ABSTRACT: Due to the serious adverse futures of some anticancer drugs, the determination of trace amounts of these drugs by simple analytical techniques is of great interest. In this regard, knowing about the mechanism of the analyte with the sensing material plays an important role. Nickel oxide nanoparticles (NiO NPs) modified by a carbon paste electrode (NiO-CPE) showed an irreversible cyclic voltammetric (CV) behavior in the NaOH (pH 13) supporting electrolyte based on the peak separation of 311 mV. Its peak current was decreased by adding tamoxifen (TAM), confirming that TAM molecules can consume NiO before participating in the electrode reaction. For this goal, TAM can be oxidized or reduced, and the corresponding mechanisms are schematically illustrated in the text. This study focused on the kinetic aspects of the process. Based on the CV results, a surface coverage ($\Gamma$) value of $2.72 \times 10^{-5}$ mol NiO per cm$^2$ was obtained with charge transfer coefficients $\alpha_a$ and $\alpha_c$ of 0.317 and 0.563, respectively. $\alpha_a$ and $\alpha_c$ values were changed to 0.08 and 0.72 in the presence of TAM. Further, the rate constant ($k_s$) value was $0.021 \pm 0.01$ s$^{-1}$ in the presence of TAM. In linear sweep voltammetry (LSV), an $\alpha$ value of about $0.636 \pm 0.023$ and an exchange rate constant ($k_o$) value of about $0.097 \pm 0.031$ s$^{-1}$ were obtained in the absence of TAM, which changed to $0.62 \pm 0.081$ and $0.089 \pm 0.021$ s$^{-1}$ in the presence of TAM, respectively. Despite more published papers, when the TAM analyte was added to the NaOH supporting electrolyte, both anodic and cathodic peak currents of the modified NiO-CPE decreased. We suggested some reasons for this decreased peak current, and four mechanisms were illustrated for the electrode response in the presence of TAM.

1. INTRODUCTION

In recent decades, a significant disease leading to more deaths worldwide has been cancer.\textsuperscript{1,2} Unfortunately, due to the increase in industrial activities and environmental pollution, by 2040, it is expected that there will be more than 2.7 million cancer patients worldwide. Most of these patients suffer from one of four major types of cancer, including lung cancer, prostate cancer, bowel cancer, and female breast cancer. Chemotherapy and anticancer drugs are the mainstays of treatment for more cancers. Accordingly, the side effects of anticancer drugs, their effectiveness, and the effects of their dose in the chemotherapy process are essential research areas that are of great importance for global health.\textsuperscript{3–5}

An oral nonsteroidal antiestrogen drug is tamoxifen (TAM: \((Z)-2-(4-(1,2-diphenylbut-1-en-1-yl)phenoxy)-N,N-dimethylethan-1-amine\)), which has been worldwide used to prevent and treat breast cancer for the past 30 years. TAM is a triphenylethylene antiestrogen that effectively binds to estrogen receptors and forms some complexes. These complexes cannot be translocated into the target tissues’ nucleus. In addition, these complex compounds cannot bind to the receptor sites in chromatin and can block estrogen action in the uterus and the breast.\textsuperscript{3} Unfortunately, some major side effects, including thromboembolic diseases and endometrial cancer, have limited the use of TAM in healthy women.\textsuperscript{5} Severe side effects of TAM are known as its proliferative effect on the endometrium, which is dose-dependent. This reveals that TAM formulation and lower TAM dose with colloidal delivery systems are influential factors for long-term breast cancer chemoprevention. This method provides optimal conditions for achieving sufficient and required amounts of TAM at tumor sites for a specified time and minimizing the side effects of TAM on other body organs.\textsuperscript{3}
According to the discussion illustrated above, quantification, detection, and separation of TAM in biological fluids and pharmaceutical formulations have been followed by researchers. For this goal, various analytical techniques including high-performance liquid chromatography (HPLC), gas chromatography (GC), nonaqueous capillary electrophoresis, potentiometry, GC-mass spectrometry, polarography, single sweep voltammetry, and spectrophotometry have been used.\textsuperscript{7–12} Compared to the mentioned analytical techniques, electrochemical methods are more important to analytical chemists for analyzing various compounds containing electroactive functional groups due to their excellent advantages such as low cost, high sensitivity, and relatively short analysis time.\textsuperscript{13–15} Accordingly, introducing novel catalysts/compounds with simple/eco-friendly synthesis procedures for various chemical applications has great interest.\textsuperscript{16–19} Thus, electrochemical methods have adopted great application in detecting and determining various compounds such as pharmaceutics and biomolecules.\textsuperscript{19–37} Anticancer drugs have OH and NH\textsubscript{2} electroactive functional groups, which can generate electroanalytical signals due to electrooxidation or due to oxidative cyclization reactions.\textsuperscript{38} To enhance selectivity, sensitivity, and other characteristics of the electrode, surface modification of electrodes has been used. An important group of electrode surface modifiers is transition metal oxides with various oxidation states. The NiO modifier can be oxidized to Ni(III) as NiOOH species with good electrocatalytic activity.

Among electrochemical techniques, voltammetric-based techniques have been frequently used for quantification of drugs and other chemicals by electrochemical sensors, especially chemically modified ones. Most of the voltammetric reports focused on the quantitative determination of the subjected compounds. For example, electrochemical quantification of tamoxifen has been reported by VO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} GCE,\textsuperscript{39} DNA-CPE, ionic liquids-N-CQD/Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{40} graphene-CuO-polypropylene-graphite electrode,\textsuperscript{41} carbon paste electrode,\textsuperscript{12} etc. Typically, an electrode reaction involves a charge transfer step at the electrode–solution interface, and the rate of this reaction is one of the rate-controlling steps for the overall process. Commonly, this step is the most hindered or slowest step. Further, the overall rate of the electrode reaction is related to the unit area of the interface. Various processes such as chemical reactions, structural reorganization, and adsorption may happen in the electrode–solution interface that may involve a charge transfer step. During an electrode process, current flows through the cell affecting both mass transport and electrode reaction processes. The current flow measures the electrode process kinetics because it shows the charge passed through the circuit during the time. Flowed current is proportional to the electrode surface area (A). The electrode process kinetics depends on the nature of the electrode materials. The strength of the adsorption bond is also important in the metallic electrodes. Generally, the kinetics of the semiconducting-based electrodes are drastically affected by the nature of the electrode.\textsuperscript{12–44}

Here, the behavior of a modified CPE by NiO (NiO-CPE) was studied in linear sweep voltammetry (LSV) and cyclic voltammetry (CV) approaches toward TAM. The electrochemical response of the electrode was first evaluated by CV, and then the kinetics data for the electrode response were estimated by CV and LSV techniques. Commonly, in more published papers, by adding an organic analyte into the voltammetric cell, the peak current of the used modified electrode increases. Here, when the TAM analyte was added to the voltammetric cell containing the NaOH supporting electrolyte, both anodic and cathodic peak currents of the modified NiO-CPE decreased. We suggest some reasons for this decreased peak current, and four mechanisms are illustrated for the electrode response in the presence of TAM, which are illustrated in the next sections.

\section{2. Experimental Section}

\subsection{2.1. Reagents and Preparations.} Graphite powder, nickel(II) acetate tetrahydrate, Nujol oil, citric acid (CA), and other reagents were of analytical grade and purchased from Fluka, Aldrich, or Merck companies. Every day, a stock TAM solution (0.5 \(\mu\)M) was prepared, and dilute solutions were made by the serial dilution approach using this stock solution. The pharmaceutical tablet of TAM (20 mg) was acquired from the Iran Hormone Pharmacy Company (Tehran, Iran) and employed for preparing the TAM real solution. In an agate mortar, one pulverized tablet of TAM was weighed (153.3 mg) and thoroughly powdered. An adequate amount of the powder (13.8 mg) was added to a volumetric flask (50 mL), and ethanol (5 mL) was added for complete dissolution for 5 min sonication. The solution was then diluted by NaOH solution (0.1 M). This solution contained 100 \(\mu\)M with respect to TAM species.

For the synthesis of nickel oxide nanoparticles by the sol–gel technique, nickel(II) salt (2.5 g) in water (50 mL) was added drop by drop to 1.92 g CA in a beaker, and a clear solution was obtained after adjusting the pH to 3−3.5 by nitric acid. It was then stirred magnetically at 65 °C to obtain a very dense residue. After drying in ambient conditions, it was calcined for 6 h at 200 °C to achieve NiO NPs.\textsuperscript{35–48} The CPE and Ni-CPE were prepared by the procedures described in the literature\textsuperscript{12•45, 46}

\subsection{2.2. Apparatus and Voltammetric Procedure.} The X-ray diffraction (XRD) pattern was recorded by an XRD diffractometer (X’PertPro, with Ni-filtered Ni Ka radiation at 1.5406 Å, V: 40 kV, i: 30 mA; Netherland). Fourier transform infrared (FT-IR) spectra were obtained by a PerkinElmer Spectrum 65 FT-IR spectrophotometer. The samples’ morphology was studied on a Mira 3-XMU FE-SEM. A Jenway pH meter (model 3505) was used to adjust solution pHs. A potentiostat/galvanostat (Autolab, PGSTAT-101, EcoChemic, Netherlands) with data acquisition NOVA 1.8 software was used to carry out the voltammetric runs. A three-electrode voltammetric system equipped with a Ag/AgCl electrode as the reference electrode (Azar Electrode Co., Iran), the modified NiO/CPE electrode as the working electrode, and a platinum rod as the auxiliary electrode was used to perform voltammetric runs. The working solution included a 0.3 M NaOH supporting electrolyte containing the desired amount of the TAM analyte. The solution was purged by highly pure nitrogen gas for 5 min before voltammetric runs.\textsuperscript{49, 50}

\section{3. Results and Discussion}

\subsection{3.1. Characterization.} The crystalline structure of the sample was studied by powder XRD as a suitable characterization technique for this goal.\textsuperscript{49} Some characterization techniques were used to characterize the as-prepared NiO NPs, the CPE, and NiO-CPE. These characterization techniques have been illustrated in detail in previous
works, and a summary is reported here. The XRD pattern of the CPE showed hexagonal crystals that conform to the standard pattern of JCPDS No. 00-026-1076. An amorphous phase was detected in the XRD pattern of the as-synthesized NiO NPs (calcined at 200°C that had the highest electrochemical activity, see the Voltammetric Tests section). The average crystallite sizes of NiO NPs and unmodified CPE were 42 and 36 nm, respectively, using the Scherrer and Williamson−Hall equations.

The SEM images confirmed the coating of the CPE surface with the NiO NPs and revealed a plate-like morphology for the raw CPE and the NiO-CPE. Meantime, the modification process under grinding conditions does not change the initial morphology of the CPE. Finally, the EDX results showed that the modified CPE had 10% by weight of Ni. The difference was due to the spot test future of EDX, which analyzed a very small point of the electrode surface.

3.2. Voltammetric Tests. 3.2.1. Effects of the Supporting Electrolyte and CPE Modification. In the initial steps of the work, CVs of the raw and modified CPEs were recorded in the absence and presence of TAM. CVs are displayed in Figure 1, showing no voltammetric current for the raw CPE in a 0.1 M NaOH supporting electrolyte in the absence and presence of TAM (CVs c,d). On the other hand, no electroactive species existed in the supporting electrolytes used in the interfacial region to perform the redox reactions in the applied potential range (−0.2 to 0.8 V). Moreover, the absence of a voltammetric response for the raw CPE in the presence of a 0.5 μM TAM solution confirmed the overvoltage for carrying out the redox reaction for the TAM analyte in the bare electrode was very high, and it could not perform the oxidation/reduction reactions in the applied potential range.

As shown in Figure 1 (CV a), when the modified electrode was used, a good CV response in NaOH (0.1 M) was observed by the appearance of the cathodic peak at 214 mV and the anodic one at 525 mV. The best voltammetric current was detected for 15% NiO when various electrode compositions of the NiO modifier were employed (10−25%). Furthermore, the effects of various supporting electrolytes such as NaOH, KCl, and HCl with different concentrations were studied, and the changes in the electrode response of NiO-CPE were determined. The results confirmed that there are no electroactive species at the surface of the electrode in the acidic and neutral supporting electrolytes. A drastic decrease in the peak current of NiO-CPE was detected in NaOH supporting electrolytes with lower pHs of about 9. However, a decrease in the NaOH concentration caused a sharp reduction in the NiO-CPE peak current. Thus, this concentration was used in the following steps.

The reason for creating the oxidation peak in the forward scan for NiO-CPE is the oxidation of Ni(II) to Ni(III) as NiOOH (eq 1), which occurred at a peak potential of 525 mV. This reaction needs a high strong alkaline solution. A cathodic peak at about 214 mV was observed at the reverse scan. The peak separation (525−214 = 311 mV) for a one-electron transfer reaction confirms an irreversible NiO/NiOOH redox process because it is greater than 59.2 mV for the peak separation in a redox system including one-electron transfer.

\[
\text{NiO} + \text{OH}^- \rightarrow \text{NiOOH} + \text{e}^- \quad (1)
\]

In some published papers, when an organic analyte was added to such alkaline electrolytes, the CV response of their modified electrode increased, and an electrocatalytic behavior was achieved. In contrast, in the present work, when the TAM analyte was added to the NaOH supporting electrolyte, both anodic and cathodic peak currents of the modified NiO-CPE decreased (CV b).

Based on this observation, we suggest some reasons for this decrease in the peak current in the presence of TAM. First, before NiO species participate in the electrode reaction (eq 1), they may oxidize to NiO₂ or NiOOH species by reducing the TAM molecules in the strong alkaline pH used. The overall effect of this chemical reaction is consuming NiO at the electrode surface and decrease in the peak current. Second, it
can be suggested that the chemical reaction of NiO and TAM molecules reduces NiO to Ni(I), and the produced Ni(I) (or NiOH) species cannot be oxidized in the applied conditions. The formation of Ni\(_2^+\) dimers in the gaseous phase and its reaction with molecular oxygen to yield Ni(I) and NiO\(_2\) have been reported.\(^6\) Similarly, the formation of the Ni(I) dimer as Ni\(_2\)O in the applied strong alkaline pH at the electrode surface after the reaction with TAM molecules can be suggested. If this NiO reduction had occurred, TAM molecules must have been oxidized. The various oxidation mechanisms of which are illustrated in Scheme 1.

The first pathway (pathway (A), the cyclization reaction) that has been reported before\(^13\) is the hard way because of the difficulty in the removal of two sp\(^2\)-hydrogens from carbons. In contrast, the formation of another aromatic ring acts as a driving force to perform this oxidation. In this case, *OH species formed by the oxidant may remove the mentioned sp\(^2\)-hydrogens. The produced phenyl radicals are sufficiently close to each other to bind and create a new aromatic ring.

In pathway (B), first, the oxidant may remove one electron of the nitrogen lone pair to form a cation radical of nitrogen. The \(\alpha\) hydrogen of nitrogen may also be removed by *OH species to form an iminium cation. This iminium cation performs an intermolecular electrophilic aromatic substitution with the electrons of the nearby benzene ring and produces compound (V). By comparing this pathway with pathway (A), the first pathway may be better because of formation of a new aromatic ring.

Like pathway (B), in pathway (C), one electron of the oxygen lone pair and the \(\alpha\) hydrogen of oxygen can be removed to form an oxonium cation. The oxonium cation may not be able to do an intermolecular electrophilic aromatic substitution with the electrons of the nearby benzene ring due to the production of an unstable three-member ring. Thus, the OH anion attacks the oxonium cation and forms compound (VIII) by eliminating 2-(dimethylamino)acetaldehyde. Finally, the phenyl ring can be easily oxidized to quinone, and product (X) was obtained. It should be noted that the iminium and oxonium cations are relatively stable.

Pathway (D) shows how TAM molecules are reduced, and therefore, NiO is oxidized into NiOOH or NiO\(_2\), resulting in a decrease in the peak current of NiO electrooxidation. The final product in this mechanism is similar to pathway (C) (product X).

Based on the results obtained, we believe that no reaction has occurred between the TAM molecules and produced NiOOH from the electrooxidation of NiO. If such a reaction occurred, no change was observed in the peak current of NiO electrooxidation (eq 1).

3.2.2. CV Scan Rate Results. The CVs for NiO-CPE in the 0.1 M NaOH solution at various scan rates (20−1000 mV/s) are demonstrated in Figure 2A. Similar CVs were also recorded in the presence of TAM (0.5 \(\mu\)M) and are represented in Figure 2B. As a general rule, the peak current in the CV technique increases with an increase in the scan rate up to a certain level with a shift in the peak potential toward higher values. As the scan rate exceeds the optimal level, the clarity of the peaks decreases. Here, such observations were achieved below 1000 mV/s. With the increase in scan rate, the moving charge \((q)\) increased by electrooxidation of NiO according to eq 1, resulting in the increased peak current. On the other hand, the CV current was limited by poor charge transfer at lower scan rates, and high amounts of NiO modifiers at the electrode surface required higher amounts of electrons. Thus, this limitation was overcome as the scan rate increased.\(^69\)−\(^72\)

Figure 3A shows a typical plot of the CV peak current versus the scan rate, showing a proportional relationship to line equations of \(I_{pa}: 192.698 + 0.809\nu \quad (r^2 = 0.9278)\) and \(I_{pc}: -403.6337−3.6255\nu \quad (r^2 = 0.9608)\) for the anodic and cathodic branches, respectively. This \(i−\nu\) proportional relationship proves a surface-confined behavior for the electrode response in the electrooxidation of NiO.\(^45\)^\(^73\)−\(^75\) According to eq 1, high amounts of hydroxyl anions must be present at the electrode surface for NiO electrooxidation. Thus, the diffusion of these
anions toward the electrode surface is essential. Accordingly, the electrode process should be controlled by the diffusion of hydroxyl anions. However, because of the high amounts of hydroxyl anions in the diffusion layer at this high alkaline pH, no drastic decrease in concentration is observed, and the electrode process can also be considered a surface-confined process.

The CVs in Figure 2B belong to the NiO-CPE response when the TAM analyte is added to the working cell. By comparing these CVs with their corresponding CVs in the absence of TAM, the decreased peak current, or the difference between peak currents in the presence and absence of TAM ($\Delta i$), was calculated and plotted against the square root of the scan rate. A proportional relationship is presented for the anodic reaction (Figure 3B, line equations: $\Delta i_p = -95.7913 + 115.8654\nu^{1/2}, r^2 = 0.9939$), and thus, this decreased peak current confirms the diffusion-controlled process. The increased current associated with the NiO electrooxidation needs the diffusion of the TAM species to the electrode surface.

The effective surface area of the CPE was then determined by the procedure illustrated in the literature in a 0.5 mM $\text{K}_3\text{Fe(CN)}_6 + 0.5 \text{ M KCl}$ solution. The value was 0.24 cm$^2$, which is greater than the geometric one (0.031 cm$^2$) because the effective surface area is drastically affected by the surface porosity. Using the $I_p = n^2F^2\Gamma\nu/4RT$ equation in which $\Gamma$ is the surface coverage of the electrode, and using the slope of the $I_p - \nu$ plot in Figure 3A, the $\Gamma$ value for the modified NiO-CPE was about $2.74 \times 10^{-5}$ mol NiO per cm$^2$.

The typical plots of $E_p$ versus log($\nu$) were constructed based on the CVs recorded in the NaOH supporting electrolyte (Figure 2A) to calculate the apparent charge transfer coefficient ($\alpha$, Figure 3C). The plot equations of $E_{pa} = 0.2885 + 0.0766\log(\nu), r^2 = 0.9263$ and $E_{pc} = 0.2711 - 0.0914\log(\nu), r^2 = 0.9949$ were achieved and their slopes were compared with their actual values (anodic branch: $2.3RT/[(1 - \alpha)nF]$, cathodic branch: $-2.3RT/(\alpha nF)$). Finally, the $\alpha$ and $\alpha_1$ values of 0.317 and 0.563, respectively, were obtained.

Typical Laviron plots are shown by the following equations stating the relationship between peak potential and $\nu$, $\alpha$, and $k$.

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**Figure 2.** Selected CVs of NiO-CPE (10% NiO) in NaOH (0.1 M) at various scan rates (10–1000 mV/s) in the absence (A) and presence (B) of TAM (0.5 $\mu$M).
In an electrode process based on the surface confinement reaction, when the peak separation of the cathodic and anodic signals is higher than 200/n mV (n: the number of electrons transferred), the Laviron model is applicable. 

According to these equations, and using the CVs in Figure 2A,B, typical plots of $E_p$ versus log(ν) were constructed in the presence and absence of the TAM analyte (Figure 3C,D). The average $k_s$ values for the cathodic and anodic directions in the absence of the TAM analyte were $0.0095 \pm 0.047$ and $0.066 \pm 0.03$ s^{-1}, respectively. The α values were changed to 0.08 and 0.72 for the $\alpha_a$ and $\alpha_c$ parameters according to the plot slopes, respectively, and $k_s$ values of 0.021 ± 0.01 and 0.0079 ± 0.04 s^{-1} in the presence of the TAM analyte. $k_s$ values of 0.021 ± 0.01 s^{-1} (anodic branch) and 0.0079 ± 0.04 s^{-1} (cathodic branch) were also achieved according to the intercepts of the plots.

Comparing $k_s$ values in the presence (0.021 s^{-1}) and absence (0.066 s^{-1}) of TAM for the anodic branch demonstrates that in the presence of the TAM analyte, the rate of anodic oxidation of NiO is somewhat slower.

$$E_{pa} = E^0 + \frac{RT}{(1 - \alpha)nF} \ln[(RTk_s)/(1 - \alpha)nF] + \frac{RT}{(1 - \alpha)nF} \ln(\nu)$$

$$E_{pc} = E^0 + \frac{RT}{\alpha nF} \ln[(RTk_s)/\alpha nF] - \frac{RT}{\alpha nF} \ln(\nu)$$

$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha)\log \alpha - \log(RT/nF\alpha) - \alpha(1 - \alpha)nF\Delta E_p/2.3RT$

$\Delta E_p = 0.34 \pm 0.085$ mV

According to the slope of the curve and the Randles–Sevcik equation, the diffusion coefficient ($D$) was calculated for the TAM analyte. A $D_x$ value of $2.87 \times 10^{-5}$ cm^{2}/s and a $D_z$ value of $4.87 \times 10^{-4}$ cm^{2}/s were estimated based on a geometric area of 0.0314 cm^{2}, while a $D_x$ value of $3.89 \times 10^{-7}$ cm^{2}/s and a $D_z$ value of $5.59 \times 10^{-6}$ cm^{2}/s were achieved based on an effective surface area of 0.24 cm^{2}.

### 3.2.3. Linear Sweep Voltammograms

LSV characteristics are affected by some critical factors, including the electron transfer reaction rate, the chemical reactivity of the electroactive compounds, and the scan rate. A higher scan rate increases the voltammetric current and shifts the peak potentials toward higher values. In general, the shift in the peak position in a fixed scan rate depends on the type of the reaction to be reversible, quasi-reversible, or irreversible. These reactions are classified based on the amplitude of the exchange rate constant ($k_x$) values and the rate constant, which decrease from a reversible to an irreversible reaction. This is due to the longer times that the current need to respond to the applied voltage than that in a reversible process. Accordingly, with a....

Figure 3. Corresponding plots of the peak currents versus scan rate for the modified NiO-CPE in 0.1 M NaOH in the absence (A) and presence of TAM (B) based on the CVs in Figure 2A,B. The plots of peak potentials versus log(ν) in the absence (C) and presence of TAM (D) based on the CVs in Figure 2B,C.
decrease in the $k$ or $k_o$ value, the overvoltage tends to increase, and thus, the peak position shifts to higher values. In a diffusion-controlled process, a higher analyte flux (higher diffusion rate) occurs with the increase of the scan rate. Generally, in an electrochemical reaction, determining the charge transfer rate is an essential aspect of the work, and in a typical irreversible reaction, commonly, Tafel equations are correct. But the Marcus model, a simple mathematical model, demonstrated that the Tafel equation might not be accurate for all irreversible reactions, and the transfer coefficient, $\alpha$, may depend on the applied overpotential. Commonly, chronomperometry has been used to determine the rate constant for a typical surface-confined redox reaction, which has a limitation in applying a potential step at individual overpotentials.

In LSV, proper diagnostic criteria to evaluate the mechanistic analysis of systems involving follow-up chemical reactions are following the change in the peak potential during the change in the experimental variables such as sweep rate or the initial concentration of the electroactive species. More common electrode systems include a rapid electron transfer, and their rate-determining step is a chemical reaction or a diffusion process. Thus, to study the kinetics of the charge transfer step for such rapid systems, common kinetics equations could be applied. Both the activation energy and Gibbs free energy of the electrochemical systems commonly change with the change in the applied overvoltage. The slope of the Tafel equation depends on the applied overvoltage used to run a typical redox reaction. Thus, the slope value of this equation may be used to estimate the redox process activation energy. Commonly, for a redox process involving one-electron transfer, 1 V alteration in the applied overvoltage produces 1 eV alteration in the Gibbs free energy. A slight shift in the activation energy could change the Tafel slope. Further, the Tafel slope can be affected by the change in “$\alpha$”, the charge transfer coefficient, or the symmetry factor. Thus, the estimation of the $\alpha$ value is important to obtain the Tafel slope characteristics. Commonly, the $\alpha$ value measures the energy barrier for a redox reaction, and a value of 0.5 results in symmetric barrier energy and a Tafel slope of 120 mV for a one-step redox process involving one-electron transfer. When we counter a multistep electrode process, the nature and number of the preceding steps or the rate-determining step determine the Tafel slope among the various electron transfer steps. In this multistep electron transfer reaction, each step does not essentially involve one-electron transfer. Based on this discussion, knowing about the Tafel equation characteristics, especially its slope, helps us to determine which chemical reaction or electron transfer reaction is the determining factor of the rate-determining step. Accordingly, the Tafel slope can estimate the number of.

Figure 4. Linear sweep voltammograms of NiO/CPE (10% of the modifier) at scan rates of 1–10 mV/s in a 0.3 M NaOH solution in the absence (A) and presence of 0.5 μM TAM (B). Typical Tafel plots derived from the above linear sweep voltammograms in the absence (C) and presence of TAM (D).
In the NiO-TAM reaction, if NiO is oxidized to NiOOH or the reaction with TAM molecules before it underwent the solution. We suggested that the NiO modifier participated in electrode response decreased when TAM was added to the redox process. Despite more modified metal oxide CPEs, the 59.2 mV for the proposed NiO/NiOOH one-electron transfer irreversible, since the peak separation of 311 mV is greater than 4.

4. CONCLUSIONS

The cyclic voltammetric response of the proposed NiO-CPE in a high alkaline supporting electrolyte (NaOH pH 13) is irreversible, since the peak separation of 311 mV is greater than 59.2 mV for the proposed NiO/NiOOH one-electron transfer redox process. Despite more modified metal oxide CPEs, the electrode response decreased when TAM was added to the solution. We suggested that the NiO modifier participated in the reaction with TAM molecules before it underwent the electrode reaction, and thus, its electrode response decreased. In the NiO-TAM reaction, if NiO is oxidized to NiOOH or NiO₂, TAM should be reduced. If NiO is reduced to Ni(I) (as NiOH or Ni₂O species), TAM should be oxidized. Both of these non-electro-reactions consume NiO before participating in the electrode reaction, and thus, the peak current decreases. Based on the results obtained, we believe that no reaction has occurred between the TAM molecules and produced NiOOH from the electrooxidation of NiO. If such a reaction occurred, no change was observed in the peak current of NiO electrooxidation (eq 1). The electrode response obeyed the surface-confined process because of a proportional relationship in the \( i_p - v \) plot. Such behavior was also observed in TAM’s presence, confirming that the peak current belonged to the NiO/NiOOH redox process and NiO was present on the electrode surface. But when the plot of \( \Delta i_p - v^{1/2} \) (\( \Delta i \) is the decreased peak current or the difference between peak currents in the presence and absence of TAM) was constructed, a diffusion-controlled behavior is suitable for the decreased peak current because it relies on TAM diffusion to the surface of the electrode.

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Notes

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