Study of a Cobalt-Based Surface Modified Glassy Carbon Electrode: Electrocatalytic Oxidation of Sugars and Alditols

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Abstract

Sugars and alditols undergo an electrocatalytic oxidation in alkaline solution at cobalt-oxide-based glassy carbon (Co/GC) electrodes. The catalytic deposit was investigated by cyclic voltammetry and scanning electron microscopy (SEM). It is pointed out that, at relatively low coverage of cobalt, two main redox processes, $Co^{II} \rightarrow Co^{III}$ and $Co^{III} \rightarrow Co^{IV}$, are observed in 0.2 M NaOH. The redox behavior of the Co/GC electrode is strongly dependent on hydroxide ion concentration, and no electrocatalytic activity is observed at pH lower than 11.5. Under voltammetric conditions the modified electrode exhibits a *non-Nernstian* potential/pH shift (-88 ± 3 mV per pH unit). A reasonable explanation of the *E*/pH behavior in alkaline solution is given and an oxidation mechanism of Co^{II} to Co^{III} is proposed in terms of hydrous cobalt oxides. No detrimental effects on the electrocatalytic oxidation of polyhydric compounds are observed in the presence of high acetonitrile concentrations (up to 40%). Inspection by SEM of the cobalt-based deposit evidenced the presence of grain-like microcrystallites on the glassy carbon surface.

Keywords: Electrocatalysis, Sugars, Cobalt, Modified electrodes

1. Introduction

In the last few years copper [1–5], ruthenium [6–10], nickel [11–13], and cobalt [14] based glassy carbon and carbon paste electrodes have attracted considerable attention, mainly because of their analytical application as stable amperometric detectors in flowing streams. Several chemically modified electrodes (CMEs) made with inorganic films and their electroanalytical use have been reviewed by Cox et al. [15]. High valence metal oxides and/or hydroxides of Cu^{III}, Ni^{III}, Ru^{IV}/Ru^{V}, and Co^{III}/Co^{IV} seem to be very effective as oxidizing agents of recalcitrant substrates in basic media [16–19]. Recently, it was also shown that cobalt-oxide-based glassy carbon (Co/GC) electrodes can be used in liquid chromatography (LC) and flow injection analysis (FIA) with electrochemical detection, allowing a sensitive determination of carbohydrates at low and fixed potentials [14]. The Co/GC electrode is prepared by droplet evaporation of a Co^{II} solution on a glassy carbon substrate and the detection system takes advantage of the high valence species of cobalt formed at positive potentials in alkaline solution. In this respect, stable Co^{III} species on the Co/GC electrode was identified by X-ray photoelectron spectroscopy (XPS), while under conditions of electrochemical detection, the occurrence of Co^{IV} was also invoked in order to account for the significant enhancement of the anodic current observed at potentials more positive than +0.35.

In this article, we provide additional evidence of Co^{IV} involvement in the electroxidation process of organic compounds. Detailed analysis revealed that the redox behavior is strongly dependent on cobalt loading levels. Thus, scanning electron microscopy (SEM) was used to examine the distribution and morphology of the cobalt-based deposit on the glassy carbon substrate. The strategy for electrode modification adopted here offers some advantages over massive metal electrodeposition on common carbon substrates. First of all, the surface of the bulk electrode is rapidly passivated in alkaline solutions with a noticeable increase in electric resistance. Secondly, it seems that the dispersed catalytic sites provide a greater electrocatalytic efficiency compared to bulk metal electrodes [13]. Thirdly, the modification procedure herewith used is very simple and allows the combination of several stoichiometric ratios of transition metals such as Ni, Co, Cu, Ru, and Ag to enhance the oxidation rate of scarcely electroactive compounds. Very recently, several transition metal oxides supported on a graphite substrate have been prepared by pyrolytic decomposition of metal nitrates [20]. These heat-treated modified electrodes exhibit high catalytic activity toward nitrite ion reduction and oxidation in ClO_4^- solutions at pH 2. Interestingly, also in this case it has been pointed out that the catalytic current became greater at lower amounts of catalyst loadings.

In order to characterize further the role of electrochemically generated higher valence cobalt oxides and oxyhydroxides and, particularly, the current enhancement obtained in the presence of polyhydric compounds, a series of cyclic voltammetry (CV) experiments were performed in alkaline solutions. The catalytic activity of Co/GC electrodes was also verified in aqueous solution plus acetonitrile (MeCN), a well-known organic modifier utilized for high performance liquid chromatographic separations of complex mixtures. Interestingly, the addition of MeCN to the supporting electrolyte does not significantly affect the oxidation capability of the modified electrode for the electrochemical oxidation of carbohydrates and alditols.

2. Experimental

2.1. Reagents

All the solutions were prepared from deionized, double distilled water. Sodium hydroxide pellets, $Co(NO_3)_2 \cdot 6H_2O$ (Carlo Erba, Italy), carbohydrates, and alditols (Aldrich Chemical Co.) were used without further purification. Dilute sodium hydroxide solutions were prepared from carbonate-free 50% NaOH. Due to the slow decomposition of carbohydrates in alkaline media, stock solutions were prepared daily, just prior to measurement. Test solutions of compounds were prepared by diluting with hydroxide solution appropriate volumes of stock solutions. All other reagents used were reagent grade or equivalent.

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2.2. Apparatus

Cyclic voltammetry was performed by an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat interfaced to an IBM compatible personal computer using the 270 Electrochemical Analysis Software (EG&G, PAR) for data acquisition. All experiments employed a three-electrode cell with a saturated Ag/AgCl reference electrode and a platinum wire auxiliary electrode.

Flow injection experiments were conducted with a Varian Model 2510 pump and a Rheodyne Model 7125 injection valve with a 10-μL sample loop. The amperometric detection was performed at an EG&G PAR Model 400 electrochemical detector equipped with a dual glassy carbon thin-layer cell assembled in parallel-adjacent configuration. The flow rate of carrier electrolyte was 1.0 mL/min. All experiments were run at 22 ± 1 °C.

Scanning electron micrographs were obtained by a Cambridge Stereoscan microscope (Mod. 250 Mk2).

2.3. Working Electrodes

Glassy carbon plates (Sigradur K, 10 × 10 × 2 mm) used for SEM investigation were obtained from HTW Hochtemperatur-Werkstoffe GmbH (Meitingen, Germany) while glassy carbon electrodes (4 mm in diameter) used in cyclic voltammetry were purchased from EG&G (PAR). Before the modification procedure, the glassy carbon surface was polished with an abrasive slurry on polishing microcloth (PAR), sonicated in concentrated nitric acid, and thoroughly rinsed with distilled water. Cobalt-based glassy carbon electrodes were prepared as previously reported [14]. Briefly, 5 μL of a 50 mM cobalt(II) nitrate solution was deposited on the glassy carbon electrode and allowed to evaporate in an air-oven at ca. 60 °C. The modified electrode was then cycled between −0.3 and 0.7 V for ca. half an hour at 100 mV/s until a steady voltammetric profile was reached.

The surface concentration of cobalt electrocatalytic sites (Γ_{Co}) was evaluated at low scan rate (5 mV/s) by integration of the charge (Q_A) under the anodic wave centered at 0.18 V and corresponding to the Co^{II}/Co^{III} oxidation process. By the relationship $\Gamma_{Co} = Q_A/(FA)$, where A is the nominal area of glassy carbon electrode and F is Faraday's constant, the surface loading of cobalt catalyst entrapped on the GC surface was estimated [21]. It is assumed that all the cobalt redox sites are electroactive on the voltammetric time scale.

3. Results and Discussion

3.1. Electrochemistry of Co/GC Surface Modified Electrodes

The actual processes occurring at the Co/GC electrode in alkaline solution are relatively complex because several oxidation states of cobalt and a variety of oxides and hydroxides are involved, such as CoO, $Co(OH)_2$, Co_3O_4, CoOOH, and CoO_2, which are also strongly influenced by hydration effects [22]. Figure 1 shows the cyclic voltammograms of two cobalt-based modified electrodes having different cobalt loadings (Γ_{Co}). Two main redox processes are recognizable both at relatively low (Fig. 1A) and high (Fig. 1B) Γ_{Co}. Peaks I–I′ are attributable to the redox couple Co^{II}/Co^{III}, while the increase in the anodic and cathodic currents above 0.40 V (peaks II–II′) is probably due to the Co^{III}/Co^{IV} redox couple [23, 24]. The first transition occurs at a potential consonant with the [Co(1,10-phenanthroline)]$^{2+/3+}$ redox couple in basic media using a GC unmodified electrode ($E_p^A = 220$ mV vs. Ag/AgCl, $\Delta E_p = 60$ mV at 0.020 V/s and 2 mM of [Co(1,10-phenanthroline)]$^{2+}$ in 0.15 M NaOH). As pointed out earlier [14], the predominant species formed at peak I is the Co^{III} oxyhydroxide, (i.e., CoOOH or its equivalent hydrated oxide, $Co_2O_3 \cdot xH_2O$) [25]. The ill-defined redox transition II–II′ is particularly evident only at high scan rates (see Fig. 1A) and/or in strongly alkaline solution. According to Burke et al. [24] the oxidation process II involves the formation of CoO_2 (see Sec. 3.2). The voltammetric behavior of the Co/GC electrodes is essentially similar in alkaline solution prepared with sodium, potassium, or lithium hydroxide.

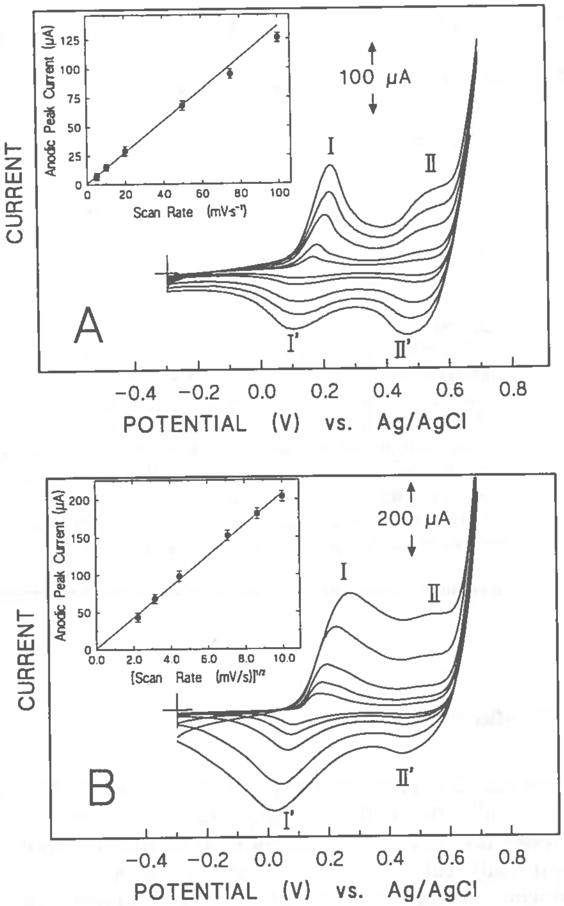

Fig. 1. Cyclic voltammograms at Co/GC electrodes in 0.20 M NaOH non-degassed solution. Cobalt loadings: A) $\Gamma_{Co} = 9.2 \times 10^{-9}$ mol/cm^2, B) $\Gamma_{Co} = 9.5 \times 10^{-8}$ mol/cm^2. Plots of the anodic peak current against v and $v^{1/2}$ are also shown (insets). Coverages were measured from the anodic charge above the base line current at 5 mV/s. Scan rates: A) 10, 20, 50, 75, and 100 mV/s; B) 5, 10, 20, 50, and 100 mV/s.

At relatively low cobalt coverage the voltammograms are asymmetrically shaped, suggesting a slow electron transfer between catalytic sites and the glassy carbon electrode. An example is depicted in Figure 1A ($\Gamma_{Co} = 9.2 \times 10^{-9}$ mol/cm^2), which exhibits a linear plot of the anodic peak current vs. scan rate, v, up to ca. 60 mV/s (see Fig. 1A, inset). Usually, this behavior is expected for a reactant confined to the electrode surface [21]. The anodic (cathodic) peak is shifted with scan rate towards more (less) positive potential values with an increasing peak separation (ΔE_p) from 60 mV to 130 mV at $v = 10$ and 200 mV/s, respectively. Further and significant alterations in the symmetry of the voltammetric waves are observed at higher cobalt loadings. Probably this behavior indicates that the rate at which oxycobalt sites are oxidized and re-reduced is kinetically controlled [26, 27]. Figure 1B shows the cyclic voltammograms at different scan rates of a Co/GC electrode exhibiting a catalyst loading of 9.5×10^{-8} mol/cm^2. In this case, the anodic peak current is proportional to $v^{1/2}$ at least up to 100 mV/s, as illustrated in the inset of Figure 1B, while peak separation exhibits a more pronounced increment indicative of a more resistive deposit.

The coverage of cobalt catalytic sites can be varied either by changing the concentration of Co^{II} solution used to modify the glassy carbon surface or after prolonged use of the modified electrode in alkaline solution. To calculate cobalt loadings, the geometrical cross section of the glassy carbon electrode was considered in place of the real surface area. The latter is obviously affected by the roughness of the graphitic support and by the density and morphology of the cobalt-oxide deposit, hence, in this context the comparison between cobalt loadings purely reflects the charge under the Co^{II}/Co^{III} oxidation peak evaluated at a low scan rate.

3.2. Electrocatalytic Oxidation of Sugars and Alditols at a Co/GC Electrode

Figure 2 shows cyclic voltammograms at a Co/GC electrode in the presence of 2.4, 4.8 and 16.5 mM glucose (curves a, b, and c, respectively) in 0.20 M sodium hydroxide, along with the run in blank NaOH solution (solid line). Millimolar solutions of glucose give rise to an increase in the anodic current and a decrease in the cathodic. Such behavior is what would be expected for an electrocatalytic oxidation process. At about 0.4 V the extent of both the oxidation increase and the reduction decrease is proportional to the glucose concentration. Notably, in the presence of relatively high glucose concentrations, the anodic peak corresponding to the Co^{II}/Co^{III} oxidation process is slightly shifted to more positive values (curve c) whereas the corresponding cathodic peak disappears, indicating that the electrochemically generated Co^{III} and/or Co^{IV} species are rapidly reduced in the presence of a high concentration of substrate. This aspect is more pronounced at low scan rates. A similar electrocatalytic behavior was observed for the oxidation of other sugars and alditols.

Although the nature of the catalytic deposit cannot be easily controlled, as confirmed by SEM investigation (see below), the electrocatalytic effectiveness of the Co/GC electrodes is always preserved at all cobalt loadings, showing good stability and high sensitivity to the oxidation and detection of carbohydrates and alditols [14]. This may be related to the fact that the electrocatalytic process is confined to the outermost film of cobalt catalytic sites.

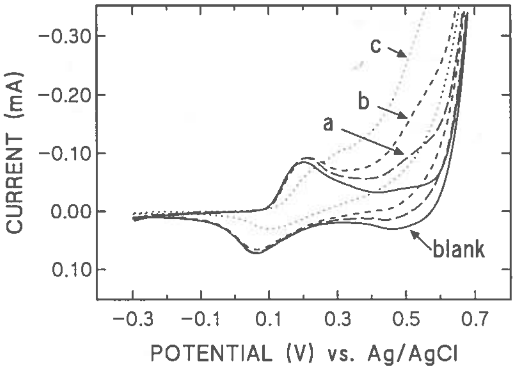

Fig. 2. Cyclic voltammograms at a Co/GC electrode in 0.20 M NaOH before (blank) and after addition of glucose, 2.4 mM (a), 4.8 mM (b), and 16.5 mM (c). Scan rate was 10 mV/s.

In accordance with previous studies on the cobalt metal electrode in alkaline solution [23, 24], the significant enhancement of the oxidation of polyhydric compounds occurring at a Co/GC electrode can be attributed to the catalytic capability of high-valence cobalt species formed under anodic polarization. Based on the anodic oxidation of organic substrates such as amines, alcohols, and carbohydrates at nickel-based electrodes [28–30], and supposing that in the present case a similar process takes place, the following mechanism may be considered, which proceeds via the formation of Co^{III}/Co^{IV} oxides and hydroxides [31]:

$$\mathrm{CoO} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{CoOOH} + e^- \tag{1}$$

$$\mathrm{CoOOH} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{CoO_2} + e^- \tag{2}$$

$$\mathrm{CoO_2} \longrightarrow \mathrm{CoO} + \tfrac{1}{2}\mathrm{O_2} \tag{3}$$

$$\mathrm{Co^{III,IV}} + \text{Substrate} \xrightarrow{\text{—rds—}} \mathrm{Co^{II}} + \text{Radical intermediates} \tag{4}$$

$$\text{Radical intermediate} \longrightarrow \text{Products} + (n-1)\,e^- \tag{5}$$

Here, OH$^-$ represents the ion inserted or extracted in the course of the redox transitions (see Eqs. 1 and 2). Once formed, the trivalent oxyhydroxide, CoOOH and tetravalent oxide, CoO_2, act as strong oxidizing agents of substrates in solution. At more positive potentials than 0.6 V, oxygen gas evolution takes place through Equation 3. The Co^{II} species formed through Equation 4 are re-oxidated via Steps 1 and 2. The overall reaction proceeds according to an electrocatalytic mechanism in which the rate determining step (rds) is given by Step 4, and reaction intermediates rapidly react, leading to decomposition products. In agreement with this scheme there is the following experimental evidence [14]: i) XPS characterization of the cobalt deposit on the glassy carbon surface held in NaOH solution under anodic polarization revealed the presence of Co^{III}, probably as CoOOH; ii) hydrodynamic voltammograms obtained by flow injection experiments in addition to cyclic voltammetry of glucose and other substrates at Co/GC electrodes also suggest an involvement of the Co^{IV} species, at least at potentials more positive than 0.45 V, because in that region a further enhancement of the oxidation current occurs; iii) the catalytic response is strongly dependent on NaOH concentration (see Sec. 3.3).

3.3. Effects of pH

It is well known that an alkaline medium is required for enhancing the electrocatalytic activity of transition-metal-based electrodes such as nickel [11–13, 16, 17], copper [1–5], ruthenium [6–8], and cobalt [14, 18]. A series of cyclic voltammograms of a Co/GC electrode obtained at different pH values are shown in Figure 3. A significant displacement of the main redox couple (I–I′) occurs on changing pH, regardless of cobalt loading. Peak heights are progressively attenuated on lowering the hydroxide ion concentration and disappear almost completely at pH lower than 11. Plots of the anodic and cathodic peak potentials vs pH exhibit negative slopes equal to -88 ± 3 and -92 ± 3 mV per pH unit, respectively (Fig. 3, inset), i.e., values close to $3/2\,(2.303\,RT/F)$ at 25 °C, rather than the Nernstian 59 mV value. The adsorption of intermediate hydroxyl radicals, which is pH dependent, has been invoked to account for these unusual potential/pH dependences [32]. Here,

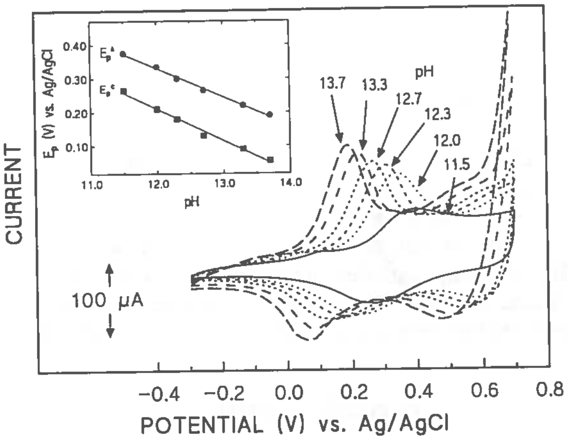

Fig. 3. Effects of pH on cyclic voltammograms obtained at a Co/GC electrode ($\Gamma_{Co} = 2.7 \times 10^{-8}\,\mathrm{mol/cm^2}$) in a solution of constant ionic strength (1.0 M NaOH + $NaNO_3$). Scan rate was 50 mV/s. The inset shows anodic and cathodic (E_p^A, and E_p^C) peak potentials vs. pH.

however, a different and more reasonable approach will be considered. The *non-Nernstian* behavior of the Co/GC electrode is not unique and similar dependences are reported by Burke's group for iridium [33–35], gold [36], iron [37] and nickel [38] electrodes in strongly alkaline solutions. These authors suggested the first successful approach which accounts for the apparent non-Nernstian *E*/pH shift. The key point of this approach is to consider the cobalt-based deposit in terms of hydrous oxides instead of an anhydrous system. By analogy with nickel [38] and other hydrous transition metal oxides, characterized by extended bridging, the first redox process of the Co/GC electrode may be rewritten as

$$[\mathrm{Co^{II}O}\cdot(n+1)\mathrm{H_2O}] + \tfrac{1}{2}\mathrm{Na^+} + \tfrac{3}{2}\,\mathrm{OH^-}$$

$$\rightleftharpoons [\mathrm{Co^{III}OOH}\cdot\tfrac{1}{2}(\mathrm{OH^-})\cdot\tfrac{1}{2}(\mathrm{Na^+})\cdot n\mathrm{H_2O}] + \mathrm{e^-} + \mathrm{H_2O} \qquad (1')$$

where the hydrated oxyhydroxides species are regarded as weakly cross-linked chains with the cobalt ion octahedrally coordinated. Equation 1′ is in agreement with the observed (3/2)(2.303 RT/F) slope and is equivalent to the corresponding Reaction 1 formulated in terms of anhydrated oxide species as indicated by XPS results [14]. Generally, the hydrous oxide layer is regarded as a porous gel or polymer in which an extensive cross-linking between polymer chains is inhibited by coordinated water molecules. In turn, the relatively open structure strongly influences the rate of electron transfer of metal-oxide electrodes [33, 34] and might explain the slow electron transfer kinetics observed at the Co/GC electrode.

The extent of the catalytic oxidation current as a function of pH for a representative mono-, di- and trisaccharide, such as glucose, lactose and maltothreose, respectively, is summarized in Table 1. The response was evaluated in CV experiments at 0.50 V because of the better signal-to-noise ratio observed in flow-through amperometric detection at that potential. Comparison of responses obtained under the same experimental conditions indicates that the catalytic current of glucose is greater than those of lactose and maltothreose, which both exhibited very similar responses. At pH lower than 11.5 no catalytic current was noted for all examined carbohydrates. This electrochemical behavior is consistent with an electrocatalytic oxidation process which mainly occurs at highly basic solutions and takes place in the potential range where high oxidation states of cobalt are generated.

Table 1. Effect of pH on the current response of three sugars at the Co/GC electrode [a].

pH	*Current, [b] μA*		
	Glucose (5 μM)	*Lactose (5 μM)*	*Maltothreose (5 μM)*
11.5	64	38	37
12.0	96	39	52
12.3	110	47	68
12.7	157	59	72
13.0	207	74	78
13.3	261	95	98
13.7	305	142	138

[a] Molar solutions of constant ionic strength 1.0 M NaOH + $NaNO_3$. The third scan was recorded at each tabulated experiment; scan rate, 50 mV/s. [b] The analytical current was obtained in CV by subtracting the background current measured at the modified electrode in the supporting electrolyte from the anodic current evaluated at 0.50 V.

3.4. Effects of Acetonitrile on the Co/GC Electrode

Generally, the selectivity of liquid chromatographic separations can easily be enhanced by addition of organic modifiers to aqueous mobile phases. High-grade MeCN is often used in order to provide adequate resolutions of complex mixtures without detrimental effects on the detector response. When electrochemical detection is applied in LC, the use of organic modifiers in the mobile phase needs to be considered with care, since some electrode materials may be poisoned or the heterogeneous electron-transfer rate may be slowed down or even inhibited. Furthermore, large amounts of MeCN are not allowed when carbon paste chemically modified electrodes are used. In this situation a test was necessary to verify whether the Co/GC electrode retains its catalytic oxidation capabilities in the presence of MeCN.

The addition of MeCN to aqueous sodium hydroxide produces quantitative differences in the voltammetric profile of the Co/GC electrode. Figure 4 compares cyclic voltammograms recorded using the same Co/GC electrode in 0.20 M NaOH solution (solid line) and with an increasing amount of MeCN: 6%, 25% and 40%. Two revealing features can be observed in the voltammetric profiles as the MeCN percentage is raised; i) the anodic and cathodic peak currents are shifted towards less positive values, and ii) both anodic and cathodic peak currents are lowered in magnitude. When the acetonitrile concentration is increased to 40% by volume, ΔE_p exhibits only a 10% increase while both anodic and cathodic peak current decrease by as much as 50%. Although a more drawn-out voltammogram is recorded with the anodic peak current nearly

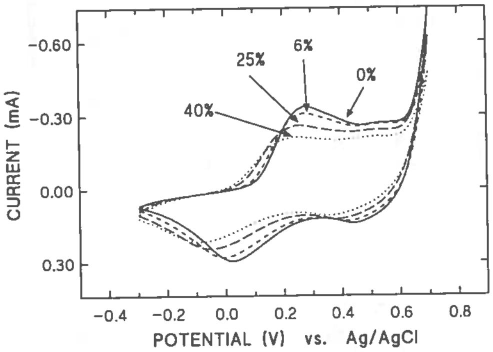

Fig. 4. Cyclic voltammograms at a Co/GC electrode recorded at 100 mV/s in 0.20 M NaOH aqueous electrolyte containing different amounts of acetonitrile (percentages by volume).

disappearing in the presence of a large amount of MeCN, the electrocatalytic oxidation of scarcely electroactive compounds (see below) is not suppressed at all. A probable explanation of the diminished background current may be due to decreased activity of the hydroxide ions in solution, which provokes more sluggish electron-transfer rates of the cobalt redox couples (Eqs. 1 and 2). It is worthwhile to note that the MeCN effects on the Co/GC were completely reversible. In fact, after removal of the modified electrode from the aqueous solution containing 40% MeCN and replacing the Co/GC electrode into the sodium hydroxide, CVs qualitatively similar to those seen before adding the organic modifier were again observed.

To monitor the effects of MeCN on the anodic oxidation of polyhydric compounds, some CVs were recorded in the presence of sorbitol (Fig. 5). Voltammograms A and B were obtained at a Co/GC electrode in 0.20 M NaOH solution and in the same supporting electrolyte plus 40% (v/v) of the organic modifier, respectively. Millimolar concentrations of sorbitol give rise to comparable responses in both electrolyte media, thus implying that electrocatalytic oxidation of sorbitol at the Co/GC electrodes is not suppressed in the presence of MeCN. In contrast, an attenuation of response was observed at Pt and Au working electrodes in alkaline solution plus MeCN [39, 40], probably as a consequence of a poisoning of the catalytic sites. It seems that at the Co/GC electrode the interactions between molecules of MeCN and oxycobalt redox centers are probably quite weak, thus in the presence of a substrate the organic modifier is easily displaced from the catalytic sites, allowing the electrocatalytic oxidation without apparent detrimental effects. This indicates that the substrate favorably competes with the molecules of MeCN to occupy the cobalt catalytic sites.

The good reactivity towards polyhydric compounds displayed at Co/GC electrodes in the presence of MeCN was also evaluated in FIA using a conventional thin-layer electrochemical cell. The responses obtained under constant-potential operation for glucose and sorbitol with 0.20 M NaOH (A and C) and 0.20 M NaOH plus MeCN (B and D) as carrier solutions are compared in Figure 6. The current response is not influenced by MeCN up to 40% (v/v), confirming that the organic modifier does not hinder the catalytic oxidation of the substrates.

3.5. Scanning Electron Microscopy Studies

In order to obtain more information on the nature of the catalytic film, the morphology of the cobalt-oxide deposit was investigated by scanning electron microscopy (SEM). Electron micrographs of a freshly prepared modified electrode (Fig. 7) were rather different from those held in sodium hydroxide solution before and after anodic polarization (Figs. 8 and 9). After each treatment the samples were thoroughly rinsed with pure water prior to being inspected by SEM. As expected, the glassy carbon surface of Co/GC electrodes appears profoundly modified. Apparently, two types of cobalt-based deposit (Fig. 7)

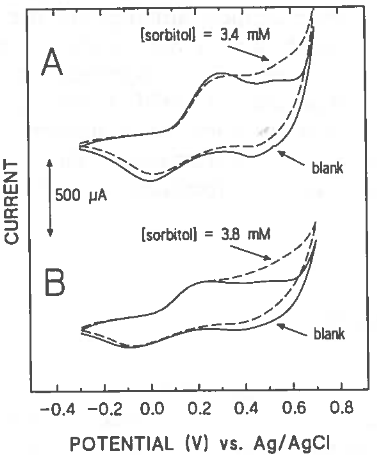

Fig. 5. Cyclic voltammograms for the oxidation of sorbitol at a Co/GC electrode. A) 3.4 mM in 0.20 M NaOH aqueous solution; B) 3.8 mM in 0.20 M NaOH + acetonitrile (40%, v/v). Scan rate was 100 mV/s.

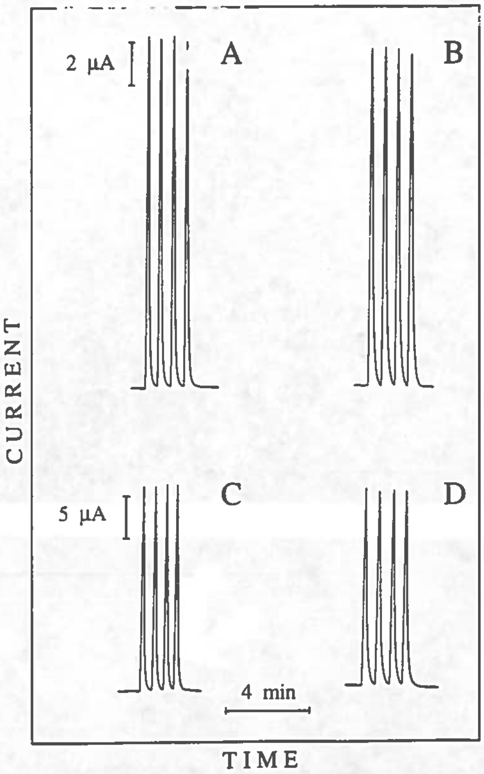

Fig. 6. Amperometric detection of 1×10^{-3} M glucose (A and B), and sorbitol (C and D) solutions in FIA obtained at a Co/GC electrode using 0.20 M NaOH (A and C) and 40 : 60 (by volume) acetonitrile/0.20 M NaOH (B and D) as carrier electrolyte. Applied potential, 450 mV (vs. Ag/AgCl); flow rate 1.0 mL/min.

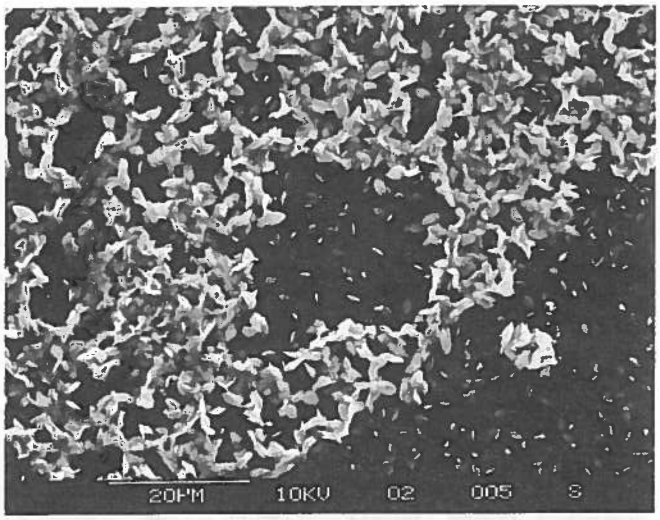

Fig. 7. SEM micrograph of GC surface that has been deposited with cobalt(II) nitrate, dried in an air-oven at 50 °C and washed with copious distilled water. Two different types of cobalt-based deposit are distinguishable: a more densely packed layer accompanied by many microcrystallites morphologically not well defined.

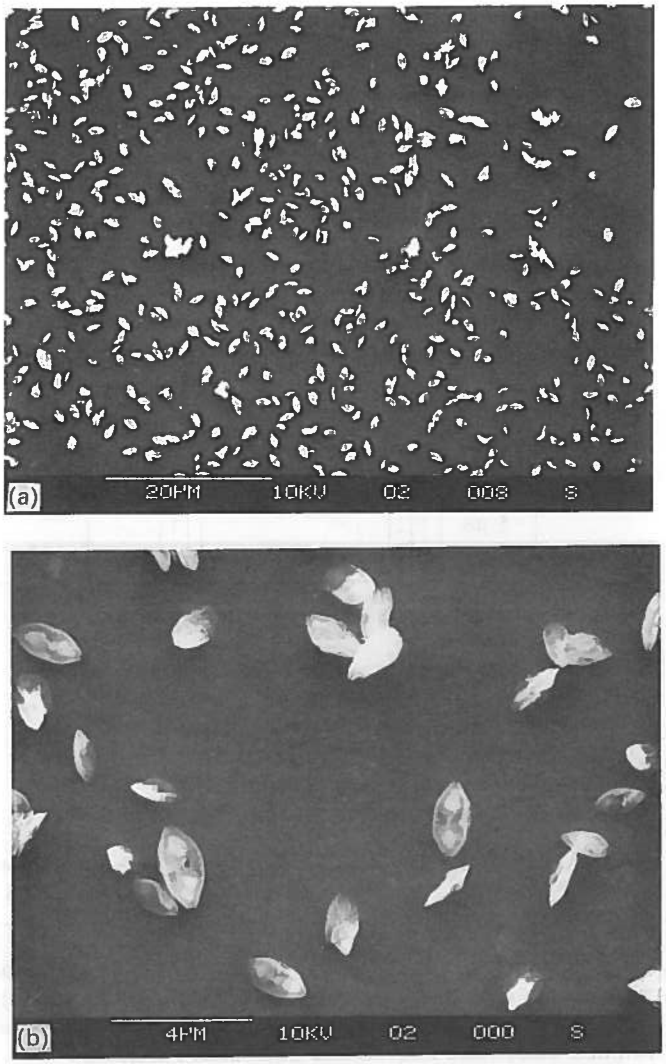

Fig. 8. A) Scanning electron micrograph of cobalt-based deposit on GC surface after immersion in 0.2 M NaOH solution for 14 h. In this image many grains evenly covering the surface are visible while the outermost layer has been almost all removed. B) Higher magnification of the same electrode assembly showing individual microcrystallites, many of which display grainlike morphology. Typical lengths of crystallites are about 1–3 μm.

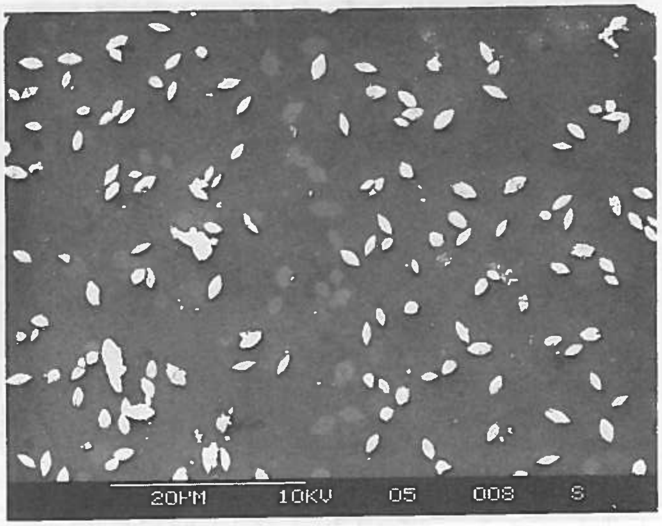

Fig. 9. Scanning electron micrograph of Co deposit on GC polarized at 0.50 V (vs. Ag/AgCl) for 8 h in alkaline solution.

are present: a relatively dense-packed outermost deposit and a grain-like evenly distributed microcrystallite. While the latter remains attached even after 14 h of immersion in alkaline environment, dissolution of the outermost deposit occurs (Fig. 8A). Since it is known that $Co(OH)_2$ is slightly more soluble than Co_3O_4 and CoOOH in alkaline solution [23], the outermost layer may be $Co(OH)_2$. The microcrystalline deposit remaining on the glassy carbon surface can be considered as the catalytically active component and although it is not chemically and morphologically well defined should consist of mixed oxides and hydroxides of cobalt [14].

Figure 8B shows a close-up of some microcrystallites randomly distributed on the glassy carbon surface with an average length of 1–3 μm. These microcrystallites may be regarded as an ensemble of cobalt-based microelectrodes lying on the GC surface. Well-separated arrays of microelectrodes are of particular interest because they offer amplification of the current compared to usual bulk electrodes, while retaining the advantageous properties of single microelectrodes, such as high mass flux, radial diffusion with steady-state current, and low ohmic potential drop [41, 42]. The characteristic steady-state voltammetric behavior of microelectrode arrays is dependent on the reciprocal distance between individual microelectrodes. In the case of microelectrode ensembles with insufficient spacing, the overlap of diffusion layers gives rise to a peak-shaped voltammetric profile. We suggest that in the case of Co/GC electrodes the situation may be considered as a random distribution of an array of microelectrodes with small separations between individual microscopic cobalt-based crystallites. Under the condition of relatively high density of microelectrodes, the microscopic model leads to the conclusion that the radial diffusion changes into linear. However, as far as we know, no microscopic models exist which deal with surface-confined redox processes, therefore, at present only a speculative rationalization of the voltammetric behavior of Co/GC electrodes is possible.

The surface of the Co/GC electrode immersed in NaOH solution and polarized at +0.5 V for 8 h exhibits a relatively low density of crystallites along with spots of deposit which seem tightly attached to the GC surface (Fig. 9). Thus, while numerous microcrystallites remain randomly distributed across the GC surface, the spots may be considered as residuals of the bulk deposit after the rinsing operation. Previously, we have evaluated that after 4 h of flow-through operation the electrode response was lowered by almost 7% [14]. Interestingly, examination of Figure 9 reveals that the morphology of the crystallites is better defined, although the deposit consists of rudimentary crystals with a not clearly recognizable shape. Immersion of the samples for a longer time (up to two months) in alkaline solution did not modify either the morphology or the average length of cobalt-based microcrystallites, thereby indicating that the growth of crystals is inhibited or alternatively is very slow under the experimental conditions used in this study.

4. Conclusions

It seems that high-valence oxidation states of cobalt, i.e., Co^{III} and Co^{IV}, are involved in the electrocatalytic oxidation of polyhydric compounds such as sugars and alditols. Electrolyte solutions with pH higher than 11.5 are necessary for analytical detection since the formation of surface catalytic sites is favored at relatively high hydroxide concentrations. An electrooxidation mechanism of the hydrous cobalt-oxide is proposed based on the peak potential dependence on pH, which accounts for the experimentally observed potential/pH shift.

Stable and sensitive catalytic oxidation has been obtained also in the presence of MeCN, thus suggesting that no poisoning of catalytic sites occurs at the Co/GC electrode. These findings make the analytical application of cobalt-based modified electrodes very attractive, especially in conjunction with chromatographic separations, where the use of MeCN as organic modifier is required to enhance column selectivity. Although micrographs of anhydrous cobalt oxides deposits taken under vacuum do not strictly represent the situation in solution, the main feature which arises from their analysis is that the strongly attached deposit is formed by grain-like microcrystallites, which may be considered the catalytic sites.

Further work needs to be done in order to gain deeper insight into the electrocatalytic oxidation mechanism of carbohydrates and alditols. By examining other substrates, we hope to characterize the major factors affecting the oxidation process on Co/GC electrodes.

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6. References

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