Cyanide and Phenol Oxidation on Nanostructured Co_3O_4 Electrodes Prepared by Different Methods

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Nanostructured cobalt oxide (Co_3O_4) electrodes were prepared by two different methods. The first one involved the synthesis of Co_3O_4 nanoparticles through a nanocasting route using commercial silica gel as a sacrificial template, and in the second one, the Co_3O_4 electrodes were prepared by thermal decomposition. The electrodes were characterized by different techniques, such as scanning electron microscopy, energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD), transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. EDX, XRD, and XPS show a characteristic spinel-type structure and a similar chemical composition for the two nanostructured cobalt oxides. However, the surface morphology is different. The electrochemical oxidation of cyanide and phenol in alkaline medium were used as test reactions. The electrocatalytic activity of the nanocrystalline Co_3O_4 electrodes for cyanide and phenol oxidation turned out to be highly dependent on the electrode preparation method.

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Conductive transition-metal oxides (TMOs) form important and diverse materials that have attracted much attention in many fields of technological interest because of their outstanding electronic, optical, magnetic, and catalytic properties.^{1,2} Tetragonal rutilelike TMOs containing noble-metal cations have been successfully applied as anode coatings [commonly known as dimensionally stable anodes (DSAs)] in a number of important electrolytic processes, such as oxygen and chlorine evolution and the electrochemical oxidation of biorefractory organic pollutants in wastewaters.³⁻⁹ However, spinel-type cobalt oxide-based coatings have emerged as a cheaper alternative to DSA electrodes in alkaline media because they possess long-term stability under anodic conditions, good electrical conductivity, and high electrocatalytic activity toward several reactions.^{2,3,10-16} In addition, these materials have found use in a host of solid-state applications, such as magnetic materials, electrochromic devices, Li-ion rechargeable batteries, etc.¹⁷⁻²¹

A substantial amount of information is now available on the crystallography, structural chemistry, thermal reactivity, and surface properties of both the precursors and thermally decomposed oxide materials. However, much less attention has been paid to the morphological- and size-controlled synthesis of nanoparticles, although it has been well documented that different electrical, optical, magnetic, and mechanical properties could be reached by reducing particle dimensions to the size of 1–100 nm.²²⁻²⁴

In spite of the lesser attention, cobalt oxide nanoparticles have been prepared by sol-gel,^{18,25} reduction/oxidation route,²⁶ homogeneous precipitation,²⁷ metalloorganic chemical vapor deposition,^{28,29} and nanocasting approaches.^{30,31} It is well known that the behavior of nanophase materials strongly depends on the shapes and sizes of the particles, which are thus a key factor in their ultimate performance and applications.

Different preparation processes often lead to materials exhibiting widely differing electrocatalytic behavior. Therefore, it is desirable to study the structural and chemical properties that may condition the electrochemical performance of nanocrystalline Co_3O_4 spinels formed with various synthetic methods in order to help establish a structure-performance correlation, which will guide us to newer materials design and the development of more sophisticated synthetic methods.³²

This work is aimed at the study of the influence of the method of preparation of Co_3O_4 electrodes on their electrochemical activity

toward cyanide and phenol oxidation in alkaline medium. The microstructure, composition, and crystalline state of the differently prepared Co_3O_4 electrodes have been investigated by different techniques.

Experimental

Synthesis of Co_3O_4 nanoparticles and preparation of the electrodes.—Two different synthetic methods have been applied for the preparation of Co_3O_4 nanoparticles.

Nanocasting route (XT).—In this way, spinel-type Co_3O_4 nanoparticles were synthesized by means of a nanocasting technique employing a commercial silica xerogel (Aldrich, 28,851-9) as the sacrificial hard template (pore-confinement method).³¹ The synthetic method was comprised of the following steps: (i) the pores in the silica were filled by a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) in ethanol, with a metallic cation concentration of 1.6 M, (ii) the sample was dried at 80°C and the cycle impregnation-drying was repeated up to three times in order to attain a high loading of cobalt nitrate, (iii) the impregnated silica was heat-treated in air up to 400°C (5°C/min) for 4 h, and (iv) the synthesized Co_3O_4 nanoparticles were obtained after dissolution of the silica framework with 2 M NaOH.

The electrodes were prepared by supporting the Co_3O_4 nanoparticles on different substrates, such as glassy carbon (GC) rods and Ti plates. To achieve an adherent layer, the nanoparticles were previously dispersed in Teflon (Aldrich)-water suspensions. The concentration of the Co_3O_4 nanoparticle dispersions was 25 mg mL⁻¹, and the Teflon content (as solid) was 33% of the total solid content (Co_3O_4 nanoparticles + Teflon). All dispersions were homogenized in an ultrasonic bath for at least 30 min. The suspension was then applied over the substrates and left to dry at room temperature. These samples are referred to as $\text{Co}_3\text{O}_4(\text{XT})$.

Prior to the deposition processes, the ends of GC rods (3 mm diam) (0.071 cm² of geometric area) were sandpapered and rinsed with distilled water, and Ti plates (0.5 × 0.7 × 0.05 cm, Goodfellow 99.6%) (0.7 cm² of geometric area) were degreased in acetone, etched in a boiling 10% oxalic acid solution for 1 h, and finally rinsed with distilled water.

Thermal decomposition route (TD).—In this way, the Co_3O_4 nanoparticles were obtained as thin films by TD of appropriate salt precursors onto a Ti support. The salt precursor was $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ACS Aldrich) dissolved in absolute ethanol (J. T. Baker). The metallic cation concentration was 0.5 M. Prior to the decomposition process, a Ti plate (1 × 1 × 0.05 cm, Goodfellow 99.6%) (2 cm²

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of geometric area) was degreased in acetone, etched in a boiling 10% oxalic acid solution for 1 h, and finally rinsed with distilled water. Details of the synthesis are described elsewhere, in which the precursor solution was spread over the Ti surface and calcined at 350°C.³³ These samples are designated as Co₃O₄(TD).

Characterization of the electrodes.—The surface texture of the electrodes was studied by scanning electron microscopy [(SEM) Hitachi S-3000N], which was coupled to a Rontec X-ray detector for energy dispersive X-ray (EDX) microanalysis. X-ray diffraction (XRD) measurements were performed using a Seifer JSO-Debye flex 2002 diffractometer with Ni-filtered Cu K α radiation (λ = 1.541 Å), a graphite monochromator, and a proportional pulse-height discriminator PW 1711/10. The profile intensities were measured step by step (0.05° in 2θ and step time 3 s) for a whole time of 3600 s for one scan. The position of the Ti peaks was used as an internal calibration for peak shift. Cell parameters were calculated by a computer program using the peak position relevant to the K α 1 monochromatic radiation, obtained by fitting the experimental range with a pseudo-Voigt function per peak plus a background line. Line-broadening analysis was performed in order to determine the volume-weighted average crystallite size. The optimized pseudo-Voigt function obtained for each diffraction peak was Fourier transformed and deconvoluted from the instrumental broadening by Stokes' method.

Transmission electron microscopy (TEM) images were obtained using a JEOL microscope (model no. JEM-2010). In order to obtain the required powder amount for the TEM analysis, a Co₃O₄(TD) electrode was scraped and in the case of Co₃O₄(XT), Co₃O₄ nanoparticles were used as prepared.

The X-ray photoelectron spectroscopy (XPS) spectra have been obtained in a VG-Microtech Multilab electron spectrometer, by using the unmonochromated Mg K α (1253.6 eV) radiation from a twin anode source operated at 300 W. Photoelectrons were collected into a hemispherical analyzer working in the constant energy mode at a pass energy of 50 eV. The base pressure in the analysis chamber was maintained at 5×10^{-10} mbar. The binding energy (BE) scale was referenced against the main C 1s line of adventitious impurities set at 284.6 eV. Peak energies are given to an accuracy of ± 0.2 eV. All XPS curves were fitted with mixed Gaussian (70%)-Lorentzian (30%) line shape functions after nonlinear Shirley background subtraction. Peak areas were normalized by using appropriate atomic sensitivity factors. The analyzed samples were conducting well enough to prevent surface charging effects.

Electrochemical measurements were carried out in a conventional three-electrode cell. The counter electrode was a platinum electrode, and the potentials are referred to a reversible hydrogen electrode (RHE) immersed in the same solution. The aqueous 0.1 M NaOH solutions were prepared from Merck p.a. and ultrapure water (Purelab Ultra from Elga-Vivendi, 18.2 M Ω cm). Sodium cyanide and phenol were also from Merck p.a. Cyclic voltammograms were obtained at a constant sweep rate of 20 mV s⁻¹. The current densities were calculated using the geometric area of the electrodes.

Results and Discussion

Structural properties of the electrodes of Co₃O₄ nanoparticles.—Figures 1a and b show the SEM images of a GC-supported Co₃O₄(XT) electrode. In this case, a uniform coating can be observed. It is worth emphasizing the lack of cracks and the presence of some roughness. When the Co₃O₄(XT) sample is supported on a Ti substrate (image not shown), a poorly adherent coating with large and deep cracks and aggregates of 1–10 μ m is observed. Therefore, this support has not been used in the electrochemical characterization and electro-oxidation of cyanide and phenol. However, a good adherence on GC support is obtained. Figures 1c and d show the morphology of a Ti/Co₃O₄(TD) electrode. The substrate is uniformly covered by the oxide, and the coating surface appears rather smooth and compact, especially when

Figure 1. SEM images of GC/Co₃O₄(XT) (a) $\times 500$ and (b) $\times 3000$, and Ti/Co₃O₄(TD) (c) $\times 500$, and (d) $\times 3000$ electrodes.

compared to those obtained by others onto Ti or Ni substrates via the thermal decomposition or sol-gel methods.³⁴ The magnified images point out the presence of small cracks and a high level of well-defined aggregates that provide the coating with a porous granular morphology at small scale. From the comparison of SEM results between both electrodes, it can be stated that the differently prepared electrodes present different surface morphologies.

The bulk composition of the Co₃O₄ coatings was determined by EDX microanalysis. Table I summarizes the experimental atomic composition and the O/Co values determined by EDX. From Table I, it can be concluded that both spinels possess a similar composition. It also appears that the amount of oxygen is higher than the theoretical one (O/Co > 1.33), pointing out the nonstoichiometry of this type of oxide. It has been reported earlier^{35,36} that the oxygen excess (Co₃O_{4+x}), which depends on the calcination temperature, is inherent for cobalt spinels. The excess oxygen is believed to be closely related to the electrocatalytic properties of structure defect sites in which a part of M⁺² and M⁺³ are converted into M⁺³ and M⁺⁴ ions, hence, increasing the electrical conductivity.³⁴

Figure 2 shows the X-ray diffractograms of Co₃O₄(XT) and Co₃O₄(TD) samples. For comparison purposes, Fig. 2 also includes the experimental diffraction patterns of the Ti substrate and the cobalt spinel powder standard. The XRD for Co₃O₄(TD) shows reflections at 2θ = 31.20, 36.90, 44.90, 59.55, and 65.30°, which could be indexed to a cubic spinel lattice belonging to the Fd3m space group. Both the position and the relative intensities of the above diffraction lines are in agreement with data corresponding to a pure Co₃O₄ phase (JCPDS-ICDD 9-418) (Fig. 2). Extra lines can be attributed to reflections at (002) and (103) planes of the underlying Ti substrate. The position, the width, and the relative intensity of the spinel-phase diffraction peaks of Co₃O₄(XT) are essentially indistinguishable from those of Co₃O₄(TD).

Table I. Atomic composition of the different nanostructured Co₃O₄ electrodes obtained by EDX.

Sample	Atomic composition (%)			
	Co	O	Ti	(O/Co) _{EDX}
Co ₃ O ₄ (XT)	33.51	66.49	—	1.98
Ti/Co ₃ O ₄ (TD)	35.24	63.25	1.51	1.79

Figure 2. XRD patterns of the titanium support, Co_3O_4 powder standard, and the $\text{Ti}/\text{Co}_3\text{O}_4(\text{TD})$ and $\text{GC}/\text{Co}_3\text{O}_4(\text{XT})$ electrodes.

Figure 3. TEM images of (a, b) $\text{Co}_3\text{O}_4(\text{TD})$ and (c, d) $\text{Co}_3\text{O}_4(\text{XT})$ powders.

206 The unit-cell parameter for the two samples has been calculated
207 according to Bragg's formula for face-centered-cubic crystals and
208 using the main indexed planes of the cobalt spinel, namely, (220),
209 (311), (400), (511), and (440). The resulting mean values of the
210 lattice parameter as well as the unit cell volume are shown in Table
211 II. The cell parameters of $\text{Co}_3\text{O}_4(\text{TD})$ and $\text{Co}_3\text{O}_4(\text{XT})$ are slightly
212 different from those reported for standard powders (JCPDS-ICDD
213 9-418 file). Overall, these results demonstrate that a pure cubic spi-
214 nel phase with virtually identical unit cell dimension is obtained
215 irrespective of the method of synthesis.
216 The average crystallite size, calculated according to the Scherrer
217 equation,³⁷ was also found to be very similar for both materials
218 (Table II). From XRD results, it can be stated that both preparation
219 methods lead to nanocrystalline Co_3O_4 coatings with similar pri-
220 mary particle size (i.e., the size of a single crystallite).³⁸ However,
221 whether or not the typical size of an agglomerate of crystallites is
222 within the nanometric domain still needs to be checked. This ques-
223 tion can be answered with the aid of TEM.
224 The TEM images of $\text{Co}_3\text{O}_4(\text{TD})$ and $\text{Co}_3\text{O}_4(\text{XT})$, respectively,
225 are shown in Fig. 3. In the case of $\text{Co}_3\text{O}_4(\text{TD})$, the particle size was
226 higher than the average crystallite size. $\text{Co}_3\text{O}_4(\text{XT})$ particles were of
227 ~ 10 nm, in close agreement with XRD data, and approximately
228 half the size of the $\text{Co}_3\text{O}_4(\text{TD})$ ones. A greater aggregation of
229 $\text{Co}_3\text{O}_4(\text{TD})$ particles can also be observed in Fig. 3. Differences in
230 particle size and aggregation suggest that the nanocasting method-
231 ology prevents nanoparticle growth. Taking into account that the
232 synthesis of the $\text{Co}_3\text{O}_4(\text{XT})$ nanoparticles occurs within the con-
233 fined space provided by the pores of the silica, the size of the Co_3O_4
234 nanoparticles will be limited by the size of these mesopores. The
235 analysis of the textural properties of the silica used as the template
236 shows that the porosity of this material is made up of mesopores
237 with a mean pore size of 12 nm. In consequence, the synthesised
238 nanoparticles should have a diameter around this value. This is cor-
239 roborated in three different ways: (i) The value obtained from the
240 XRD patterns is 11 nm (see Table II), (ii) the size deduced by TEM
241 inspection is ~ 10 nm (see Fig. 3d), and (iii) the nanoparticle diam-
242 eter obtained from BET surface area is ~ 9 nm. It can be seen that
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the values obtained for the size of the $\text{Co}_3\text{O}_4(\text{XT})$ nanoparticles are
very close and are similar to the size of the pores of the template.
XPS is a surface-sensitive probe that can provide valuable infor-
mation on the surface composition and allow distinction of the dif-
ferent local atomic environments (i.e., valence state and coordina-
tion) of an element. Because electrochemical charge-transfer is
essentially an interfacial phenomenon, an account of the surface
chemistry of Co_3O_4 would assist in the understanding of the role of
the method of preparation on the electrochemical behavior of these
electrodes.
The detailed XPS spectra of the Co 2p transitions are stacked in
Fig. 4. In order to study the effect of the support on the nanopar-
ticles, the spectrum of $\text{Co}_3\text{O}_4(\text{XT})$ on Ti is also included. The BE of

Figure 4. XPS spectra of the Co 2p region for $\text{Co}_3\text{O}_4(\text{XT})$ powders, the $\text{Ti}/\text{Co}_3\text{O}_4(\text{XT})$, and the $\text{Ti}/\text{Co}_3\text{O}_4(\text{TD})$ electrodes.

Table II. Lattice parameters and unit cell volume of the different nanostructured Co_3O_4 electrodes calculated from diffraction patterns.

Electrodes	Lattice parameter		Crystallite size (Å)
	a (Å)	V (Å ³)	
$\text{Co}_3\text{O}_4(\text{JCPDS})$	8.084	528.29	—
$\text{Co}_3\text{O}_4(\text{XT})$	8.091	529.67	110
$\text{Ti}/\text{Co}_3\text{O}_4(\text{TD})$	8.076	526.73	117

Table III. Photoelectron binding energies and peak energy gaps for the Co 2p photoemission line.

Electrode	Co 2p _{3/2}	fwhm	Δ _{split}	Δ _{sat}
Co ₃ O ₄ (XT)	779.9	3.1	15.3	10.4
Ti/Co ₃ O ₄ (XT)	779.9	3.2	15.2	10.0
Ti/Co ₃ O ₄ (TD)	779.9	3.0	15.1	10.2

Δ_{sat} = BE_{main peak} - BE_{sat}.

AQ: #6

the main Co 2p_{3/2}, the full width at half maximum (fwhm), the spin-orbit splitting (Δ_{split}), and the energy shift of the shake-up satellite (Δ_{sat}) are summarized in Table III.

The Co 2p spectrum of the Co₃O₄(TD) (Fig. 4, bottom) shows two broad and asymmetric main peaks separated by a spin-orbit splitting of 15.1 eV. The Co 2p_{3/2} component is centered at 779.9 eV (fwhm = 3.0 eV) and is accompanied by a shake-up satellite of low intensity shifted by 10.2 eV to higher BEs. The satellite is characteristic of paramagnetic Co(II) high-spin complexes. The general line shape of the Co 2p spectrum and the position of the above spectral features are all in close agreement with data reported earlier for pure Co₃O₄ crystals with a spinel structure.^{33-35,39} The spectral features for Co₃O₄(XT) are quite similar to those of the thermally prepared Ti/Co₃O₄ electrode, suggesting that both Co₃O₄ thin films present a similar surface chemical composition. The XPS results also evidence that there is no effect of the Ti support.

Table IV shows the surface atomic composition of the Co(III) and Co(II) contributions, obtained from the main Co 2p_{3/2} component deconvolution. The ratio Co(III)/Co(II) is similar in all the electrodes and close to 2, which is in agreement with the stoichiometric formula of the spinel-type cobalt oxide (CoCo₂O₄). Again, the route of synthesis does not affect the surface composition of the nanostructured spinels.

Electrochemical characterization of Co₃O₄ electrodes.— Figures 5a and b show the steady-state cyclic voltammograms for Ti/Co₃O₄(TD) and GC/Co₃O₄(XT) electrodes, respectively, in a 0.1 M NaOH solution, in the range of 0.9–1.67 V (RHE) at a scan rate of 20 mV s⁻¹. In order to compare both voltammograms, and due to the different oxide loads achieved by the different methods, the current density is corrected by the mass of Co₃O₄ deposited and the current axis is expressed as microamperes per centimeters squared per milligram.

In both cases, a typical response of a spinel-type Co₃O₄ electrode is observed, with two characteristic redox peaks in the voltammogram at a half-wave potential of 1.22 V (A₁/C₁) and 1.50 V (A₂/C₂), respectively, the first redox process being much more evident for the Ti/Co₃O₄(TD) sample. The sharp current rise occurring at potentials above the A₂ peak corresponds to the oxygen evolution reaction (OER). As previously reported in the literature,^{21,40,41} the two redox features below the OER can be assigned to Co(II) ↔ Co(III) and Co(III) ↔ Co(IV) surface transitions according to the following reversible half-reactions

Table IV. Surface relative abundance of Co(III) and Co(II) for the different nanostructured Co₃O₄ electrodes obtained by XPS analysis.

Electrode	Co 2p		
	Co(III)	Co(II)	Co(III)/Co(II)
Co ₃ O ₄ (XT)	67.3	32.7	2.05
Ti/Co ₃ O ₄ (XT)	67.4	32.6	2.06
Ti/Co ₃ O ₄ (TD)	67.4	32.6	2.06

Figure 5. Steady-state voltammograms for (a) Ti/Co₃O₄(TD) and (b) GC/Co₃O₄(XT) electrodes in 0.1 M NaOH solution at v = 20 mV s⁻¹.

yet the nature of the A₁/C₁ redox couple could also be related to⁴²

It should be stressed from XPS spectra (Fig. 4) that the absence of a strong satellite at 5.0–6.0 eV above the main Co 2p_{3/2} component allows the growth of CoO or Co(OH)₂ electrochemically inactive phases to be ruled out.³³ Accordingly, the surface redox transition at 1.22 V in Fig. 5 should be exclusively attributed to the reaction in Eq. 1.

The main difference between both voltammograms of Fig. 5 is the higher corrected current density obtained for the GC/Co₃O₄(XT) electrode in relation to the Ti/Co₃O₄(TD) sample. It suggests a higher active surface area per mass unit for the GC/Co₃O₄(XT), which is in accord with the fact that the nanoparticle size of Co₃O₄(XT) is smaller than that of Co₃O₄(TD), as shown in the previous section.

Electrochemical oxidation of cyanide.— The voltammetric response of Ti/Co₃O₄(TD) and GC/Co₃O₄(XT) electrodes was tested in cyanide-containing 0.1 M NaOH solutions with cyanide concentrations ranging from 100 to 5000 ppm. Figure 6 shows steady-state cyclic voltammograms for Ti/Co₃O₄(TD) (Fig. 6a) and GC/Co₃O₄(XT) (Fig. 6b) electrodes recorded at room temperature in a 500 ppm CN⁻ + 0.1 M NaOH solution at a scan rate of 20 mV s⁻¹.

In the case of Ti/Co₃O₄(TD), a slight increase in the anodic current in the region of the A₂ wave is recorded in a 500 ppm cyanide solution during the first forward scan (Fig. 6a). This current rise can be attributed to a small cyanide oxidation current. The first-scan cyanide oxidation current becomes larger as the cyanide concentration is raised up to 5000 ppm (Fig. 7). In the second and following cycles, both the anodic and cathodic currents passed in the A₂/C₂ potential region decay progressively below the values for the steady-state voltammogram in the background electrolyte. This behavior is exacerbated at concentrations of >500 ppm and suggests that the product of cyanide oxidation partially blocks the surface active sites, thus gradually inhibiting both the cyanide electro-oxidation process and the surface Co(III)/Co(IV) redox transition. Cyclic voltammograms recorded in a secondary cell filled with

Figure 6. Cyclic voltammograms for (a) Ti/Co₃O₄(TD) and (b) GC/Co₃O₄(XT) electrodes in 0.1 M NaOH + 500 ppm cyanide solution. Dashed line: steady-state voltammogram in 0.1 M NaOH solution at $v = 20 \text{ mV s}^{-1}$. Number indicates cycle number in the presence of cyanide.

cyanide-free background electrolyte, after withdrawal of the electrode from the working cell and thorough rinsing with ultrapure water, reveal that the surface remains blocked, and hence, the inhibiting oxidation product is irreversibly adsorbed.

In contrast, the behavior of GC/Co₃O₄(XT) is rather different. In this instance, the cyanide oxidation current is significantly enhanced in the potential region of the A₂ wave. The cyanide current falls slowly with the increasing number of cycles to achieve the steady state shown in Fig. 6b (solid line), which still remains higher than the blank voltammogram (dashed line). In addition, it should be emphasized that the cathodic peak C₂ is completely missing in the reverse sweeps.

Figure 7. Cyclic voltammograms for Ti/Co₃O₄(TD) electrode in 0.1 M NaOH + 5000 ppm cyanide solution. Dashed line: steady-state voltammogram in 0.1 M NaOH solution at $v = 20 \text{ mV s}^{-1}$.

Figure 8. Cyclic voltammograms for (a) Ti/Co₃O₄(TD) and (b) GC/Co₃O₄(XT) electrodes in 0.1 M NaOH + 1000 ppm phenol solution at $v = 20 \text{ mV s}^{-1}$; — 1st and 20th cycle; - - - steady-state voltammogram in 0.1 M NaOH solution.

In agreement with previous reports,¹⁶ the voltammogram in Fig. 6b suggests that cyanide is indirectly oxidized at GC/Co₃O₄(XT) electrodes by highly powerful oxidant Co(IV) surface species that are electrochemically generated within the A₂ wave region. The cyanide oxidation proceeds through an electrochemical-chemical (EC) two-step oxidation pathway that can be envisaged as follows

the overall process being the well-known cyanide oxidation reaction

The consumption of surface Co(IV) species by solution cyanide regenerates surface Co(III) species and accounts for the hindrance of the reversal of half-reaction (Reaction 2), thus explaining the absence of the cathodic C₂ peak.

From the voltammetric results described thus far, it follows that there exists a remarkable effect of the method of preparation of Co₃O₄ electrodes on the electrocatalytic activity toward cyanide oxidation. The improved electrocatalytic response toward cyanide oxidation of the GC/Co₃O₄(XT) electrode is probably a consequence of the higher active area of the nanostructured spinel obtained by the xerogel template method. Nevertheless, a size-induced increase of highly reactive corner or edge surface sites compared to plane sites and electronic effects derived from changes in the bandgap width and/or the occurrence of midgap electronic states above the valence band³⁸ should not be ruled out as additional factors.

Electrochemical oxidation of phenol.—Figure 8 shows the 1st and 20th voltammetric cycles, recorded between 0.9 and 1.67 V, for the Ti/Co₃O₄(TD) (Fig. 8a) and GC/Co₃O₄(XT) (Fig. 8b) electrodes in a 0.1 M NaOH solution containing 1000 ppm of phenol. In both cases, an increase in the current density above 1.3 V, peaking at 1.57–1.59 V [i.e., within the range of the Co(III) to Co(IV) transition], is observed during the first voltammetric scan. This current is associated with phenol electro-oxidation. As above, the phenol oxidation current is much higher in electrodes based on template-formed Co₃O₄ nanoparticles than in thermally prepared thin films. This may be a result of the higher effective surface area of the former electrodes. An additional side peak occurs at 1.46 V on GC/Co₃O₄(XT) electrodes. This feature is gradually better defined as the phenol concentration increases from 100 to 1000 ppm, but it appears as a barely discernible side shoulder on Ti/Co₃O₄(TD) electrodes, even at the highest phenol concentration studied (Fig. 8a).

On both electrodes, the current involved in the oxidation of phenol drops gradually with increasing number of cycles (Fig. 8). This inhibition process might be attributed to the electrode fouling produced by the formation of a nonconductive polymeric product coming from phenol oxidation that blocks the electrode surface.⁴³

The identification and assignment of the various anodic features to any particular phenol-involving oxidation process is difficult at the present time. The phenol electro-oxidation is known to be a complex process. The first step in phenol oxidation is believed to involve the formation of an adsorbed layer of phenoxy radicals on the surface. Such radicals remain on the electrode surface and then they are oxidized forming different products, such as quinones, aliphatic acids, carbon dioxide, dimers, and a surface polymeric film through coupling reactions involving adjacent phenoxy and dimeric radicals.⁴⁴ Indeed, the conditions for polymer film formation are known to be favorable in alkaline media.⁴⁵ The formation of the initial oxidation intermediates can proceed either through an unspecific direct electron transfer between the organic and the electrode surface or thanks to electrogenerated high-valent metal oxides that function as heterogeneous mediators.⁴⁶ As a first approach, we propose that the anodic prepeak corresponds to an unspecific direct electrolysis of phenol, which also occurs on platinum and GC electrodes at about the same potential value, and the peak within the potential window of the A₂ transition is related to a surface Co(IV)-mediated mechanism, as in the case of cyanide.

The much higher phenol electro-oxidation currents observed for the GC/Co₃O₄(XT) electrode, with the more defined unspecific phenol oxidation peak, indicate that again there exists a remarkable effect of the method of preparation of Co₃O₄ electrodes on the electrocatalytic activity toward phenol oxidation.

Conclusions

We report the fabrication of electrodes made up of Co₃O₄ nanoparticles synthesized through two different routes (i.e., nanocasting and thermal decomposition). Both materials exhibit a similar crystalline structure and chemical composition, typical of spinel structure. Differences between the samples are related to the morphology of the surface. Thus, Co₃O₄(XT) shows a more porous surface and a smaller particle size than Co₃O₄(TD).

The voltammograms for both samples also show a very similar profile, although the corrected current density of Co₃O₄(XT) electrodes is much higher than that of Co₃O₄(TD), which is indicative of a higher active surface area for the material obtained by the nanocasting route, which is in agreement with the increased surface roughness and the smaller particle size of this material.

In the case of thermally prepared Ti/Co₃O₄(TD) electrodes, a slight cyanide electro-oxidation is only observed during the first voltammetry cycle; however, cyanide electro-oxidation is clearly manifested on the GC-supported Co₃O₄(XT) electrode under the same experimental conditions. It is proposed that cyanide electro-oxidation involves an EC mechanism in which an electrogenerated powerful oxidant Co(IV) species is responsible for the chemical oxidation of cyanide. With regard to phenol electro-oxidation, the recorded corrected currents are also much higher for the electrodes fabricated with Co₃O₄(XT) nanoparticles rather than the Co₃O₄(TD) ones. At both electrodes, the oxidation of phenol seems to proceed with two anodic features, which are tentatively related to an unspecific direct electron transfer at low potential and a Co(IV)-mediated oxidation process at higher potentials. Irrespective of the type of electrode employed, the electro-oxidation of phenol appears to be accompanied by severe electrode inhibition most likely owing to the formation of an insulating polymeric film. The better performance of the GC/Co₃O₄(XT) electrode for both cyanide and phenol oxidations is clear evidence of the enormous influence of the preparation method of Co₃O₄ electrodes on its electrocatalytic activity.

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References

- P. A. Cox, *Transition Metal Oxides: An Introduction to Their Electronic Structure and Properties*, Clarendon Press, Oxford (1992).
- L. G. Tejuca, J. L. F. Fierro, and J. M. Tascon, *Advances in Catalysis*, Vol. 36, Academic Press, New York (1989).
- S. Trasatti, Editor, *Studies in Physical and Theoretical Chemistry*, Vol. 11, Elsevier Science, Amsterdam (1980/1981).
- S. Trasatti, *Electrochim. Acta*, **45**, 2377 (2000).
- F. Montilla, E. Morallón, A. De Battisti, and J. L. Vázquez, *J. Phys. Chem. B*, **108**, 5036 (2004).
- F. Montilla, E. Morallón, and J. L. Vázquez, *J. Electrochem. Soc.*, **152**, B421 (2005).
- P. Canizares, F. Martinez, M. Diaz, J. Garcia-Gomez, and M. A. Rodrigo, *J. Electrochem. Soc.*, **149**, D118 (2002).
- J. D. Rodgers, W. Jedral, and N. J. Bunce, *Environ. Sci. Technol.*, **33**, 1453 (1999).
- L. Szpyrkowicz, C. Juzzolino, and S. N. Kaul, *Water Res.*, **35**, 2129 (2001).
- E. B. Castro and C. A. Gervasi, *Int. J. Hydrogen Energy*, **25**, 1163 (2000).
- A. C. Tavares, M. A. M. Cartaxo, M. I. D. Pereira, and F. M. Costa, *J. Electroanal. Chem.*, **464**, 187 (1999).
- R. N. Singh, J. P. Pandey, N. K. Singh, B. Lal, P. Chartier, and J. F. Koenig, *Electrochim. Acta*, **45**, 1911 (2000).
- R. Boggio, A. Carugati, G. Lodi, and S. Trasatti, *J. Appl. Electrochem.*, **15**, 335 (1985).
- P. Cox and D. Pletcher, *J. Appl. Electrochem.*, **20**, 549 (1990).
- P. Cox and D. Pletcher, *J. Appl. Electrochem.*, **21**, 11 (1991).
- A. Stavart and A. Van Lierde, *J. Appl. Electrochem.*, **31**, 469 (2001).
- Y. Wang, C. M. Yang, W. Schmidt, B. Spliethoff, E. Bill, and F. Schüth, *Adv. Mater. (Weinheim, Ger.)*, **17**, 53 (2005).
- F. Švegl, B. Orel, M. G. Hutchins, and K. Kalcher, *J. Electrochem. Soc.*, **143**, 1532 (1996).
- P. Poizat, S. Laurelle, S. Grugeon, L. Dupont, and J. M. Tarascon, *Nature (London)*, **407**, 496 (2000).
- X. Wang, X. Chen, L. Gao, H. Zheng, Z. Zhang, and Y. Qian, *J. Phys. Chem. B*, **108**, 16401 (2004).
- L. Mendoza, V. Albin, M. Cassir, and A. Galtayries, *J. Electroanal. Chem.*, **548**, 95 (2003).
- A. Henglein, *Chem. Rev. (Washington, D.C.)*, **89**, 1861 (1989).
- L. E. Brus and J. K. Trautman, *Philos. Trans. R. Soc. London, Ser. A*, **353**, 313 (1995).
- A. D. Yoffe, *Adv. Phys.*, **42**, 173 (1993).
- F. Švegl, B. Orel, I. Grabec-Švegl, and V. Kaučič, *Electrochim. Acta*, **45**, 4359 (2000).
- Y. Ni, X. Ge, Z. Zhang, and H. Liu, *Mater. Res. Bull.*, **36**, 2383 (2001).
- X. Zhu, L. Liao, and Y. Chui, *Inorg. Chem. Ind.*, **34**, 1 (2001).
- D. G. Colombo, D. C. Gilmer, V. G. Young, S. A. Campbell, and W. L. Gladfelter, *Chem. Vapor. Deposition*, **4**, 220 (1998).
- D. Barreca, C. Massign, S. Daolio, M. Fabrizio, C. Piccirillo, L. Armelao, and E. Tondello, *Chem. Mater.*, **13**, 588 (2001).
- A. B. Fuertes, *J. Phys. Chem. Solids*, **66**, 741 (2005).
- T. Valdés-Solís, G. Marbán, and A. B. Fuertes, *Chem. Mater.*, **17**, 1919 (2005).
- R. Xu and H. C. Zeng, *J. Phys. Chem. B*, **107**, 12643 (2003).
- A. La Rosa-Toro, R. Berenguer, C. Quijada, F. Montilla, E. Morallón, and J. L. Vázquez, *J. Phys. Chem. B*, **110**, 24021 (2006).
- T. C. Wen and H. M. Kang, *Electrochim. Acta*, **43**, 1729 (1998).
- S. Angelov, G. Tyuliev, and Ts. Marinova, *Appl. Surf. Sci.*, **27**, 381 (1987).
- G. H. Li, L. Z. Dai, D. S. Lu, and S. Y. Peng, *J. Solid State Chem.*, **89**, 167 (1990).
- B. D. Cullity and S. R. Stock, *Elements of X-Ray Diffraction*, p. 170, Prentice Hall, Englewood Cliffs, NJ (2001).
- M. Fernández-García, A. Martínez-Arias, J. C. Hanson, and J. A. Rodríguez, *Chem. Rev. (Washington, D.C.)*, **104**, 4063 (2004).
- T. J. Chuang, C. R. Brundle, and D. W. Rice, *Surf. Sci.*, **59**, 413 (1978).
- R. Boggio, A. Carugati, and S. Trasatti, *J. Appl. Electrochem.*, **17**, 828 (1987).
- M. Longhi and L. Formaro, *J. Electroanal. Chem.*, **464**, 149 (1999).
- N. Fradette and B. Marsan, *J. Electrochem. Soc.*, **145**, 2320 (1998).
- R. Lapuente, F. Cases, P. Garces, E. Morallon, and J. L. Vazquez, *J. Electroanal. Chem.*, **451**, 163 (1998).
- M. Ferreira, H. Varela, R. M. Torresi, and G. Tremiliosi-Filho, *Electrochim. Acta*, **52**, 434 (2006).
- Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.*, **21**, 703 (1991).
- G. Fóti, D. Gandini, and Ch. Comninellis, *Curr. Top. Electrochem.*, **5**, 71 (1997).

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