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The Electrochemical Oxidation: a New Way for Preparing Highly Oxidized Ferrites

J.-C. Grenier, A. Wattiaux, L. Fournes, M. Pouchard and J. Etourneau

Institut de Chimie de la Matière Condensée de Bordeaux, C.N.R.S., Château Brivazac, avenue du Dr. Schweitzer, 33608 Pessac, France

Abstract. The electrochemical oxidation is depicted as a novel and powerful route for preparing highly oxidized ferrites. The reaction is achieved at room temperature, in air, in alkaline solution (1M KOH or NaOH). This process has been used for preparing various new compounds and especially perovskite-type ferrites such as $SrMO_3$ (M = Fe or/and Co) or $Sr_2LaFe_3O_{9-\varepsilon}$. The characterization of the samples shows that they remain well crystallized after the electrochemical treatment and bulky oxidized. The reaction can be described as an intercalation process of oxygen atoms into the host lattice of the starting material. For instance, the chemical analysis as well as Mössbauer spectroscopy data of $SrFeO_3$ or of Sr_2FeCoO_6 reveal iron cations to be exclusively tetravalent. On the other hand, $Sr_2LaFe_3O_{9-\varepsilon}$ exhibits at decreasing temperature a disproportionation of the mixed valence of iron. Potentiostatic and galvanostatic experiments have shown that the amount of intercalated oxygen can be controlled and that the process is reversible. A mechanism involving the formation of O^- species that can diffuse inside the bulk of the material, is proposed.

1. INTRODUCTION

In the synthetic chemistry of oxides, obtaining highly oxidized materials requires high oxygen pressures and annealing at rather low temperatures, typically 400 to 700 °C. However, in the last two decades, other ways belonging to the field of the so-called 'Chimie Douce' have been investigated, which allowed to obtain metastable forms of highly oxidized materials. The first one that can be quoted is the chemical oxidation at room temperature, which uses strong oxidizing agents in solution such as MnO_4^-, BrO^- or ClO^- species [1, 2]. Solid-gas reactions with F_2, Cl_2 or NO_2 gases have also been successfully used at moderate temperatures (typically t < 400°C) [3-6]. In the field of the 'Chimie Douce', the electrochemical processes that use the electric potential as a 'driving force' instead of chemical agents appear very interesting preparation methods, especially in the intercalation chemistry [7]. For instance, they are well known for intercalating cations such as H^+, Li^+ or Na^+ whose ionic sizes are rather small in oxide host lattices, but oxidizing materials supposes to insert (or add) oxygen anions whose size is rather big ($r_{O^{2-}} \approx 1.40$ Å) since the oxide lattice is oxidized and collapses; therefore, such a reaction seemed quite doubtful. However, in 1990, we demonstrated for the first time the promising possibilities provided by the electrochemical oxidation in alkaline solution for preparing highly oxidized oxides by "Chimie Douce" at room temperature ; that was successfully achieved on La_2CuO_4 ceramics for which, surprisingly oxygen overstoichiometry and superconductivity were induced [8, 9]. Then similar experiments were repeated by several groups [10-12] ; we described here results more especially concerned with the electrochemical oxidation of some strontium ferrites $Sr_2Fe_2O_5$, Sr_2FeCoO_5 and $Sr_2LaFe_3O_8$.

2. EXPERIMENTAL AND ELECTROCHEMICAL REACTION

Electrochemical experiments were carried out at room temperature, in a solution of 1M NaOH or KOH, under air or nitrogen flow, in a two compartment cell, using a three electrode device. The working electrode is either a rotating disc electrode (500-5000 rpm) or a fixed electrode, the surface area of which can be large, which allows to prepare a big quantity of material. This working electrode is usually a pellet (density 80-85%) but it can be also a crystal or a thin film [13, 14]. Dense pellets (∅ 8 mm, thickness 2 mm, weight 0.4 g) were obtained from powders of the starting materials prepared by solid-state reaction.

Electrochemical reactions were carried out either at steady potential (E = 450 - 800 mV, *potentiostatic mode*) or at constant current intensity (I < 1 mA), *galvanostatic mode*). Typical (I,E) curves (Fig. 1) exhibit a current plateau before the oxygen evolution reaction occurring at high anodic potentials according to the reaction :

$$4\,OH^- \longrightarrow O_2\nearrow + 2\,H_2O + 4\,e^-,\ E_{th} = 0.303\ V/(Hg/HgO) \qquad (1)$$

This plateau is the signature of the oxidation process of the material which can be written as follows :

$$A_xM_zO_y + 2\delta\,OH^- \longleftrightarrow A_xM_zO_{y+\delta} + \delta\,H_2O + 2\delta\,e^- \qquad (2)$$

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According to the Nernst relation ($E = E_{th} + (RT/4F)\ln(a_{O_2}/[OH^-]^4)$), the oxygen activity in reaction *(1)* can be estimated: for usual applied overpotentials ($E_{appl.} - E_{th.} = \eta_{O_2} \approx 0.2$ V); it is equivalent, at room temperature, to very high oxygen pressures ($p_{O_2} \approx 10^{15}$ Pa), which might explain why such a reaction is achieved.

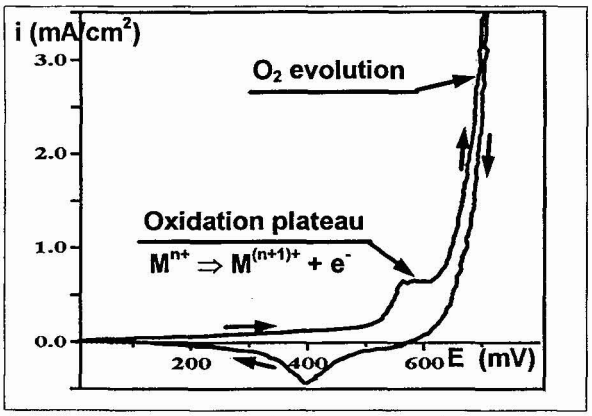

Fig. 1 Typical oxidation plateau observed in a cyclic voltammogram of an oxide

Accurately weighed amounts of $SrCO_3$, La_2O_3 and Co and Fe nitrates (of high purity) were dissolved in diluted nitric acid (HNO_3/H_2O = 1/1) and dried. So formed powder was slowly fired up to 1473 K and annealed for 48 h before quenching in air. Pellets were pressed under an uniaxial pressure of 2 MPa for 2 minutes and finally annealed for 2 h before quenching in liquid nitrogen. The final thermal treatment was : for $Sr_2Fe_2O_5$, 1273 K under a flow of argon, for Sr_2FeCoO_5, 1473 K in air and for $Sr_2LaFe_3O_8$, 1173 K in purified argon.

The characterization of samples was achieved by X-ray diffraction and chemical analysis using the Mohr's salt method. The as-prepared samples show the orthorhombic symmetry characterizing the brownmillerite-type or G-type structures as well as the expected oxygen stoichiometry. These structures represented in Fig. 2, are built up of 1 or 2 octahedral layers separated by a tetrahedral one in which oxygen vacancy rows can be clearly seen along directions equivalent to the $[110]_C$ of the cubic perovskite cell.

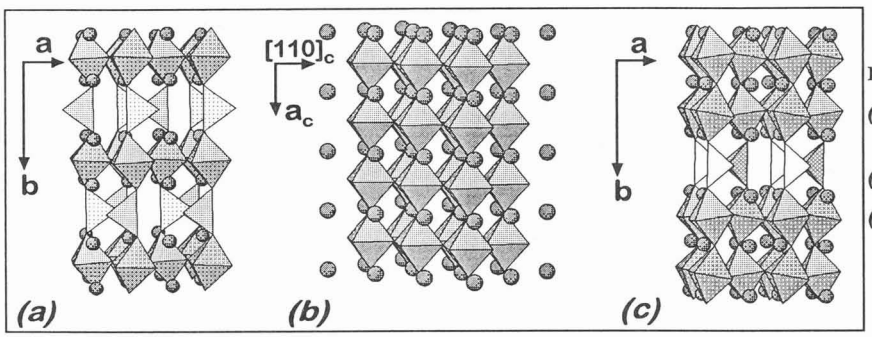

Fig. 2 Typical structures of :
(a) the brownmillerite-type $Sr_2Fe_2O_5$.
(b) the cubic perovskite-type
(c) the G-type $Sr_2LaFe_3O_8$.

3. RESULTS

Table I summarizes the electrochemical conditions of oxidation and the final composition of the oxidized ferrites.

Table I

Starting compound	Electrochemical conditions	Final composition	Cell parameter (a_C pm)	ΔV/V (%)
$Sr_2Fe_2O_5$	400 mV; 60 h.	$SrFeO_3$	384.5(2)	- 6.3
Sr_2FeCoO_5	I = 250 µA; 9 days	Sr_2FeCoO_6	383.7(2)	- 6.7
$Sr_2LaFe_3O_8$	500 mV ; 8 days	$Sr_2LaFe_3O_{8.90}$	387.7(2)	- 5.2

$Sr_2Fe_2O_5$ was oxidized at constant potential, for 60 hours, which finally involved ΔE_{OCV} (Open Circuit Potential) ≈ 400 mV [15]. Sr_2FeCoO_5 was oxidized for a duration calculated as the time necessary for the total charge transfer of $2e^-/Sr_2CoFeO_5$ (corresponding to the complete oxidation $\delta = 1$) using the following formula $t = 2\delta mF/MI$ (m being the sample mass, M its molecular weight, I the oxidation current, *F* the Faraday constant); however, assuming a part of the current to be used for the oxygen evolution, an additional polarization time was added [16]. $Sr_2LaFe_3O_8$ was obtained using either the potentiostatic method (500 mV for 8 days) or the galvanostatic one(100µA for 20 days).

After electrochemical oxidation all samples show X-ray diffractograms characterizing a well crystallized material with the cubic perovskite-type pattern. The chemical composition is close to the expected oxygen composition for stoichiometric perovskite attesting that the oxygen intercalation is complete (or almost complete for $Sr_2LaFe_3O_8$). Comparing the unit cell parameter a_C with the mean reduced cell parameter of the starting material, one can point out a significant

volume shrinkage (≈ 6%) due to the oxidation process leading to the occurrence tetravalent Fe(IV) or Co(IV) whose ionic radii are somewhat smaller than those or Fe(III) or Co(III).

In addition, these compounds exhibit a metallic (or semi-metal) behavior while the starting materials are insulating. From a magnetic viewpoint, they are all antiferromagnetically ordered before oxidation and, when fully oxidized, $SrFeO_3$ shows helimagnetism below T_N = 140 K , Sr_2FeCoO_6 becomes ferromagnetic below T_C = 327 K, and exhibit a drastic magnetic transition at 195 K assigned to the spin ordering and charge disproportionation (see below).

Starting materials as well as oxidized samples were also characterized using Mössbauer spectroscopy. The Mössbauer resonance spectra were obtained with a constant acceleration Halder-type spectrometer with a room temperature ^{57}Co (Rh matrix) source in a transmission geometry in the range of temperatures $4.2 \leq T \leq 350$ K. The spectra were fitted to the sum of Lorentzians by a least squares refinement ; all isomer shifts given in this study refer to α-Fe at 293 K.

All starting materials exhibit Mössbauer spectra characterizing magnetically ordered materials and trivalent iron in octahedral (O_h) and tetrahedral (T_d) sites. Typical spectra are given in Fig. 3. The intensity ratio between these lines well agree with the distribution of iron in both sites with regard to the structure : for $Sr_2Fe_2O_5$, O_h/T_d = 47/53, for Sr_2FeCoO_5, O_h/T_d = 46/54 (Fig. 3a), which implies a random occupancy of iron and cobalt in both sites, and for $Sr_2LaFe_3O_8$ (Fig. 3b), O_h/T_d = 68/32.

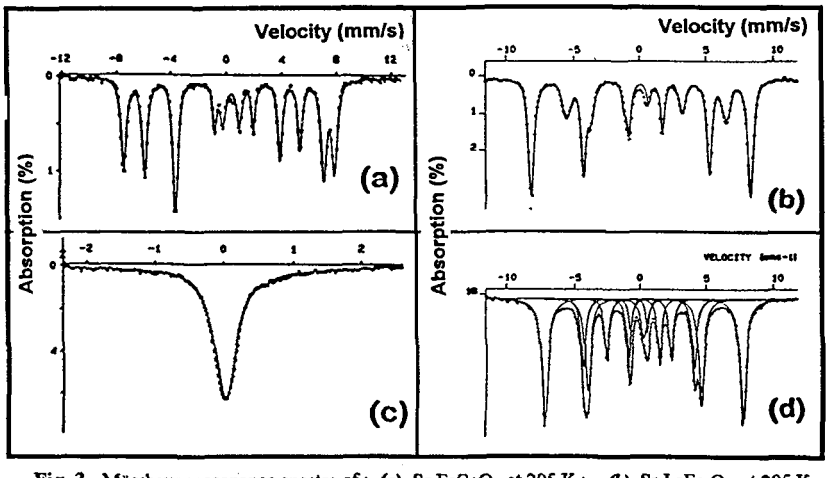

Fig. 3 Mössbauer resonance spectra of : *(a)* Sr_2FeCoO_5 at 295 K ; *(b)* $Sr_2LaFe_3O_8$ at 295 K *(c)* Sr_2FeCoO_6 at 340 K *(d)* $Sr_2LaFe_3O_{8.90}$ at 4.2 K

After electrochemical oxidation, the spectra show a complete change and no trace of the starting materials. All patterns exhibit paramagnetic lines whose Mössbauer parameters characterize the oxidation of trivalent iron :

- for $SrFeO_3$, at 293 K, it is a single symmetrical line (δ = 0.082 mm/s) demonstrating the presence of only Fe(IV).
- for Sr_2FeCoO_6 (Fig. 3c), the thermal dependence of the spectra shows that the magnetic ordering Curie temperature T_c is close to 327 K in agreement with magnetic susceptibility data. Above T_c, at 340 K, the spectrum was fitted by a broad single line with δ = 0.07 mm/s characterizing again the presence of Fe(IV).
- for $Sr_2LaFe_3O_{8.90}$, at room temperature, the spectrum exhibit a single symmetrical line, somewhat broadened, which was fitted by a quadrupolar doublet (Δ = 0.16 mm/s) ; the value of the isomer shift (δ = 0.14 mm/s) is characteristic of a mixed valence of iron and, as expected, intermediate of Fe(III) and Fe(IV), which implies a fast electron transfer. At decreasing temperature magnetic ordering is observed below 195 K and, at 4.2 K, two sextets can be observed (Fig. 3d). The Mössbauer parameters (δ_1 = 0.36 mm/s, H_1 = 46.6 T and δ_2 = -0.03 mm/s, H_2 = 26.4 T) involve a charge disproportionation of the average mixed valence of iron into $Fe^{(3+\lambda)+}$ and $Fe^{(5-\lambda)+}$. The intensity ratio I_1/I_2 = 70/30 well agrees with the chemical analysis.

4. CONCLUSION : CONSIDERATIONS ABOUT THE ELECTROCHEMICAL PROCESS

These experiments being performed in concentrated [OH] solution, one should address the question about the nature of the intercalated species, the formation of oxyhydroxides being the most obvious assumption. Early works using T.G.A., ^{H}N.M.R. as well as I.R. spectroscopy clearly demonstrated the absence of (OH) species in the final oxidized materials [17]. The above reported results clearly show that it is indeed oxygen atoms that have been intercalated, which nicely corroborates the reaction *(2)*. Such conclusions were also confirmed by quantitative galvanostatic experiments at very low current intensity, the results being in excellent agreement with iodometric titration of the samples [10]. As O^{2-} anions, with respect to their ionic size, are not likely to be the diffusing species, therefore the addressed question is : which are the diffusing species ?

The oxidation process occurring at potentials close to the oxygen evolution reaction, we assumed that this process should involve electroactive species concerned with the mechanism of the oxygen evolution.

Various electrochemical studies have been carried out (cyclic voltammetry (I_{ox} *vs.* $v^{-1/2}$ (sweep rate) or Tafel behavior (log(E) = f(i)), experiments at steady potential (I_{ox} *vs.* $t^{-1/2}$ (time) [18, 19]), which led to conclude to the formation, at the surface of the electrode, of O^- species that are immediately consumed and to determine the value of the diffusion

coefficient $D_{ox.}$ of the electroactive species to be about 10^{-9}-10^{-11} cm^2/s. This value appears somewhat greater than the value usually found for the O^{2-} diffusion in oxides at room temperature (< 10^{-15} cm^2/s). Therefore, we proposed the oxygen diffusion to be possible thanks to the formation of O^- species considering that most oxides concerned by electrochemical oxidation belong to the class of materials [20] for which the following equilibrium, $M^{(n+1)} + O^{2-} \Longleftrightarrow M^{n+} + O^-$, is characterized by a very small energy Δ ($\approx$ 0 eV, the charge transfer energy), which involves the existence of a mixed valence of oxygen (O^{2-}/O^-) or, in other words, an easy electron transfer from the oxygen to the metal cation. Then, one may expect that the formation of O^- species is rather easy which would explain why oxygen atoms can easily move into the oxide network, even at nearly room temperature. Such a mobility was early reported by Jorgensen et al. [21] from neutron diffraction experiments and also from NMR data, conductivity measurements ...[22]. However, such a migration requires easy diffusion paths within the parent structure ; in brownmillerite compounds or G-type compounds, this path clearly appears along $[001]_O \equiv [110]_{per.}$ vacancy files (Fig. 2).

Recently discovered the electrochemical oxidation has rapidly appeared as a powerful technique of 'Chimie Douce' for bulky oxidizing oxides, capable to replace the use of high oxygen pressures in some specific cases. The preparation and the characterization of some fully oxidized ferrites has clearly demonstrated the intercalation of oxygen to be successful. Various new 'overoxidized' oxides (such as the superconducting cuprate $La_2CuO_{4.09}$ [8, 23]) have been thus prepared in a metastable state. The galvanostatic mode appears however the most efficient way for controlling the kinetics of this process.

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