(II)-BA-MWCNT-PE ^g	2.21	4.78×10^4	3.58×10^{-5}	1.54	[60]
RGSs/GCE ^l	—	—	—	1.86	[61]
Ni(II)(Salen)Y/GCE	7.74	1.54×10^8	3.47×10^{-7}	1.57	[62]
Co(II)BBAEDI-MWCNT-MCPE ^h	1.5	—	4.5×10^{-6}	0.85	[64]
Quinizarine/GCE	4.44	4.83×10^3	1.1×10^{-6}	—	[65]
GC/Nafion/poly(Ni)	—	1.6×10^3	1.3×10^{-8}	—	[66]
NiPCNF ^k	—	5.8×10^3	8.0×10^{-6}	—	[67]
Ni(OH) ₂ -MnO ₂	—	—	—	1.23	[68]
Ni(II)-SalenA/CPE	0.087	1.03×10^5	1.18×10^{-7}	1.53	This work

^a MOF/GCE: Metal–organic framework/glassy carbon electrode.^b CuNPs-PANI-Nano-ZSM-5: Copper nanoparticles-polyaniline-ZSM-5 nanozeolite.^c G/NiCuCo: Graphite/nickel copper cobalt ternary alloy.^d NPA-NiCuP: Nanoporous nickel copper phosphorous amorphous alloy.^e MBCPE/Fe₃O₄NPs/DPB: Magnetic bar carbon paste electrode/Fe₃O₄ magnetic nanoparticles/2-(3,4-dihydroxyphenyl)benzothiazole.^f DBC-IL/CNPE: Benzofuran derivative-ionic liquids/carbon nanotube paste electrode.^g Ni(II)-BA-MWCNT-PE: Nickel(II)-baicalein-multiwall carbon nanotube-paste electrode.^h Co(II)BBAEDI-MWCNT-MCPE: Cobalt(II) bis(benzoylacetone)ethylenediimino-multiwall carbon nanotube-modified carbon paste electrode.^k NiPCNF: Ni-pentacyanonitrosylferrate.^l RGSs/GCE: Reduced graphene sheets modified glassy carbon electrode.^m E_p (RHE) = E_p (Ag/AgCl/KCl (3 mol/L)) + 0.197 + 0.0591 pH.

the diffusion coefficient of N₂H₄. The charge response under diffusion control is described by the following equation [52]:

$$Q = 2nFAcD^{1/2}\pi^{-1/2}t^{1/2} \quad (9)$$

Fig. 10(b) displays experimental plots of Q vs. $t^{1/2}$ for all concentrations of N₂H₄ (5–60 mmol/L) at the surface of Ni(II)-SalenA/CPE. In the next step, the slopes of the resulting straight lines were plotted against N₂H₄ concentration (Fig. 10(c)). From the slope of the resulting plot and using Eq. (9), the mean value of D was determined to be 1.27×10^{-7} cm²/s in the range of 5.0–60.0 mmol/L N₂H₄, which is similar to the D value obtained from double-step chronoamperometry.

3.8. Repeatability, reproducibility, and stability of Ni(II)SalenA/CPE

For a novel electrode, long-term stability is an important parameter. The reproducibility and stability of Ni(II)-SalenA/CPE were evaluated via the comparison of the currents of five different electrodes containing 15% Ni(II)-SalenA using the CV technique. The anodic current of these electrodes in the presence of 20 mmol/L N₂H₄ was tested independently and the RSD% was 3.75%. A reproducible current response with an RSD of 3.08% was observed for five successive assays at 20 mmol/L N₂H₄. The long-term stability was explored by measuring a N₂H₄ solution intermittently, with the

electrode stored at room temperature when not in use. After 1 and 3 months, the electrode response to electrocatalytic oxidation of N₂H₄ retained about 95% and 88% of the initial value, respectively.

In order to investigate the long-term stability of Ni(II)-SalenA/CPE, this electrode was subjected to 50 cycles between 0.0 and 0.9 V at a scan rate of 100 mV/s in 0.1 mol/L NaOH solution (Fig. S5(a)). The electrode retained 98.7% of its initial current response after 50 cycles and no significant change was detected in the peak potential values. These results indicate mechanical and chemical stability as well as a reproducible response of Ni(II)-SalenA/CPE in the absence of N₂H₄. The stability of Ni(II)-SalenA/CPE was also evaluated in 0.1 mol/L NaOH solution containing 10.0 mmol/L N₂H₄ (Fig. S5(b)). After 50 repetitive cycles, the electrode retained about 79.5% of its initial anodic current response with no significant alteration in the peak potential value, which indicates long-term stability of the modified electrode toward N₂H₄ electrooxidation. This decrease in the current response can be attributed to a small leak of nickel species into the solution and/or slight contamination of the active sites by the adsorption of N₂H₄ oxidation products, such as N₂ gas [49].

For further evaluation of the electrocatalytic activity and long-term stability of the catalysts, chronoamperograms were recorded for Ni(II)-SalenA/CPE at a peak potential of 0.65 V in

Fig. 10. (a) Chronocoulomograms of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution in the absence and presence of different concentrations of N_2H_4 . The potential steps were 0.65 and 0.30 V vs. Ag|AgCl|KCl (3 mol/L). (b) Dependence of Q on $t^{1/2}$ at each concentration of N_2H_4 . (c) Plot of the slopes of the straight lines vs. N_2H_4 concentration. (d) Current–time transient for oxidation of 10 mmol/L N_2H_4 on the surface of Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution at a potential step of 0.65 V vs. Ag|AgCl|KCl (3 mol/L).

0.1 mol/L NaOH solution containing 10 mmol/L N_2H_4 (Fig. 10(d)). As can be seen in this figure, the decrease in current density at initial times is relatively large. However, when the time is greater than 25 s, the current density reaches a relatively stable value. Fluctuations in current during continuous operation may be due to the generation of N_2 gas bubbles on the catalytic active sites of Ni(II)-SalenA/CPE. It is obvious that this electrode exhibits good stability toward N_2H_4 oxidation [13]. In addition, Ni(II)-SalenA remained stable in the structure of the fabricated electrode in 0.1 mol/L NaOH solution.

4. Conclusions

In this study, organic-template-free synthesis of nanozeolite LTA was performed. A new nanozeolite-encapsulated catalyst (Ni(II)-SalenA) was successfully prepared using the flexible ligand method and then this catalyst was used for the modification of a CPE. The experimental results revealed that Ni(II)-SalenA/CPE has good electrochemical stability, reproducibility, and electrocatalytic activity in 0.1 mol/L NaOH solution. Ni(II)-SalenA/CPE showed higher catalytic performance for the electrocatalytic oxidation of N_2H_4 than other electrodes in this work and some in previous studies. The porous structure of nanozeolite LTA provides a framework for Ni^{2+} uptake and encapsulation of salen ligands in nanozeolite supercages, which are converted to $\text{Ni}(\text{OH})_2$ and NiOOH during anodic ox-

idation in alkaline solution and participate in the electrooxidation of N_2H_4 . The effects of potential scan rate and N_2H_4 concentration were considered, and the results showed that oxidation of N_2H_4 on Ni(II)-SalenA/CPE in 0.1 mol/L NaOH solution was a diffusion-controlled electrocatalytic process in a wide potential range, which proceeds via an EC' mechanism. The diffusion coefficient and the catalytic rate constant for N_2H_4 electrooxidation were determined using chronoamperometric and chronocoulometric methods. In addition, the general reaction mechanism for the electrooxidation of N_2H_4 on the surface of Ni(II)-SalenA/CPE in alkaline solution was established to involve a one-electron-transfer reaction as the rate-limiting step followed by a three-electron process to produce environmentally friendly nitrogen and water as final products.

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Graphical Abstract

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Encapsulation of a nickel salen complex in nanozeolite LTA as a carbon paste electrode modifier for electrocatalytic oxidation of hydrazine

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Organic template free synthesis of nanozeolite NaA, LTA (Linde Type A) structure, was performed and nickel salen complex was encapsulated in the supercages of the nanozeolite NaA using the flexible ligand method. The prepared Ni(II)-SalenA was used for modification of CPE to obtain Ni(II)-SalenA/CPE. This modified electrode was applied for electro-catalytic oxidation of hydrazine in alkaline medium.

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纳米分子筛LTA包裹Ni-Salen配合物为修饰碳糊电极用于电催化氧化肼反应

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摘要: 采用柔性配体法将Ni-salen配合物包裹在纳米分子筛LTA的超笼中, 用来修饰碳糊电极制得Ni(II)-SalenA/CPE, 并采用循环伏安法、计时电流法和计时库仑法考察了该电极电催化氧化0.1 mol/L NaOH溶液中肼反应性能。首先采用无有机模板剂法合成纳米分子筛LTA, 并用各种技术进行了表征。XRD和粒径分析结果分别显示LTA晶体的平均粒径为56.1和72nm。在Ni(II)-SalenA/CPE电极氧化还原位上水合肼催化氧化反应电子转移系数为0.64, 速率常数为 $1.03 \times 10^5 \text{ cm}^3/(\text{mol} \cdot \text{s})$ 。电催化反应机理研究表明, 水合肼氧化反应通过它与 $\text{Ni}^{3+}(\text{Salen})\text{O}(\text{OH})$ 反应或直接进行电氧化反应。阳极峰电流与扫描速率的平方根呈线性关系, 表明反应受扩散控制, 水合肼的扩散系数为 $1.18 \times 10^{-7} \text{ cm}^2/\text{s}$ 。结果表明, Ni(II)-SalenA/CPE对水合肼氧化反应表现出高的电催化活性, 这是由于纳米分子筛LTA的多孔结构以及Ni(II)-Salen的存在。最后研究了水合肼在碱性溶液中Ni(II)-SalenA/CPE电极上的氧化反应机理, 发现其为四电子过程, 第一个电子转移反应为速率控制步骤, 然后是一个三电子过程, 产生环境友好的最终产物氮气和氨。

关键词: 纳米分子筛LTA; Salen配合物; Ni(II)-SalenA/CPE; 肼; 电催化氧化; 燃料电池

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