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ORIGINAL PAPER

FAD-modified $SiO_2/ZrO_2/C$ ceramic electrode for electrocatalytic reduction of bromate and iodate

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Abstract $SiO_2/ZrO_2/C$ carbon ceramic material with composition (in wt%) SiO_2=50, ZrO_2=20, and C=30 was prepared by the sol–gel-processing method. A high-resolution transmission electron microscopy image showed that ZrO_2 and the graphite particles are well dispersed inside the matrix. The electrical conductivity obtained for the pressed disks of the material was 18 S cm^{-1}, indicating that C particles are also well interconnected inside the solid. An electrode modified with flavin adenine dinucleotide (FAD) prepared by immersing the solid $SiO_2/ZrO_2/C$, molded as a pressed disk, inside a FAD solution (1.0×10^{-3} mol L^{-1}) was used to investigate the electrocatalytic reduction of bromate and iodate. The reduction of both ions occurred at a peak potential of −0.41 V vs. the saturated calomel reference electrode. The linear response range (lrr) and detection limit (dl) were: BrO_3^-, lrr=4.98×10^{-5}–1.23×10^{-3} mol L^{-1} and dl=2.33 μmol L^{-1}; IO_3^-, lrr=4.98×10^{-5} up to 2.42×10^{-3} and dl=1.46 μmol L^{-1} for iodate.

Keywords $SiO_2/ZrO_2/C$ ceramic electrode · Electrical conductive ceramic · Flavin adenine dinucleotide · Electrochemical detection of bromate and iodate · Electrochemical sensor

Introduction

Materials obtained by the sol–gel-processing method to construct electrochemical devices have attracted great interest over the past decades due to their remarkable facilities of obtaining homogenous electrochemical studies and applications [1–4]. Growing interest has been focused on sol–gel-derived carbon ceramic electrodes (CCEs), which are generally prepared by incorporating graphite powder into a silicate gel matrix [5, 6]. The advantages presented by CCE, such as low cost, high stability, good surface-renewable repeatability, and easy preparation and modifying, have proportionate many efforts devoted to the preparation of modified CCE with different electroactive species for electroanalytical applications [7–14].

Flavoproteins play an important biological role in the electron transfer reactions in living systems, primarily due to the presence of flavin adenine dinucleotide (FAD). Other members of the flavin family include flavin mononucleotide, riboflavin (vitamin B_2), and lumiflavin [15, 16]. FAD in particular has been extensively studied on several solid electrodes such as Au [17–19], Pt [20], glassy carbon [21–23], and titanium oxide-modified electrodes [24, 25].

Disinfection of drinking water by chlorine sometimes forms carcinogenic trihalomethanes, and therefore, recently, ozone has been alternatively used for the treatment. However, the bromate ion can be generated during the ozone treatment, if the water source contains bromide ion [26–28]. This powerful oxidant is a genotoxic carcinogen [29, 30].

Table salt is iodized with potassium iodate or iodine in most countries. The iodized salt is recognized as the method of choice and the most successful strategy for preventing iodide deficiency disorders [31]. Otherwise, an excess of iodine or iodate can produce goiter and hypothyroidism as well as hyperthyroidism [32].

Materials and methods

Preparation of $SiO_2/ZrO_2/C$

The $SiO_2/ZrO_2/C$ composite material, hereafter designated as SZC, was prepared by the sol–gel method according to a

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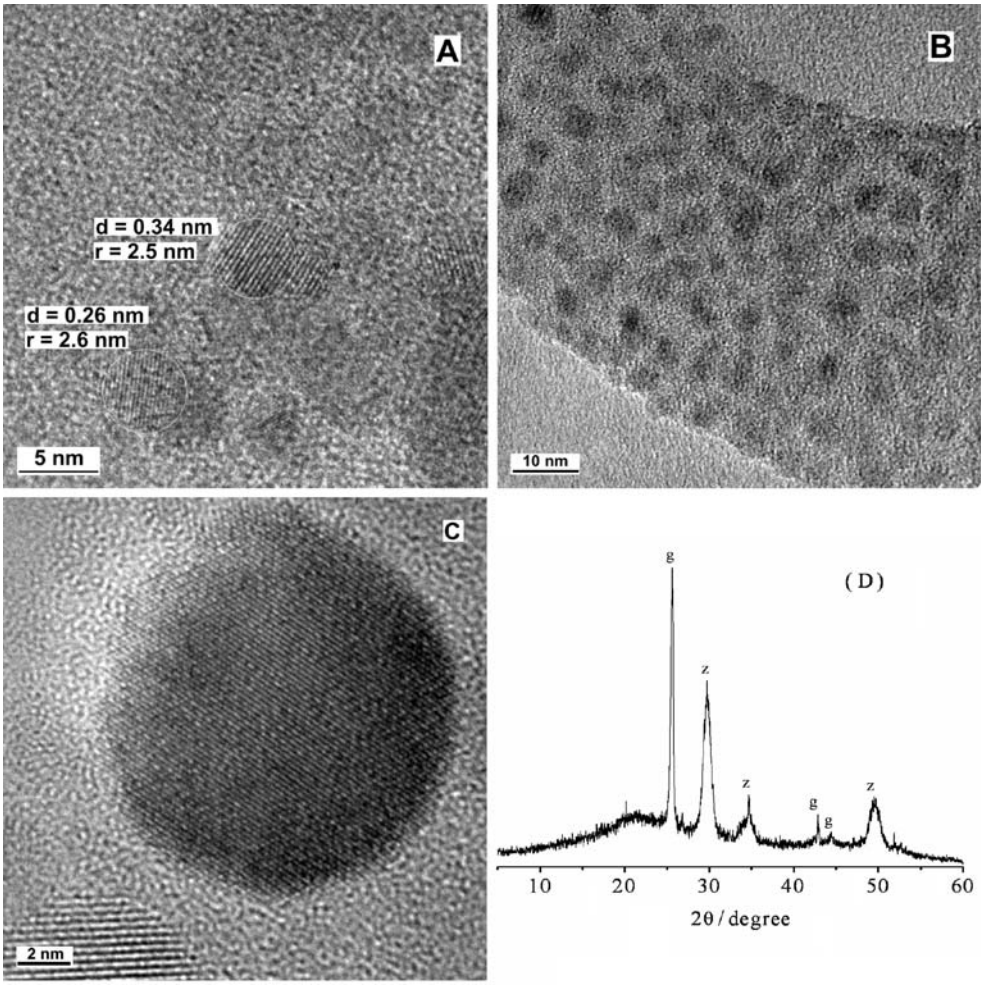


Fig. 1 **a** HRTEM image for SZC heated at 343 K. **b** Image obtained by mass contrast for SZC heat treated at 1,273 K. **c** HRTEM of ZrO_2 heat treated at 1,273 K. **d** The X-ray diffraction patterns obtained for sample heat treated at 1,273 K

previously described procedure [33]. In a solution of tetraethyl orthosilicate (TEOS; Aldrich) in pure ethanol in a 1:1 (*v*/*v*) proportion, an aqueous acid solution was added, and the mixture was stirred for few hours at room temperature. An appropriate amount of zirconium tetrabutoxide (Aldrich) and graphite (Fluka) were added to the prehy-

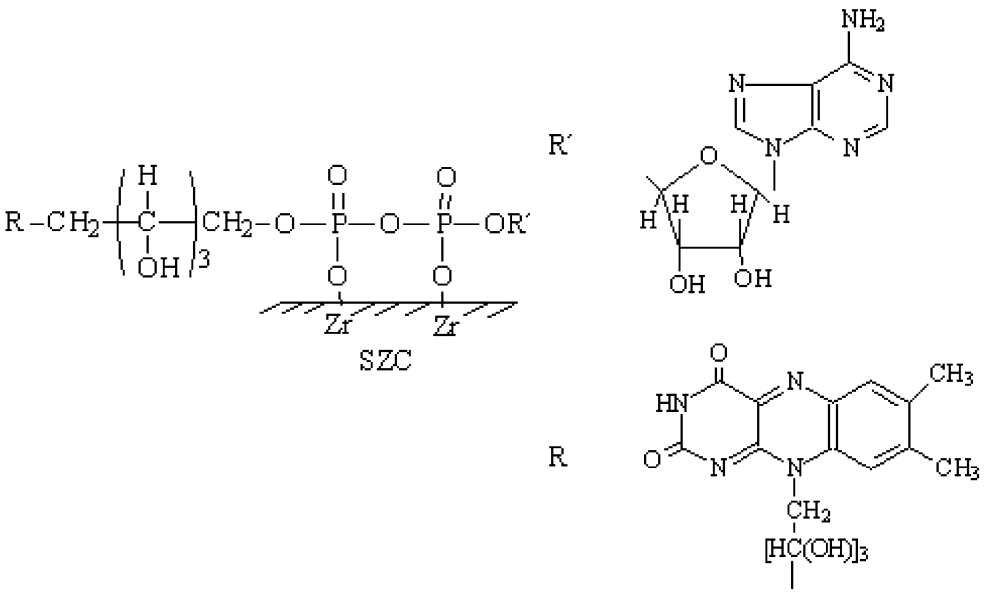


Fig. 2 Schematic representation of FAD immobilized on the SZC surface

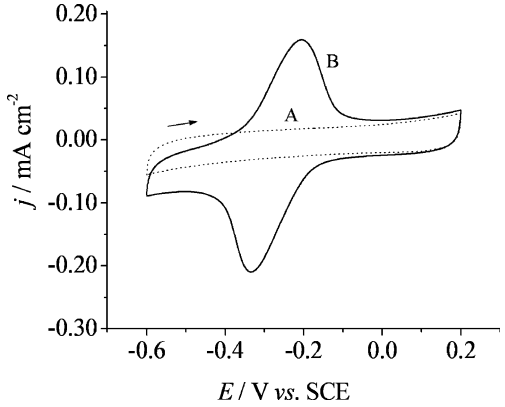


Fig. 3 Cyclic voltammograms obtained for: **a** bare SZC electrode and **b** on SZC/FAD electrode, in 0.1 mol L^{-1} KCl solution, pH 4, at a sweep rate of 5 mV s^{-1}

drolyzed TEOS solution, followed by an additional small amount of the aqueous acid solution. The mixture was stirred and allowed to rest. The solvent was evaporated until gelation, and the obtained xerogel was ground to a fine powder. It was exhaustively washed with bidistilled water and ethanol and, finally, dried under vacuum.

Preparation of the SZC carbon ceramic electrode and modification with FAD

About 12 mg of the dried and powdered SZC was pressed at a pressure of 2.5×10^3 kg cm^{-2} in a disk format. The pressed disk presenting an 8-mm diameter was glued at the end of a glass tube with the same external diameter and 15 cm length. The electrical contact was made by a copper wire, and pure graphite powder paste was inserted inside the glass tube [34]. The electrode modification was achieved by immersing the electrode into a 1.0×10^{-3}-mol L^{-1} FAD solution for 15 h. The FAD phosphate group reacts and adheres to the SZC surface resulting in a surface-modified electrode. The electrode surface is rinsed with deionized water before using.

Trasmission electron microscopy

Images of high-resolution transmission electron microscopy (HRTEM) were obtained on a JEOL JEM-3010 with 0.17-nm resolution, operating with a voltage of 300 kV. The fine-powdered SZC material was dispersed in isopropyl alcohol and submitted to an ultrasound bath during 10 min, and the suspension was deposited on a copper grid, previously coated with a thin film of carbon (approximate thickness of 3 nm).

Electrochemical measurements

Electrochemical measurements were carried out with a conventional three-electrode electrochemical cell. A platinum wire acted as the counter electrode, and the working electrode was a SZC CCE. All the potentials were measured and referred to the saturated calomel reference electrode (SCE). The cyclic voltammograms of the adsorbed FAD were recorded, usually between −0.6 and +0.2 V in 0.1 mol L^{-1} KCl solution free of oxygen. The solution pH was adjusted by adding HCl or NaOH solution. Amperometric measurements were performed by applying a fixed potential of −0.410 V. Finally, bromate and iodate anions in the appropriate concentration were added to detect them by voltammetry and amperometry.

Results and discussions

Characteristics of the material

To obtain information about the degree of dispersion of ZrO_2 particles in the SZC matrix, it was necessary to heat at 1,273 K under a nitrogen atmosphere to observe the crystalline ZrO_2 phase. For as-prepared samples, ZrO_2 is amorphous and therefore unobservable by the HRTEM technique.

Figure 1a shows the HRTEM image for SZC heated at 343 K under vacuum (0.13 Pa), and the observed fringes at

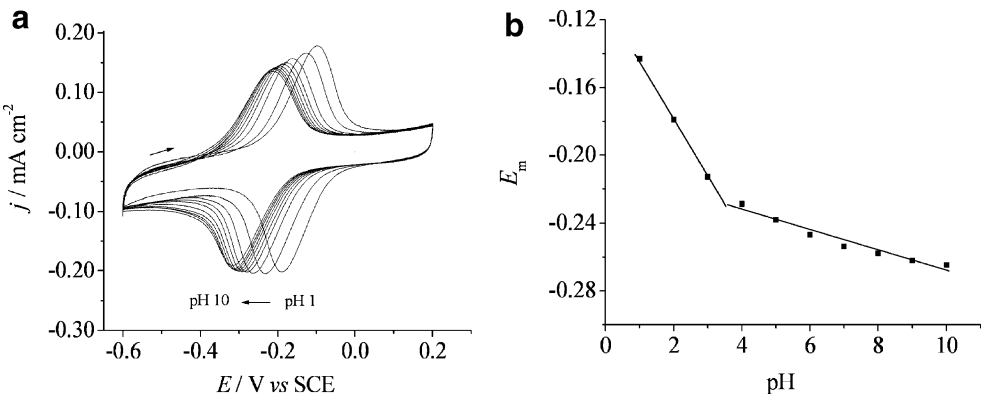


Fig. 4 **a** Variation of E_m of SZC/FAD as a function of solution pH, obtained in 0.1 mol L^{-1} KCl solution at a sweep rate of 5 mV s^{-1}. **b** Plot of E_m vs. solution pH

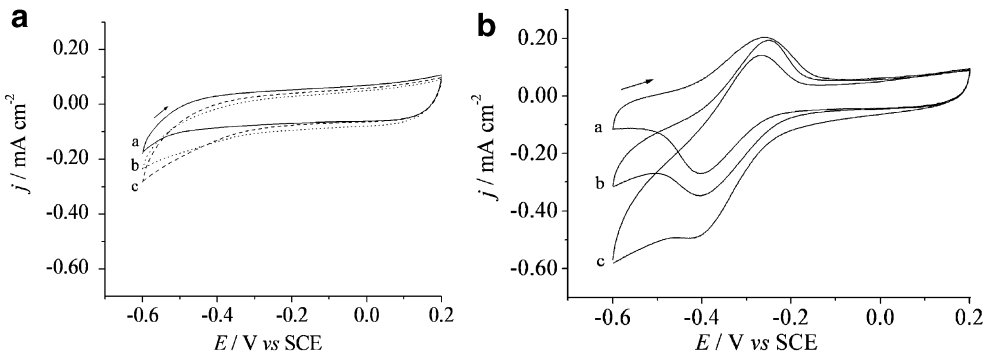


Fig. 5 **a** Cyclic voltammograms obtained with SZC electrode. *a* Immersed in the solution in absence of analyte; *b* solution containing $[BrO_3^-]=5\times10^{-3}$ mol L^{-1}; *c* solution containing $[IO_3^-]=5\times10^{-3}$ mol L^{-1}. **b** Cyclic voltammograms obtained with SZC/FAD electrode: *a* immersed in the solution in absence of analyte, *b* solution containing $[BrO_3^-]=5\times10^{-3}$ mol L^{-1}, *c* solution containing $[IO_3^-]=5\times10^{-3}$ mol L^{-1}. In **a** and **b**: solution of KCl 0.1 mol L^{-1}, pH 4.0, and a scan rate of 10 mV s^{-1}

0.26 and 0.34 nm of the nanoparticles in the micrograph are due to the crystalline phase of graphite [35]. According to the X-ray diffraction pattern (figure not shown), these two distances correspond to the (002) and (101) planes, respectively. For this sample, the HRTEM presented in Fig. 1b shows the image obtained by mass contrast, where ZrO_2 appears as darker particles, in comparison to the graphite, which is more transparent. In Fig. 1c, for the sample heated at 1,273 K, both ZrO_2 and graphite crystalline particles are clearly observed, where the larger one corresponds to the ZrO_2 phase. SiO_2 remained as an amorphous phase. The X-ray diffraction patterns obtained from this heated material is shown in Fig. 1d where peaks marked (2θ in degree, [hkl]) with *g* (graphite) and *z* (ZrO_2) refers to: (a) *g*=25.8 [002], 42.2 [100], 44.5 [101]; (b) *z*= 30.0 [101], 34.8 [002], 49.7 [002].

According to these data, it is noted that ZrO_2 particles are highly dispersed in the SZC matrix. The active centers are the ZrOH groups present on the surface of the matrix (heated at 343 K), and they are the responsible to link with the phosphate groups of FAD through the P–O–Zr bond.

Electrochemistry

The electrical conductivity of the material SZC was obtained following a procedure previously described [34]. The obtained pressed disk presented a conductivity of 18 S cm^{-1}, and then it was used to prepare the electrode as described above in the experimental part. After that, it was immersed in a FAD solution. Since this compound possesses phosphate groups, which normally have good affinity for the ZrOH groups, present on the SZC pressed disk surface, an efficient immobilization of the FAD on the electrode surface could be obtained [35]. The immobilization of this species may occur through the Z–O–P linkage, as shown in Fig. 2:

Figure 3 shows the cyclic voltammogram obtained with SZC and SZC/FAD electrodes in the solution saturated with argon. In contrast to the unmodified CCE, clear anodic and cathodic peaks were registered for the FAD-modified CCE. A well-defined redox couple with a midpoint potential of $E_m=-0.270$ V vs. SCE ($E_m=(E_{pa}+E_{pc})/2$), where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respec-

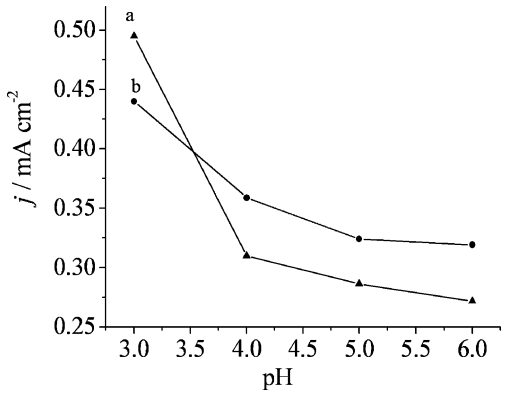


Fig. 6 Cathodic peak current for SZC/FAD in presence of 5.0×10^{-3} mol L^{-1} of **a** IO_3^- and **b** BrO_3^- obtained in 0.1 mol L^{-1} KCl solution at solutions' pH between 3.0 and 6.0 and scan rate of 10 mV s^{-1}

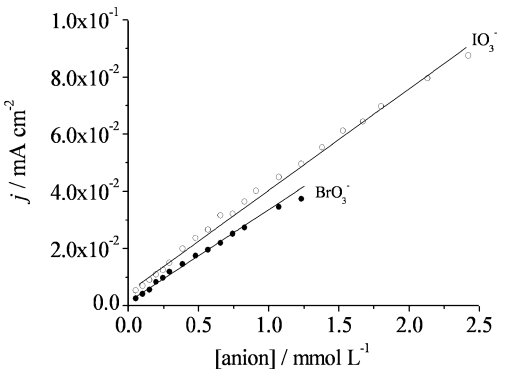


Fig. 7 Plot of current densities against concentration of bromate and iodate, obtained by chronoamperometry on SZC/FAD-modified CCE. Applied potential of −0.41 V and solution pH 4.0

Table 1 Analytical parameters of SZC/FAD electrode for detection of BrO_3^- and IO_3^- at pH 4.0

Analyte	Linear response range, mol L^{-1}	r^2 (n)	Detection limit, μmol L^{-1}
BrO_3^-	4.98×10^{-5}–1.23×10^{-3}	0.997 (14)	2.33
IO_3^-	4.98×10^{-5}–2.42×10^{-3}	0.998 (21)	1.46

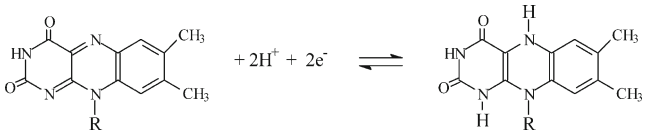
tively, is observed for the SZC/FAD-modified electrode. This value is similar to those found for FAD adsorbed on TiO_2-modified carbon fibers [24] and silica gel-modified zirconium oxide [36]. No decrease in the peak current was observed after many repeated cycles, suggesting that FAD is strongly adsorbed on the SZC electrode surface. The surface concentration of electroactive species Γ_c was estimated to be 2.21×10^{-8} mol cm^{-2} by the following equation [37].

$$Q = nFA\Gamma_c$$

where Q is the background-corrected charge obtained by integrating the area under the anodic peak, A is the electrode geometric surface area, and the other symbols have their usual meaning. It should be pointed out that the calculated surface coverage is an effective attribute (per cross-section of the electrode) and does not reflect the real number of FAD molecules per surface area of the exposed zirconium oxide.

The variation of E_m with the solution pH showed to be dependent between 1 and 4, while between pH 4 and 10, E_m becomes virtually independent of pH (Fig. 4).

This is not expected because it is supported that in the redox process of flavins, two protons and one or two electrons are involved [38–40]. These dependences are quite different from the electroactivity of flavins in solution: 60 mV/pH for 6.5≥pH≥10.5 and 30 mV/pH in the range of pH between 6.5 and 10.5 [41]. The first inflection point is attributed to the pK_a for the deprotonation of N-1 of the reduced flavin (the fully reduced hydroquinone form), and the second inflection point is due to the pK_a for the deprotonation of the oxidized isoalloxazine ring N-5 (the oxidized quinone form) [41], which has been explained by the FAD redox reaction:



The electrocatalytical reduction of bromate and iodate by SZC/FAD-modified electrode

To evaluate the electrocatalytic activity of the SZC CCE modified with FAD toward bromate and iodate reduction, cyclic voltammograms were obtained in the absence (Fig. 5a) and presence of these species (Fig. 5b). A cathodic peak current is observed at −0.410 V vs. SCE. These results demonstrated that the SZC/FAD-modified electrode electrocatalytically reduces BrO_3^- and IO_3^- an in aqueous solution (Fig. 5b).

The results presented above show that the SZC/FAD-modified CCE in acidic solutions had an electrocatalytic reduction activity for BrO_3^- and IO_3^- that was pronounced directly through the redox couple occurring at a potential of −0.41 V vs. SCE.

As both anions are strong oxidants at acidic conditions, the effect of pH on the potential of BrO_3^- and IO_3^- reduction was examined over the pH range between 3 and 6. A decrease in the reduction current density for BrO_3^- and IO_3^- is observed as the solutions' pH increase from 3.0 up to 6.0 (Fig. 6).

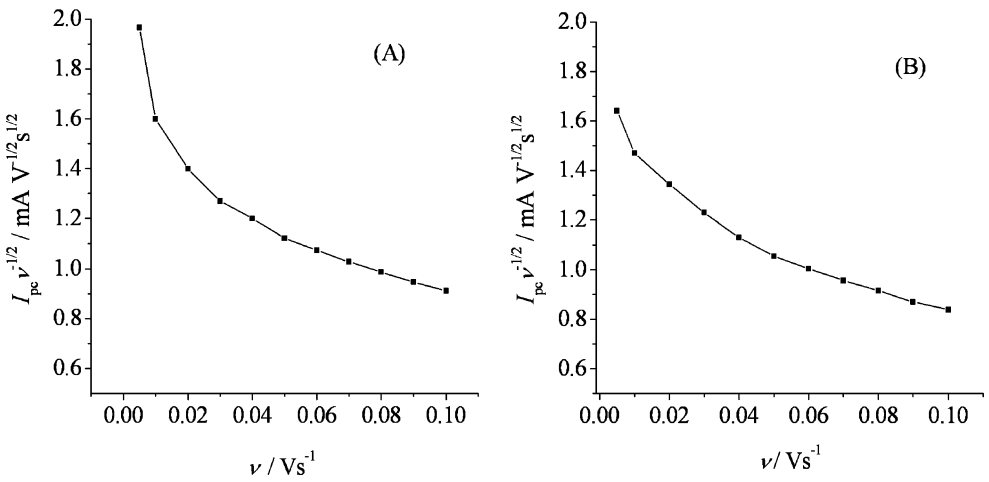


Fig. 8 Variation of the scan rate-normalized current ($I_p/\nu^{1/2}$) with a scan rate on the SZC/FAD-modified electrode in solution containing 5.0×10^{-3} mol L^{-1} bromate (**a**) and iodate (**b**). The experiments were performed in 0.1 mol L^{-1} KCl solution at pH 4.0

The reduction of both anions in acidic solutions can occur according to the reactions:

$$BrO_3^- + 6H^+ + 6e^- \rightleftarrows Br^- + 3H_2O$$
$$IO_3^- + 6H^+ + 6e^- \rightleftarrows I^- + 3H_2O$$

The chronoamperometric behavior of the SZC/FAD electrode was examined in the presence of bromate and iodate. The response time of the SZC/FAD-modified electrode was very fast for BrO_3^- and IO_3^-, i.e., about 0.5 s (figure not shown), and presented a straight line with correlation factors r^2=0.997 and 0.998, respectively (Fig. 7).

The results obtained from amperometric measurements are summarized in Table 1. This behavior shows that the SZC/FAD-modified CCE is a useful amperometric sensor for the determination of bromate and iodate.

Additional information about bromate and iodate reduction on the modified electrode surface was obtained by analyzing the catalytic current from the cyclic voltammograms. According to Andrieux and Sevéant [42], a theoretical model for the catalytic current I_p depends on the potential scan rates ν as follows:

$$I_p = 0.496FAC_o^* D^{1/2}(Fv/RT)^{1/2}$$

where C_o^* is the substrate concentration, D represents the diffusion coefficient of the substrate, F is the Faraday constant, and R and T are the gas constant and temperature, respectively. Furthermore, a catalytic system behaves as a totally irreversible system controlled by diffusion for large values of kinetic parameters (i.e., high value of the catalytic rate constant, k) [42, 43]. First, a plot of the catalytic current I_p vs. the square root of the potential scan rate, $\nu^{1/2}$, was plotted (figure not shown) suggesting that the process is controlled by mass transport. However, a deviation from the linearity for higher scan rates is clearly verified, suggesting a kinetic limitation. Second, a plot of the sweep rate-normalized current $I_p/\nu^{1/2}$ vs. the sweep rate (Fig. 8) exhibited the characteristic shape of the EC_{cat} process for bromate and iodate. The profiles of the curves (B) and (C) show that the catalytic current are still present in higher scan rates, suggesting good reaction rates between immobilized FAD and bromate and iodate. It is also clearly observed that the reduction reaction rate for iodate is about three times faster than that observed for bromate in the present system.

Conclusions

The SZC electrode was modified by immersing into a FAD solution and resulted in SZC/FAD, where the chemical species is bonded to the surface through Zr–O–P bonding. Furthermore, this electrode was used for the electrocatalytic reduction of bromate and iodate. The reduction reactions occurred at a cathodic peak potential of −0.41 V vs. SCE, and changes of the solutions' pH between 3.0 and 6.0 showed a decrease in substantial current densities for higher values of pH. The reduction current densities for bromate and iodate, at a fixed pH of 4.0, were linearly dependent over a wide range of concentrations. These studies indicated that the SZC/FAD-modified electrode can be used as an amperometric sensor for BrO_3^- and IO_3^-.

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