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Iron(IV) in Layered Cobalt−Iron Oxide Formed by Electrochemical Oxidation

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Introduction

Layered double metal hydroxides belonging to the pyroaurite group (pyroaurite-type compounds, abbreviated PTCs) consist of positively charged trioctahedral metal hydroxide layers, $[M_a{}^{II}{}_{1-x}M_b{}^{III}{}_x(OH)_2]^{x+}$, with interlayers of charge-compensating anions and water molecules,[1,2] $[A_{x/n}yH_2O]^{x-}$, with $0.15 < x < 0.70$. Compounds with hydroxide layers of mono- and trivalent metal cations are also known,[3] and the possible existence of PTCs containing tetravalent cations (Si, Ti(IV), V(IV)) has been indicated.[4]

Recently we described the synthesis of a $Co^{II}Fe^{III}$−PTC with the composition $[Co^{II}{}_{0.678}Fe^{III}{}_{0.309}(OH)_2][(CO_3)_{0.140}yH_2O]$.[5] The blue variety of $Co(OH)_2$ also has a layered structure which on anodic oxidation transforms topotactically to the layered CoOOH.[6] Hence it is likely that the Co(II)-dominated $Co^{II}Fe^{III}$−PTC also can be oxidized electrochemically and still retain its layered structure. The oxyhydroxide formed by the electrochemical reaction will be described here with emphasis on the oxidation state of the cations.

Experimental Section

$Co^{II}Fe^{III}$−PTC was synthesized as previously described.[5] SnO_2-covered glass electrodes (4 × 4 cm) were prepared according to Mochel,[7] and the PTC was deposited on the electrodes by sedimentation from aqueous suspension. The films (2.5 g m^{-2}) were oxidized electrochemically at 25 °C in 0.1 M $NaHCO_3$ at 1300 mV vs SCE for 60 min. Material from several electrodes was collected, mixed and washed with water. The chemical composition of the product (CoFe−PTC_{ox}) was determined as previously described;[5] oxidation states were determined iodometrically on dissolution in HCl and are reported relative to Co and Fe. All analyses were carried out in triplicate.

X-ray diffractograms were obtained of intact films on the electrodes or by scanning unoriented powder samples. Differential thermal analysis (DTA) was carried out in a mixture of N_2 and O_2 gases with simultaneous detection of the water and carbon dioxide liberated.[8] Mössbauer spectra were obtained between 298 and 5 K using a constant acceleration spectrometer and a source of ^{57}Co in Rh. Isomer shifts are given relative to the centroid of the room temperature spectrum of α-Fe. Lorentzian line shape was assumed in fitting of the spectra, and doublets were constrained to have all parameters identical. It is assumed that all Fe sites have identical *f* factors. We were unable to obtain infrared or Raman spectra of the product, and thus no information on hydroxyls, carbonates, and water species could be obtained in this way.

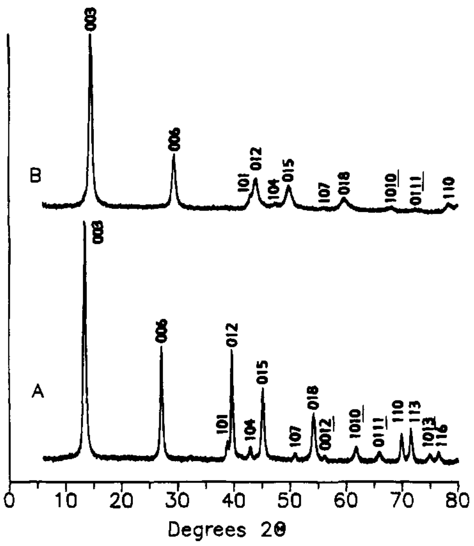

Figure 1. X-ray diffractograms: (A) starting material for electrochemical oxidations ($Co^{II}Fe^{III}$−PTC); (B) resulting oxidation product (CoFe−PTC_{ox}). (Co Kα radiation). Indices refer to a hexagonal cell.

Results and Discussion

On electrochemical oxidation the yellowish-brown color of the $Co^{II}Fe^{III}$−PTC becomes dark reddish-brown and turns black after a few minutes. The black material could not be reduced electrochemically. A similar behavior has been reported for the electrochemically produced CoOOH.[6,9] When oxidation of the solid ceased the current decreased to a stable value (2.2 A m^{-2}) determined by the rate of oxidation of water. Oxidation in nonbuffered electrolytes such as K_2SO_4 or KNO_3, or using a $SO_4{}^{2-}$ interlayered form of the $Co^{II}Fe^{III}$−PTC resulted in partly disintegration of the films probably due to lack of neutralization of the protons generated during oxidation of the hydroxide or electrolysis of water. The powder diffractogram of the CoFe−PTC_{ox} can be indexed on a hexagonal cell having lattice parameters $a = 0.2834$ nm and $c = 2.118$ nm, somewhat smaller than those for the original $Co^{II}Fe^{III}$−PTC ($a = 0.312$ nm, $c = 2.278$ nm) (Figure 1), but larger than those of anodically produced CoOOH ($a = 0.282$ nm, $c = 2.04$ nm).[6] Thus the overall structure of $Co^{II}Fe^{III}$−PTC is conserved during the anodic oxidation, with contraction in both the *a* and *c* axis directions indicating a decrease in mean cation radius and a decrease in the thickness of the interlayer. Also an increase in the width of the diffraction peaks is noted, indicating a decrease in crystallite size. The structure probably contains a number of oxo bridges and is related to that described for CoOOH with H^+ positioned between layers of $CoO_2{}^-$.[10,11] A gradual collapse in the *c* axis direction from 2.118 nm in the freshly oxidized sample was observed on drying over P_2O_5 until a minimum of 1.65 nm was achieved. For partly oxidized material (oxidation time 8 min) no intermediary 003 spacings between those of the original and the oxidized samples were observed, and at this stage all the iron is present as Fe(III) in the high spin state. This indicates that whole crystallites are uniformally transformed rather than gradually and that the change in unit cell dimensions mainly is correlated with the oxidation of the dominating cobalt cation.

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Table 1. Chemical Composition of CoFe$-$PTC$_{ox}$ and Its Precursor Phase

	wt %				
	Co	Fe	Na	CO_2	Ox/(Co + Fe)^a
Co^{II}Fe^{III}$-$PTC	35.46	15.31	0.00	5.50	0.00
CoFe$-$PTC$_{ox}$	37.70	16.14	3.39	2.23	1.10

^{a} Ratio between moles of I^- reduced in iodometrical analysis and moles of Co and Fe in the sample.

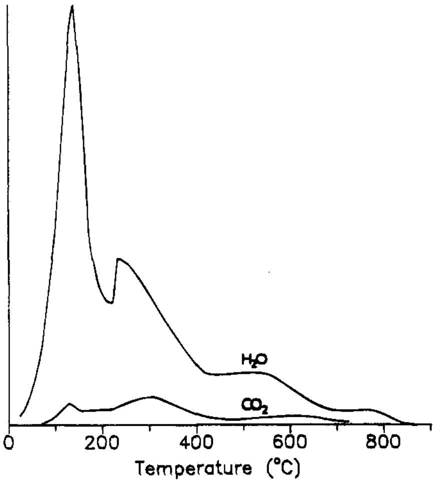

Figure 2. Water and carbon dioxide loss curves for CoFe$-$PTC$_{ox}$ during DTA.

The Co:Fe ratio (2.20:1) is unaffected following oxidation whereas Na is incorporated in the product as a counterion, demonstrating a net charge reversal of the octahedral layer (Table 1). The incorporation of alkali metal cations following oxidation has been observed for similar oxyhydroxides of Co,[6] Ni$-$Co, and Ni$-$Fe.[12,13] Different 003 spacings were observed when using different alkali metal electrolytes, indicating that the interlayer cation may influence the thickness of the interlayer. From the DTA results (Figure 2) the peak in water concentration at 140 °C is ascribed to loss of interlayer and adsorbed water. The peaks at higher temperatures on the water concentration curve are assigned to dehydroxylation in analogy to the Co^{II}Fe^{III}$-$PTC[5] showing the presence of hydroxy groups also in the oxidized product. The reactions in the temperature range above 200 °C are dominantly endothermic. CO_2 is lost over a wide range of temperatures with a maximum at approximately 300 °C. The origin of the CO_2 is not completely clear. It may be present as occlusion of gas formed in the highly acid interlayer from CO_3^{2-}. It was found that contrary to Co^{II}Fe^{III}$-$PTC, which dissolves instantaneously in dilute H_2SO_4 solutions, the CoFe$-$PTC$_{ox}$ dissolved very slowly even in 4 M H_2SO_4 as expected for oxides or (oxy)hydroxides of higher valent metals.

The iodometric analysis indicates that Co and Fe may have formal average oxidation states close to III and IV, respectively (Table 1). We therefore investigated the actual oxidation state of Fe by Mössbauer spectroscopy (Figure 3). The spectrum obtained at 298 K displays two absorption peaks which are interpreted to be the result of overlapping lines from a doublet (with peak positions at approximately -0.15 and $+0.55$ mm s^{-1}) and a singlet (with peak position at 0.14 mm s^{-1}). The spectrum obtained at 80 K reveals the same components. The singlet has isomer shifts of -0.14 and -0.06 mm s^{-1} at 298 and 80 K, respectively and a relative area of approximately 70% at both temperatures. The doublet has isomer shifts and quadrupole splittings of 0.40 and 0.70 mm s^{-1} and 0.48 and 0.71 mm s^{-1} at 298 and 80 K, respectively. All components have line widths of approximately 0.35 mm s^{-1}. The doublet displays parameters which are typical for Fe(III) high spin, e.g. coordinated to oxygen; but in comparison to that for the original Co^{II}Fe^{III}$-$PTC[5] the quadrupole splitting has increased significantly, indicating a more distorted coordination. The isomer shift for the singlet is significantly smaller than those commonly reported for Fe(III) high spin indicating that the oxidation state for 70% of the Fe is higher than III. The 12 K spectra display a singlet with increased line width, strongly overlapping the Fe(III) doublet. The broadening probably is due to incipient magnetic order and a spectrum obtained at 5 K indeed reveal that at least the major part of the Fe has ordered magnetically. The 5 K spectra is rather complex consisting of both very broad and rather sharp lines, and no detailed interpretation is offered. The overall behavior of the Fe in the oxidized product is similar to that observed for some perovskite-type oxides, which show spectra dominated by singlets due to an oxidation state close to IV at high temperature and at low temperature exhibit charge disproportionation into Fe(III) and Fe(V) and order magnetically.[14,15] For these compounds the absence of the Jahn$-$Teller-induced quadrupole splitting of the Fe(IV) high spin component at higher temperatures has been explained by the formation of a metallike delocalized σ^* band containing the e_g electrons and a symmetrical $t_{2g}{}^3$ configuration. The broadening of the absorption lines of the magnetically split components may be caused by several effects e.g. relaxation, distribution of hyperfine parameters (caused by occurrence of several non-discrete oxidation states or local structural variation). A rough estimation of the area of the sextet with hyperfine field of approximately 44 T (assigned to Fe(III)) indicates that it constitutes approximately 40% of the spectral area. Assuming that at 5 K all the Fe(IV) has disproportionated into the Fe(III) and Fe(V) states, we would expect that 35% would be present as Fe(III). Considering the approximate nature of this calculation, we

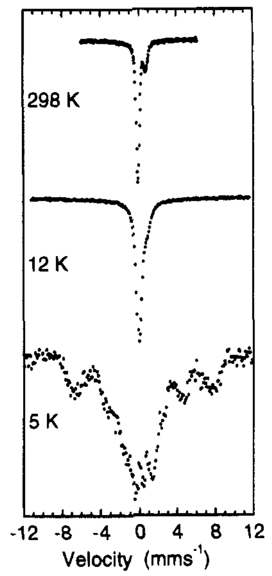

Figure 3. ^{57}Fe-Mössbauer spectra of CoFe$-$PTC$_{ox}$ at the indicated temperatures.

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consider this to be in good agreement with the estimated area of this component. Apparently the paramagnetic Fe(III) component observed in the high temperature spectra also remains paramagnetic at 5 K.

When CoFe–PTC_{ox} is stored in air and at room temperature, it was found that over a year-long period the relative intensity of the singlet decreased significantly whereas the intensity of the doublet increased. This shows that the high oxidation state is unstable, but the details of this reaction are unknown.

Based on the data presented above the composition of the PTC_{ox} may be calculated. The ratio between Fe(III) and Fe(IV) is determined from the relative areas of the components in the Mössbauer spectrum at 298 K, which in combination with the iodometric analysis gives the ratio between Co(III) and Co(IV). Assuming that no vacancies are present in the oxygen planes, electroneutrality is obtained by adjustment of the O:OH ratio. Hence the composition of CoFe–PTC_{ox} is $[Co^{III}_{0.496}Co^{IV}_{0.193}Fe^{III}_{0.093}Fe^{IV}_{0.218}O_{1.57}(OH)_{0.43}][Na_{0.159}(CO_2)_{0.055}(H_2O)_x]$, with $x = 4-5$ for air-dried samples. The electrochemical oxidation reaction may be divided into the following reactions: (i) oxidation of Co(II) to Co(III) resulting in unit cell contraction; (ii) oxidation of Fe(III) and Co(III); (iii) dissociation of OH groups due to increase in cation acidity, and neutralization of H^+ by interlayer CO_3^{2-} or HCO_3^- from the electrolyte; (iv) expulsion of CO_2 and adsorption of Na^+ in the interlayer.

Similar mixed oxyhydroxides, but of Ni with Co or Fe, prepared by hydrolysis of the corresponding substituted nickelates under strongly oxidizing and alkaline conditions have been reported.[12,13] These have been shown also to contain Co, Ni, or Fe with oxidation states above III. Hence Co(III,IV) appears not to be the only cation which may stabilize the tetravalent oxidation state of Fe in these oxyhydroxides.

The present work also shows that trioctahedral layers with all octahedral positions occupied by tri- or tetravalent cations are not inherently unstable. The phase transition induced by anodic oxidation is different from the oxidation of PTCs in air, resulting in spinel-type oxides with Fe in the trivalent state.