ORIGINAL PAPER

Voltammetric sensor for nitrite determination based on its electrocatalytic reduction at the surface of *p*-duroquinone modified carbon paste electrode

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Abstract A *p*-duroquinone (tetramethyl-*p*-benzoquinone) modified carbon paste electrode (DMCPE) was employed to study the electrocatalytic reduction of nitrite in aqueous solutions using cyclic voltammetry (CV), double potential-step chronoamperometry, and differential pulse voltammetry (DPV). It has found that under an optimum condition (pH 1.00), the reduction of nitrite at the surface of DMCPE occurs at a potential of about 660 mV less negative than that of an unmodified carbon paste electrode (CPE). The catalytic rate constant, k'_h, based on Andrieux and Saveant theoretical model was calculated as $k'_h = 4.56 \times 10^{-5}\ cm\,s^{-1}$ for scan rate 10 mV s^{-1}. Also, the apparent diffusion coefficient, D_{app}, was found as 2.5×10^{-10} and 3.61×10^{-5} cm^2 s^{-1} *for p*-duroquinone in carbon paste matrix and nitrite in aqueous buffered solution, respectively. The values for αn_α were estimated to be −0.65 and −0.19 for the reduction of nitrite at the surface of DMCPE and CPE, respectively. The electro-catalytic reduction peak currents showed a linear dependence on the nitrite concentration, and a linear analytical curve was obtained in the ranges of 5.0×10^{-5} M to 8.0×10^{-3} M and 6.0×10^{-6} M to 8.0×10^{-4} M of nitrite concentration with CV and DPV methods, respectively. The detection limits (2σ) were determined as 2.5×10^{-5} M and 4.3×10^{-6} M by CV and DPV methods. This method was also applied as a simple, selective and precise method for determination of nitrite in real samples (the weak liquor from the wood and paper factory of Mazandaran province in Iran) by using a standard addition method.

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Introduction

Nitrite ions that are produced by photolysis of nitrate ions and by photodegradation of aquatic humic substances are present in the aquatic environment. Nitrite is a key species in global nitrogen cycle. Nitrites are of both environmental and biological importance. The nitrite anion $\left(NO_2^-\right)$ is a simple oxyanion of nitrogen with a pK$_a$ of 3.2 at 20 °C [1]. Nitrite used in meat curing has at least three functions [2, 3]: (a) nitrite provides protection against food poisoning bacteria, (b) nitrite is essential for the characteristic flavor of cured meat, and (c) nitrite is converted into nitro-somyoglobin that gives the characteristic pink color to cured meat. Nitrites are used as food preservatives against food poisoning microorganisms such as clostridium botu-linum [4], and their salts are known to occur in high quantity in soil. Nitrites are known to react with amines forming nitrosamines, which are known to be carcinogenic [5–7]. Furthermore, when nitrites are present at high concentration in blood, they can react with the iron (III) of the hemoglobin, forming methemoglobin, which has no oxygen carrying ability; this disease is called methemoglo-binemia or "blue baby syndrome" [8]. For these reasons, various methods have been used to determine nitrite ions, including the following: spectrophotometry [9], chroma-tography [10], and electrochemical methods [11–17]. The later have more advantages over the other methods in terms of cost and time. Electrochemical determination of nitrite is either by reduction or oxidation. A wide variety of electrode substrates has since been investigated, which includes

nickel [18], copper–nickel alloys [19], cadmium [20], platinum [21, 22], glassy carbon [23, 24], gold [25], lead [26], silver [27], and more recently, boron-doped diamond [28]. The profusion of electrode materials demonstrates the fact that electroanalytical determination of nitrite at bare electrodes is far from facile. Despite the thermodynamic feasibility of the reduction, the kinetics of the charge transfer are slow [29], and direct reduction of nitrite has been shown poor sensitivity and reproducibility through cumulative electrode passivation effects by the species formed during the electrochemical process [30]. Therefore, the reduction of nitrite requires applying large overpotentials at the surface of these electrodes. A good way of lowering potentials is by modification of the electrodes with redox mediators that facilitate electron transfer processes. It is well documented that functionalization of an electrode surface can offer significant analytical advantages in voltammetric experiments. These chemically modified electrode electrocatalytic systems also are used to minimize the problems with poor selectivity that are commonly associated with the use of solid electrodes [31]. Details relevant to detection and determination of nitrate and nitrite have been reviewed by Compton et al. recently [32]. However, some authors have emphasized the instability of the attached or adsorbed materials on the electrodes as a problem arising in the utilization of chemically modified electrodes [33]. It seems that the incorporation of electrocatalysts into the electrode matrix can help solve these problems, and carbon paste electrodes spiked with catalyst may be suitable for this purpose. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost of carbon paste are some advantages of chemically modified carbon paste electrodes [34, 35]. In this area, we have previously reported the electrocatalytic determination of some biologically important compounds at the surface of chemically modified carbon paste electrodes [36–42].

On the other hand, the importance of quinones as a mediator for both electro-reduction and electro-oxidation processes has been known for several years; this has attracted many researchers to work in this area [43–46]. Recently, we have demonstrated the suitability of some quinonic compounds as a mediator for the electrocatalytic oxidation of ascorbic acid [47, 48] and electrocatalytic reduction of dioxygen to hydrogen peroxide [49], so that these compounds were incorporated into the carbon paste electrode. Also, according to our knowledge, there is no report on the electrochemical properties and especially the electrocatalytic activity of *p*-duroquinone in aqueous media. Therefore, in this paper, we discuss the preparation and suitability of a *p*-duroquinone modified carbon paste electrode (DMCPE) as a new modified electrode in the electrocatalysis and determination of nitrite in an aqueous buffer solution by cyclic voltammetry, double potential step

chronoamperometry and differential pulse voltammetry. In order to demonstrate the catalytic ability of this modified electrode in the reduction of nitrite in real samples, we examined this ability in the voltammetric determination of nitrite in weak liquor from the wood and paper industry of Mazandaran by using standard addition method.

Experimental

Apparatus and reagents

The electrochemical experiments were carried out using a Potentiostat/Galvanostat (BHP2061-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium III personal computer connected to an HP Laser Jet 6L printer. A platinum wire was used as the auxiliary electrode. The DMCPE and a double junction Ag|AgCl|KCl$_{sat}$ (Metrohm) electrode were used as the working and reference electrodes, respectively. A pH meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solutions.

The solvent used for the electrochemical studies was twice distilled water. Potassium chloride from Fluka was used as the supporting electrolyte. The *p*-duroquinone and nitrite were from Fluka and were used as received. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH ranges 1.00–12.00. High viscosity paraffin (density=0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter= 0.1 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Working electrode preparations

A 0.5% (*w/w*) *p*-duroquinone spiked carbon powder was made by dissolving the given quantity of tetramethyl-*p*-benzoquinone in diethyl ether and hand mixing with 99 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring. A 1:1 (*w/w*) mixture of 0.5% *p*-duroquinone spiked carbon powder and paraffin was blended by hand mixing, and the resulting paste was then inserted in the bottom of a glass tube. The electrical connection was implemented by a copper wire lead fitted into the glass tube (with internal radius 1.7 mm). A carbon paste electrode without *p*-duroquinone was used as a blank to determine the background current.

Results and discussion

Electrochemistry of DMCPE

According to our knowledge, there is no report on the study of the electrochemical properties and especially the electro-

Fig. 1 **a** Cyclic voltammograms of DMCPE in 0.1 M phosphate buffer solution (pH 1.00) containing KCl 0.1 M as supporting electrolyte at various scan rates: *A* 2, *B* 4, *C* 6, *D* 8, *E* 10, *F* 20, *G* 50, *H* 100, *I* 200, *J* 400, *K* 600, *L* 800, *M* 1,000, and *N* 1,200 mV s^{-1}. Plots of cathodic (*A*) and anodic (*B*) peak currents of DMCPE versus υ **b** for $\upsilon{\leq}50$ and $\upsilon^{1/2}$ **c** for $\upsilon{>}100$ mV s^{-1} from cyclic voltammograms of **a**
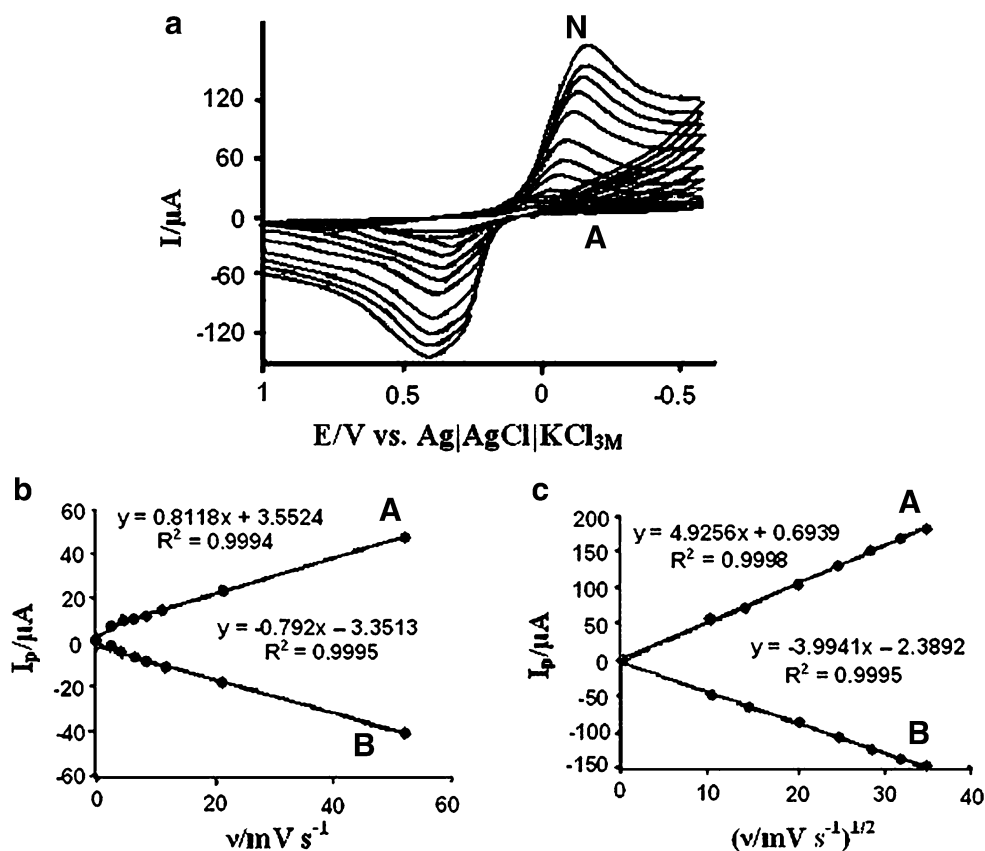
catalytic activity of *p*-duroquinone in aqueous media. Because this compound is insoluble in aqueous media, we prepared DMCPE. Therefore, we studied the electrochemical properties of DMCPE in a pure buffered aqueous solution (pH 1.00) by cyclic voltammetry. The cyclic voltammograms exhibit a cathodic (which is related to reduction of tetramethyl-*p*-benzoquinone, MQ to tetramethyl-*p*-hydroquinone, MQ^{2-}) and corresponding anodic peaks with $E_{pc}=-0.037$ V and $E_{pa}=0.417$ V vs. Ag|AgCl|KCl$_{3M}$ (Fig. 1a, curve F), whereas the cyclic voltammograms of CPE in pure supporting electrolyte show no anodic and cathodic peaks. The experimental results show that the peak separation potential, $\left(\Delta E_p = E_{pa} - E_{pc}\right)$ is greater than that 59/n mV expected for a reversible system. This result suggests that the MQ/MQ^{2-} redox couple in DMCPE shows a quasi-reversible behavior in an aqueous medium.

The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH from five separately prepared DMCPEs (Table 1). The calculated RSD for various parameters accepted as the criteria for a satisfactory surface reproducibility (0.6–3.4%). This degree of reproducibility is virtually the same as that expected for the renewal of ordinary carbon paste surface [45, 50]. However, we regenerated the surface of DMCPE before each experiment according to our previous results [36].

In addition, the effect of potential scan rate on the electrochemical properties of MQ/MQ^{2-} redox couple in DMCPE was studied in aqueous solution by cyclic voltammetry (Fig. 1a). These cyclic voltammograms were used to examine the variation of peak currents vs. sweep rates. Plots of anodic and cathodic peak currents against the scan rate, υ shows that, at low values of υ ($\upsilon{\leq}50$ mV s^{-1}), I_p varies linearly with υ (Fig. 1b); it becomes proportional to $\upsilon^{1/2}$ at higher scan rates (Fig. 1c). Such behavior has also been reported for metalloporphyrin [51] and 1, 4-

Table 1 Cyclic voltammetric data obtained from five separately constructed DMCPE in 0.1 M phosphate buffer solution (pH 1.00) at 10 mV s^{-1}

E_{pa} (V)[a]	E_{pc} (V)[a]	ΔE_p(V)	$E_{1/2}$ (V)[a]	I_{pa} (μA)	I_{pc} (μA)	Γ_a (mol cm^{-2})	Γ_c (mol cm^{-2})
0.400	−0.014	0.414	0.193	−19.03	20.46	5.62×10^{-9}	6.04×10^{-9}
(3.2)	(2.3)	(2.5)	(0.9)	(1.4)	(1.8)	(0.6)	(3.4)

The values in parentheses indicate the calculated RSD (%).

[a] Versus Ag|AgCl|KCl$_{sat}$ as reference electrode

naphthoquinone [49] modified carbon paste electrodes. This behavior indicates that the redox process is diffusion controlled at $\upsilon \geq 100$ mV s^{-1}.

Finally, the effect of aqueous solution pH on the electrode process of p-duroquinone spiked in DMCPE was investigated by cyclic voltammetry in the 0.1 M buffer solutions with various pH values, ranging from 1.00 to 12.00. In all cases, the ionic strength was adjusted to 0.1 M. The half-wave potential, $E_{1/2}$ was calculated as the average of the anodic and cathodic peak potentials, $[(E_{pa}+E_{pc})/2]$ of the cyclic voltammograms recorded at a potential scan rate of 20 mV s^{-1} in various pH. A potential-pH diagram is constructed by plotting the calculated $E_{1/2}$ values as a function of the pH values (Fig. 2). Three linear segments were found with slope values of -56.4 mV/pH, -18.3 mV/pH and 0.0 mV/pH in the ranges of pH<pK_{a1}, pK_{a1}<pH<pK_{a2} and pH>pK_{a2}, respectively. The intersection of these linear segments should correspond to the pK_{a1} and pK_{a2} of p-durohydroquinone and the intercept of each linear segments can be used for calculation of the formal potential, $E^{\circ\prime}$ of various redox system. The values obtained for pK_{a1} and pK_{a2} of p-durohydroquinone are 9.00 and 11.00, respectively. Therefore, the electrochemical response of p-duroquinone is pH dependent.

The dependence of the electrode process of DMCPE on the pH of solution was an important effective factor for its catalytic activity, when it was used as a mediator both via homogeneous and heterogeneous catalytic processes. This behavior reveals that why greater attention is required to optimize the pH of the catalytic reaction media.

Electrochemistry of nitrite at the surface of DMCPE

The electrochemical behaviors of both p-duroquinone and nitrite are dependent on the pH value of the aqueous solution. Therefore, we studied the electrochemical properties of nitrite in 0.1 M phosphate buffered solutions with
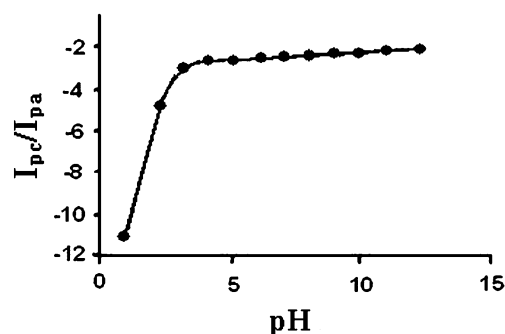

Fig. 3 Current-pH curve for electroreduction of 1.0 mM nitrite in 0.1 M phosphate buffer solution with various pH values at the surface of DMCPE at scan rate 20 mV s^{-1}

various pHs (1.00≤pH≤12.00) at the surface of DMCPE by cyclic voltammetry. The results obtained show that the reduction potentials of both nitrite and p-duroquinone shift toward more negative potentials by increasing the solution pH; their displacement can be unequal because of their different slopes of potential-pH diagrams. Consequently, in buffered solutions of pH<2.00, the conditions are favored so that the catalyzed reduction of nitrite is stared by mediation of reduced form of p-duroquinone in the DMCPE. It was found that electrocatalytic reduction of nitrite was more favored under acidic conditions than in basic medium. This appears as a gradual growth in the cathodic peak current and a simultaneous decrease in the anodic peak current in the cyclic voltammograms. Figure 3 shows the peak currents ratio, I_{pc}/I_{pa} variations against the changes of solution pH for a DMCPE in the presence of nitrite. Therefore, pH 1.00 was chosen as the optimum pH for electrocatalysis of nitrite at the surface of DMCPE.

In order to test the potential electrocatalytic activity of the DMCPE, its cyclic voltammetric responses at 20 mV s^{-1} were obtained in 0.1 M phosphate buffer (pH 1.00) in the absence and in the presence of 10^{-3} M nitrite and the data

Fig. 2 Potential-pH diagram for DMCPE in buffered aqueous medium
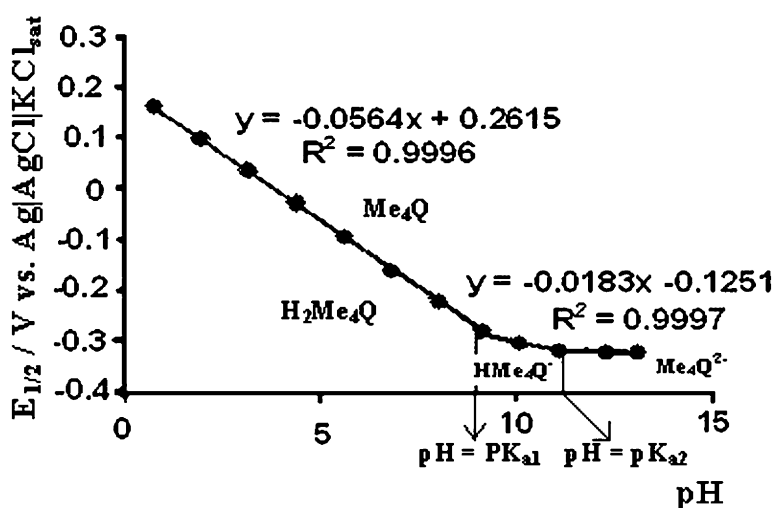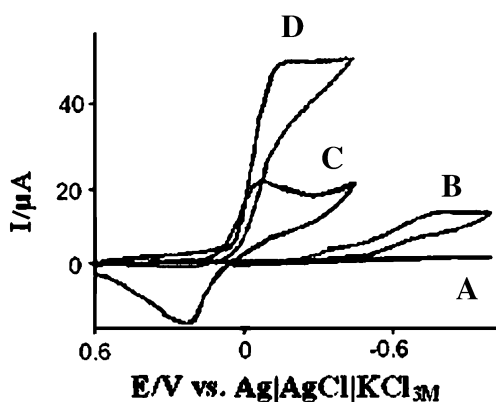
Fig. 4 Cyclic voltammograms of *A* CPE in 0.1 M phosphate buffer solution+0.1 M KCl (pH 1.00) at scan rate 20 mV s^{-1} and *B* as *A*+1 mM nitrite; *C* as *A* and *D* as *B* at the surface of DMCPE

are presented in Fig. 4. In the absence of nitrite, a pair of well-defined redox peaks of DMCPE can be observed (Fig. 4, curve C). Upon the addition of 10^{-3} M nitrite, there was a drastic enhancement of the cathodic peak current and in addition, no anodic peak was observed in the reverse scan of potential (Fig. 4, curve D). This behavior is consistent with a very strong electrocatalytic effect. Under the same experimental conditions, the direct reduction of nitrite at an unmodified carbon paste electrode shows an irreversible reduction peak with a peak potential of nearly −700 mV vs. Ag|AgCl|KCl$_{3M}$ (Fig. 4, curve B), whereas in the absence of nitrite, no peaks appear (Fig. 4, curve A). The nitrite reduction occurs at about −40 mV vs. Ag|AgCl|KCl$_{3M}$ at DMCPE surface; therefore, it is shifted about 660 mV toward less negative potential. Note that this value is comparable with other values reported by other research groups for catalytic reduction of nitrite at the surface of chemically modified electrodes by other mediators (Table 2).

The above results show the reduction of nitrite is facilitated and catalyzed by the presence of *p*-duroquinone spiked into carbon paste electrode. The presence of *p*-duroquinone as the mediator on the surface electrode provides an alternative reaction site to carbon paste for electron transfer

process of nitrite. Therefore, current due to the reduction of nitrite is increased when a DMCPE was used.

The effect of the potential scan rate on the electro-catalytic property of DMCPE toward nitrite was studied. The scan rate dependence of cyclic voltammograms for the DMCPE in 0.1 M phosphate buffer solution (pH 1.00) containing 10^{-3} M nitrite is presented in Fig. 5a. The obtained results show that the catalytic effect of the mediator appeared at scan rates up to 50 mV s^{-1}. Figure 5b (curve A) shows that a plot of the electrocatalytic peak current versus the $\upsilon^{1/2}$ is linear; suggesting that at sufficient overpotential, the reaction is diffusion limited. A plot of current function ($I_p/\upsilon^{1/2}$) vs. sweep rate (curve B of Fig. 5b) exhibits the characteristic shape typical of and EC$_{cat}$ process. Andrieux and Saveant [52] developed a theoretical model for such a mechanism and derived a relation between the peak current and the concentration of the substrate for the case of a slow scan rate, υ, and a large catalytic rate constant, k'_h:

$$I_{cat} = 0.496\, nFAc_s D^{1/2}(F\upsilon/RT)^{1/2} \tag{1}$$

where D and c_s are the diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}) of the substrate (nitrite in this case), respectively. Low values of k'_h result in value lower than 0.496 for the constant. Based on extensive computations, a working curve showing the relationship between numerical values of the constant, $I_{cat}/nFAc_s\,D^{1/2}$ $(F\upsilon/RT)^{1/2}$, and log $[k\Gamma\,D^{1/2}(F\upsilon/RT)^{1/2}]$ (Fig. 1 of [52]) is given. The value of k'_h can thus be calculated from such a working curve. For low scan rates (2–20 mV s^{-1}), we find the value of this constant to be 0.36 for a DMCPE, with a coverage of $\Gamma = 6.04 \times 10^{-9}$ mol cm^{-2}, a geometric area (A) of 0.09 cm^2 and considering $D = 8.5 \times 10^{-5}$ cm^2 s^{-1} (this is obtained by chronoamperometry as below), in the presence of 1.0 mM nitrite. The values of k'_h were found to be 3.51×10^{-5}, 4.07×10^{-5} and 4.56×10^{-5} cm s^{-1} for scan rates of 6, 8 and 10 mV s^{-1}. These values of k'_h explain well the sharp

Table 2 Comparison of the efficiency of some modified electrodes in the electrocatalytic reduction of nitrite

Electrode	Modifier	pH	Peak potential shift (mV)	LOD (M)	LDR (M)	Reference
GC	Os(bipy)$_2$(PVP)$_{10}$Cl	3.5	250	2.0×10^{-6}	5.0×10^{-6}–$1.0 \times 1\,0^{-2}$	[54]
GC	P$_2$W$_{17}$Fe	3.0	430	–	–	[55]
GC	P$_2$W$_{15}$Mo$_2$Cu	3.0	470	–	–	[55]
HMDE	Co^{III}cyclam	7.0	200	–	–	[56]
DME	(FeSCNNO)$^+$	3.0	60	1.0×10^{-8}	3.0×10^{-8}–1.0×10^{-6}	[57]
CFME	K$_8$[P$_2$W$_{17}$O$_{61}$Pd(H$_2$O)]	4.0	200	2.0×10^{-8}	1.0×10^{-7}–1.2×10^{-3}	[58]
CPE	*Fe(CN)$_6^{3-}$*	0.0	700	2.6×10^{-5}	5.0×10^{-5}–1.2×10^{-3}	[59]
CPE	poly(*o*-toluidine)	0.0	600	3.40×10^{-4}	5.0×10^{-4}–1.9×10^{-2}	[60]
CPE	*p*-duroquinone	1.0	660	4.3×10^{-6}	6.0×10^{-6}–8.0×10^{-4}	This work

LDR linear dynamic range, *LOD* limiting of detection, *bipy* 2,2′-bipyridyl, *PVP* poly (4-vinylpyridine), *Cyclam* 1,4,8,11-tetra-azacycloteradecane, *DME* dropping mercury electrode, *HMDE* hanging mercury dropping electrode, *CFME* carbon fiber microelectrode

Fig. 5 a Cyclic voltammograms of 1.0 mM nitrite at the surface of DMCPE in 0.1 M phosphate buffer solution +0.1 M KCl (pH 1.00) at various scan rates: *A* 2, *B* 4, *C* 6, *D* 8, *E* 10, *F* 20, *G* 50, *H* 100, *I* 200 and *J* 400 mV s⁻¹. **b** Variations of the electrocatalytic currents vs. $v^{1/2}$ (curve *A*) and the scan rate normalized current, current function ($I_p/v^{1/2}$) with scan rate (curve *B*)
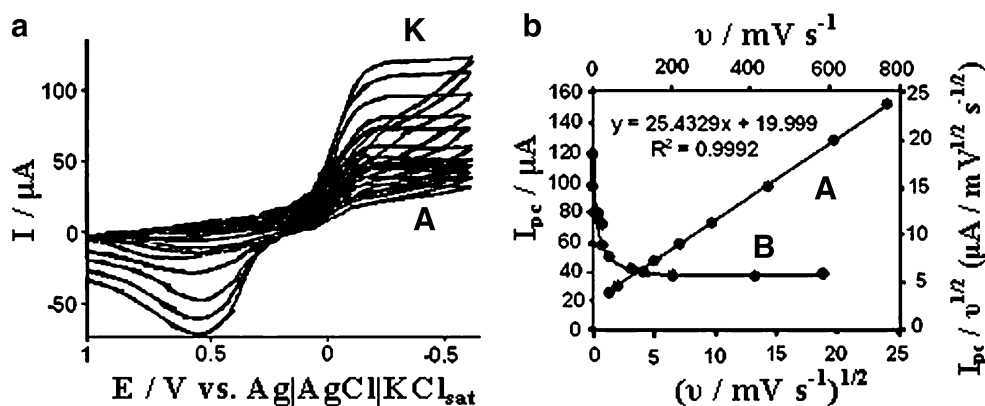
feature of the catalytic peak observed for electrocatalytic reduction of nitrite at the DMCPE.

Also, the values of αn_α (where α is the transfer coefficient and n_α is the number of electrons involved in the rate determining step) were calculated for the reduction of nitrite at pH 1.00 at both modified and unmodified carbon paste electrode according to the following equation [53]:

$$\alpha n_\alpha = 0.048/\left(E_p - E_{p/2}\right) \tag{2}$$

Here, $E_{p/2}$ is the potential corresponding to $I_{p/2}$. The values for αn_α were found to be −0.65 and −0.19 for the reduction of nitrite at the surface of the DMCPE and CPE, respectively. These values clearly show that not only the overpotential for nitrite reduction is reduced at the surface of DMCPE, but also the rate of the electron transfer process is greatly enhanced; this phenomenon is thus confirmed by the larger I_{pc} values recorded during cyclic voltammetry at DMCPE.

Chronoamperometric study

Double-step potential chronoamperometry was also employed for investigation of electrochemical processes at chemically modified electrodes [49, 61]. Therefore, double step potential chronoamperometric behavior of unmodified and modified carbon paste electrodes was examined in the absence and presence of various concentration of nitrite in aqueous buffered solution (pH 1.00) by setting the working electrode potential at −0.3 V (at the first potential step) and 0.5 V (at the second potential step) vs. Ag|AgCl|KCl₃M (Fig. 6a). As can be seen, there is no net anodic current corresponding to the oxidation of mediator in the presence of nitrite, when the potential is stepped from −0.3 to 0.5 V vs. Ag|AgCl|KCl₃M, while the forward and backward potential step chronoamperometry on the modified electrode in the blank buffered solution show very symmetrical chronoamperograms with an equal charge consumed for the reduction and oxidation of the MQ/MQ²⁻ redox system at the surface of CPE (Fig. 6b, curve A′). However, in the

presence of nitrite the charge value associated with forward chronoamperometry is significantly greater than that observed for backward chronoamperometry (Fig. 6b, curve C′). The plot of net electrolysis current of DMCPE in the absence of nitrite (Fig. 6a, curve A) vs. $t^{1/2}$ shows a straight line (Fig. 6c), which extrapolates close to the origin. Therefore, this type of near-Cottrellian behavior is not due to a linear semi-infinite diffusion process but may be caused by finite diffusion in a thin film, where the near-Cottrell equation behavior can be approximated over a short time period [46, 62]. Consequently, we can assume diffusion controlled behavior for charge transfer at DMCPE and use the potential-step chronoamperometric experiments to estimate the diffusion coefficient of *p*-duroquinone into the paraffin oil used for past preparation [49, 63]. The slope of the linear region of the $I–t^{1/2}$ plot in the short time region produces the apparent diffusion coefficient (D_{app}) of the spiked *p*-duroquinone into DMCPE by using the Cottrell equation [63]:

$$I = nFA_g D_{app}^{1/2} c\pi^{-1/2} t^{-1/2} \tag{3}$$

where D_{app} and c are the apparent diffusion coefficient (cm² s⁻¹) of spiked *p*-duroquinone in paraffin oil and the known concentration of *p*-duroquinone in paraffin oil (mol cm⁻³), respectively. A_g is the geometric area of the modified carbon paste electrode, the diameter (*d*) of the DMCPE was measured and then the geometric area of the DMCPE was calculated according to [$\pi (d/2)^2$]. Therefore, we calculated the D_{app} for *p*-duroquinone (Fig. 6c) in carbon paste matrix. It was found 2.5×10^{-10} cm² s⁻¹. While, in the equation *n*= 2, *F*=96,485 C mol⁻¹, Ag=0.09 cm², and corresponding *c* value was selected. This method has used for estimation of D_{app} for 1, 4-naphthoquinone and some its derivatives [49]. Chronoamperometry of the modified electrode in the presence of nitrite represents a typical *I–t* curve, which indicates that the observed current must be controlled by nitrite diffusion in the solution. A plot of *I* versus $t^{-1/2}$ for a modified electrode in the presence of nitrite gives a straight

Fig. 6 a Double step potential chronoamperograms obtained at the DMCPE in the *A* absence and presence of *B* 0.05, *C* 0.40, *D* 0.80, *E* 1.00 mM of nitrite in 0.1 M phosphate buffer solution (pH 1.00). First and second potential steps were −0.4 and 0.5 V vs. Ag|AgCl|KCl$_{sat.}$. b The charge-time curves: (*A′*) for curve (*A*) and (*C′*) for curve (*B*). Cottrell plots **d** for curve (*A*), **e** for curve (*B*) and **f** for curve (*C*) of **a**
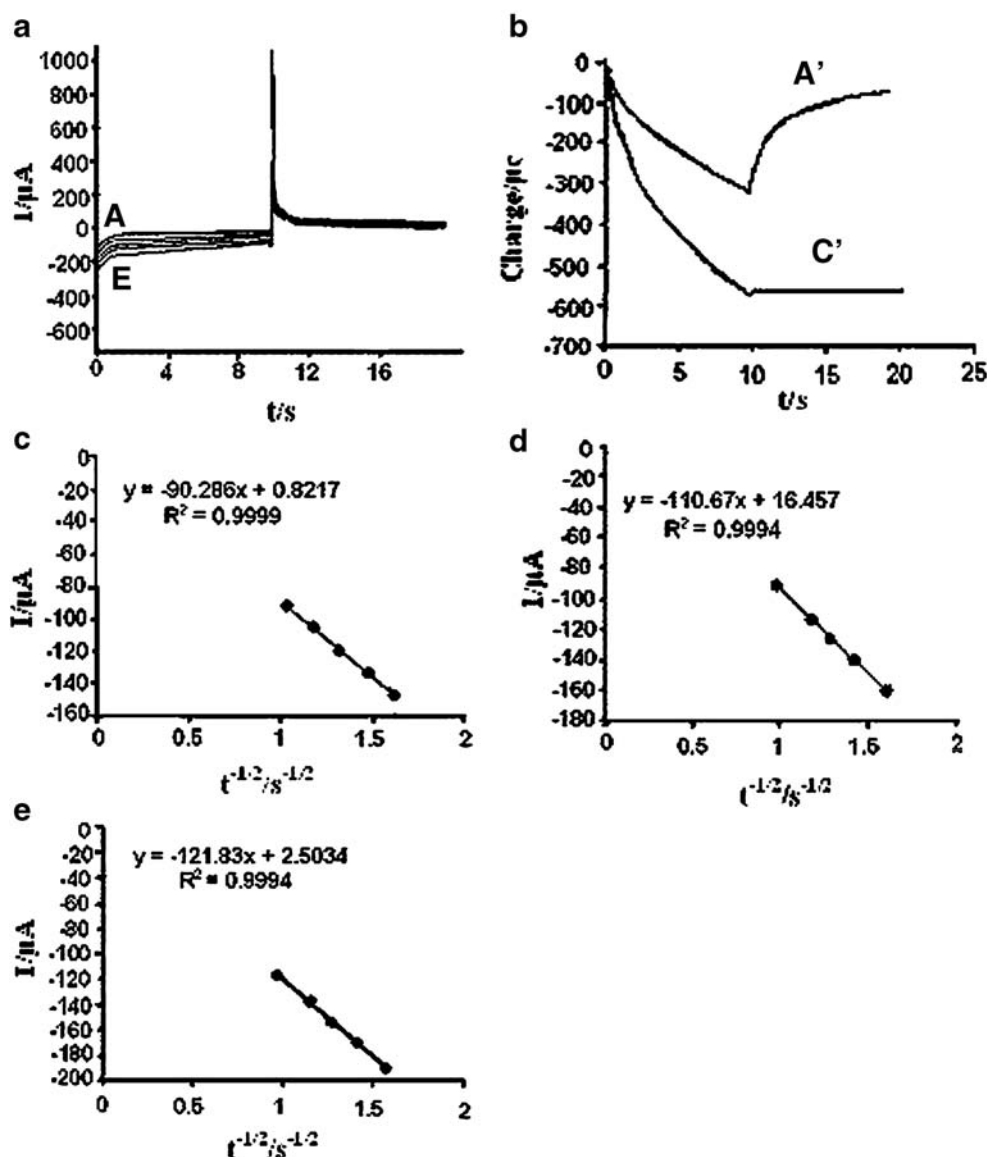
line; the slopes of such lines can be used to estimate the diffusion coefficient of nitrite (*D*) in the ranges (0.006–0.8 mM). The mean value of the *D* was found to be 8.5×10^{-5} cm^2 s^{-1} (Fig. 6d and e).

Therefore, all the above behavior is compatible with an electrocatalytic mechanism for electroreduction of nitrite at the surface of DMCPE.

Electrocatalytic determination of nitrite

The electrocatalytic peak current of nitrite reduction at the surface of the DMCPE can be used for determination of nitrite in solution. Therefore, cyclic voltammetry and differential pulse voltammetry experiments were performed

using DMCPE in phosphate buffer solution containing various concentration of nitrite. One of the main objectives of this study was the development of the electrocatalytic reduction of nitrite. The results show the electrocatalytic peak current for the reduction of nitrite on DMCPE is linearly dependent on the concentration of nitrite. The range of this linearity depends on the amount of mediator in the electrode. The mediated reduction peak currents of nitrite on a 1% DMCPE were proportional to the concentration of the substrate in the ranges 5.0×10^{-5} M to 8.0×10^{-3} M (with a correlation coefficient of 0.9993) and 6.0×10^{-6} M to 8.0×10^{-4} M (with the correlation coefficient of 0.9974) in the cyclic voltammetry and differential pulse voltammetry, respectively (Fig. 7). The detection limits (2σ) were $2.5 \times$

Fig. 7 **a** Cyclic voltammograms of nitrite at various concentrations: *A* 0.06, *B* 0.08, *C* 0.20, *D* 0.40 *E* 0.60, *F* 0.80, *G* 1.00, *H* 2.00, *I* 4.00, *J* 6.00 and *K* 8.00 mM at $\upsilon=20$ mV s^{-1} and **c** differential pulse voltammograms 1n the absence *A* and presence of *B* 0.0070, *C* 0.0085, *D* 0.0400, *E* 0.0900, and *F* 0.2400, *G* 0.3700, *H* 0.5200, *I* 0.6300, *J* 0.8100 mM of nitrite in 0.1 M phosphate buffer solution (pH 1.00) at the surface of DMCPE. Plot of electrocatalytic peak currents **b** (from CV of **a**) and **d** (from DPV of **c**) vs. nitrite concentrations
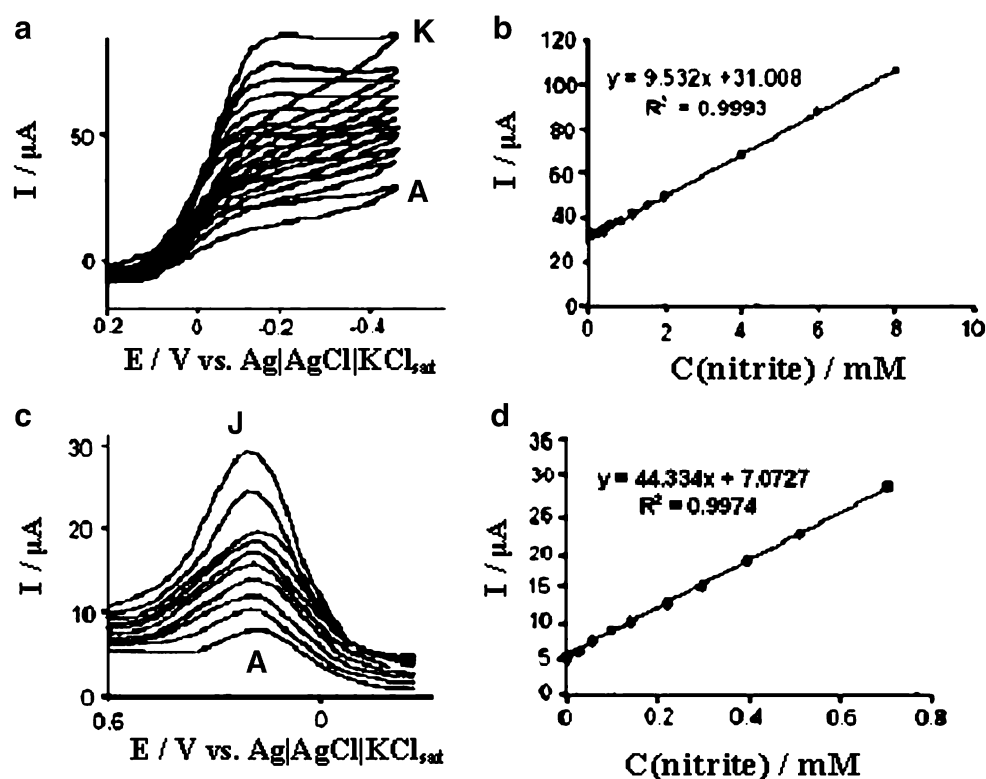
10^{-5} M and 4.3×10^{-6} M by CV and DPV methods, respectively. Thus, the catalytic reduction of nitrite can readily be applied to the determination of nitrite.

Determination of nitrite in a real sample

In order to demonstrate the catalytic reduction of nitrite in the real samples, we examined this ability in the voltammetric determination of nitrite in weak liquor from the wood and paper factory of Mazandaran province in Iran.

The determination of nitrite in a sample was carried out by the standard addition method in order to prevent of any matrix effect. Figure 8a shows related cyclic voltammograms for this purpose. As can be seen in this figure, adding nitrite to the buffer solution (pH 1.00) containing diluted weak liquor (curve A) caused an increase in the reduction peak height (curves B to F). Thus, the peak was attributed to nitrite reduction. Figure 8b shows a typical linear plot of I_{pc} versus the nitrite concentration that is usable for determination of nitrite in this sample. The concentration of nitrite in this real sample was evaluated about $(12.00\pm0.17)\times10^{-3}$ M, by this method (for $n=4$). The accuracy and precision this method was examined by comparison of data obtained from this method with a standard method (oxidation–reduction titration in acid solution of $KMnO_4$ by $Na_2C_2O_4$) for determination of nitrite. The results from the statistical calculation indicate good agreement between the mean values (*t* test) and precision (*f* test) for two methods (for $\rho=0.05$).

Fig. 8 **a** Cyclic voltammograms of *A* 10 order diluted solution of sample in 0.1 M phosphate buffer (pH 1.00) and 0.1 M KCl, and after adding nitrite *B* 0.6, *C* 0.8, *D* 2.3, *E* 4.2, *F* 6.0 mM at the surface of DMCPE, $\upsilon=20$ mV s^{-1}. **b** Plot of electrocatalytic peak currents (from CV of **a**) vs. the nitrite concentrations
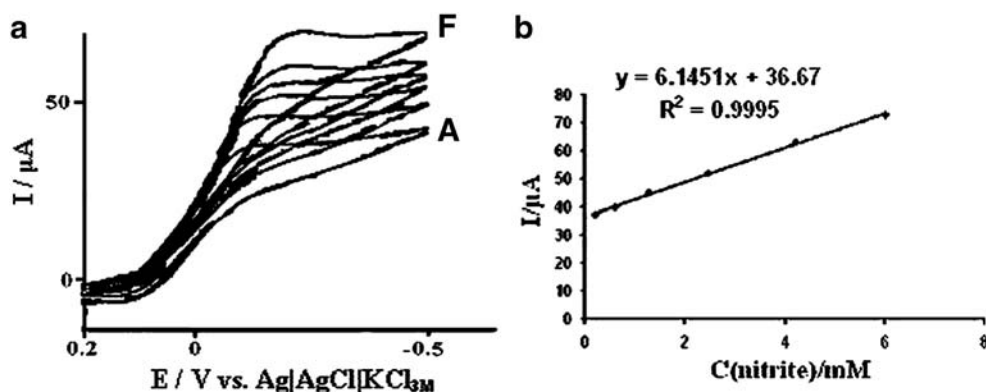
Conclusion

This work demonstrates the construction of a chemically modified carbon paste electrode by the incorporation of tetramethyl-*p*-benzoquinone as a modifying species. The value of the peak separation potential obtained for the tetramethyl-*p*-benzoquinone/tetramethyl-*p*-hydrobenzoquinone couple suggests that the couple can act as a quasi-reversible system in the carbon-paste matrix. The electrochemical behavior of the DMCPE has been studied by cyclic voltammetry, double potential-step chronoamperometry, and differential pulse voltammetry in both the absence and presence of nitrite. The results show that the reduction of nitrite is catalyzed at pH 1.00, the reduction of nitrite at the surface of this carbon paste modified electrode occurs at a potential of about 660 mV less negative than that of an unmodified carbon-paste electrode.

The mediated reduction current of nitrite at the DMCPE was used to the determination of nitrite in an aqueous solution by concentration of the substrate in the ranges 5.0×10^{-5} M to 8.0×10^{-3} M (with a correlation coefficient of 0.9993) and 6.0×10^{-6} M to 8.0×10^{-4} M (with the correlation coefficient of 0.9974) in the cyclic voltammetry and differential pulse voltammetry, respectively. The detection limits (2σ) were 2.5×10^{-5} M and 4.3×10^{-6} M by CV and DPV method. The kinetic parameters of the electrocatalytic process, the diffusion coefficients of nitrite in an aqueous solution and *p*-duroquinone in carbon paste matrix were determined.

The electrocatalytic reduction of nitrite at the surface of a DMCPE can be employed as a new method for the voltammetric determination of nitrite in real sample. The proposed voltammetric method is a rapid, simple, precise, and suitable for routine control and can be carried out directly without any pretreatment or separation.

References

1. Braida W, Ong SK (2000) Water Air Soil Pollut 118:13
2. Carlsen CU, Moller JKS, Skibsted LH (2005) Coord Chem Rev 249:485
3. Moller JKS, Skibsted LH (2002) Chem Rev 102:1167
4. Yetim H, Kayacier A, Kesmen Z, Sagdic O (2006) Meat Sci 72:206
5. Lijinsky W, Epstein SS (1970) Nature 225:21
6. Wolf IA, Wasserman AE (1972) Science 177:15
7. Choi KK, Fung KW (1980) Analyst 105:241
8. Titov VYu, Petrenko Yu M (2005) Biochem 70:473
9. Greenway GM, Haswell SJ, Petsul PH (1999) Anal Chim Acta 387:1
10. Helaleh MIH, Korenaga T (2000) J Chromatogr B 744:433
11. Cai X, Zhao Z (1988) J Electroanal Chem 252:361
12. Newbry JE, de Haddad MPL (1985) Analyst 110:81
13. Trojanowicz M, Matuszewski W, Szostek B (1992) Anal Chim Acta 261:391
14. Wen Z-H, Kang T-F (2004) Talanta 62:351
15. Thamae M, Nyokong T (1999) J Electroanal Chem 470:126
16. Obirai J, Nyokong T (2004) J Electroanal Chem 573:77
17. Davis J, Moorcroft MJ, Wilkins SJ, Compton RG, Cardosi MF (2000) Analyst 125:737
18. Bockris JO, Kim J (1996) J Electroanal Chem 143:3801
19. Moorcroft MJ, Nei L, Davis J, Compton RG (2000) Anal Lett 33:3127
20. Bodini ME, Sawyer D (1977) Anal Chem 49:485
21. Mori V, Bertotti M (1999) Anal Lett 32:25
22. Hulanicki A, Matuszewski W, Trojanowicz M (1987) Anal Chim Acta 194:119
23. Chamsi AY, Fogg AG (1988) Analyst 113:1723
24. Davis J, Compton RG (2000) Anal Chim Acta 404:241
25. Ohmori T, El-Deab MS, Osawa M (1999) J Electroanal Chem 470:46
26. Genders JD, Hartsough D, Hobbs DT (1996) J Appl Electrochem 26:1
27. Fedurco M, Kedzierzawski P, Augustynski J (1999) J Electrochem Soc 146:2569
28. Bouamrane F, Tadjeddine A, Butler JE, Tenne R, Levy-Clement C (1996) J Electroanal Chem 405:95
29. Zhao Z, Cai X (1988) J Electroanal Chem 252:361
30. Barisci JN, Wallace GG (1991) Anal Lett 24:2059
31. White PC, Lawrence NS, Davis J, Compton RG (2001) Anal Chim Acta 447:1
32. Moorcroft MJ, Nei L, Davis J, Compton RG (2001) Talanta 54:785
33. Pham MC, Dubois JE (1986) J Electroanal Chem. 199:53
34. Dryhrst G, McAallister DL (1984) Laboratory techniques in electroanalytical chemistry. In: Kissinger PT, Heinman WR (ed) Marcel Dekker, New York
35. Almeida CMVB, Giannetti BF (2002) Electrochem Commun 4:985
36. Raoof JB, Ojani R, Kiani A (2001) J Electroanal Chem 515:45
37. Raoof JB, Ojani R, Rashid-Nadimi S (2004) Electrochim Acta 49:271
38. Raoof JB, Ojani R, Hosseinzadeh R, Ghasemi V (2003) Anal Sci 19:1251
39. Raoof JB, Ojani R, Kolbadinezhad M (2005) Electroanalysis 17:2043
40. Ojani R, Raoof JB, Salmany-Afagh P (2004) J Electroanal Chem 571:1
41. Raoof JB, Ojani R, Rashid-Nadimi S (2005) Electrochimica Acta 50:4694
42. Raoof JB, Ojani R, Beitollahi Hossienzadeh HR (2006) Electroanalysis 18:1193
43. Fultz ML, Durst RA (1982) Anal Chim Acta 140:1
44. Wring SA (1992) Analyst 117:1215
45. Raoof JB, Golabi SM (1995) Bull Chem Soc Jpn 68:2253
46. Zare HR, Nasirizadeh N, Mazloum Ardakani M (2005) J Electroanal Chem 577:25
47. Ojani R, Raoof JB, Zamani S (2005) Electroanalysis 17:1740
48. Raoof JB, Ojani R, Ramine M (2006) Electroanalysis 18:1722
49. Golabi SM, Raoof JB (1996) J Electroanal Chem 46:75
50. Geno PW, Ravichandran K, Baldwin RP (1985) J Electroanal Chem 183:155
51. Takeuchi ES, Murray RW (1985) J Electroanal Chem 188:49
52. Andrieux CP, Savĕant JM (1978) J Electroanal Chem 93:163
53. Takeuchi ES, Murray RW (1985) J Electroanal Chem 188:49
54. Doherty AP, Smyth MR, Vos JG (1991) Anal Chim Acta 255:45
55. Keita B, Girard F, Nadjo L, Contant R, Belghiche R, Abessi M (2001) J Electroanal Chem 508:70
56. Taniguchi I, Nakashima N, Matsushita K (1987) J Electroanal Chem. 224:199
57. Zhao Z, Cai X (1988) J Electroanal Chem 252:361
58. Sun W, Zhung S, Jin L, Deng J (1999) J Electroanal Chem 469:63
59. Ojani R, Raoof JB, Zarei E (2006) Electrochim Acta 52:753
60. Ojani R, Raoof JB, Zarei E (2008) Electroanalysis 20:379
61. Pournaghi-Azar MH, Razmi-Nerbin H (2000) J Electroanal Chem 488:17
62. Murray RW (1986) Physical methods of chemistry, vol 12. In: Rossiter BW, Hamilton JF (ed) Wiley, New York
63. Bard AJ, Faulkner LR (2001) Electrochemical methods, fundamentals and applications. Wiley, New York