Electrochemical Synthesis of New Magnetic Mixed Oxides of Sr and Fe: Composition, Magnetic Properties, and Microstructure

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An electrochemical method for the preparation of magnetic nanoparticles of new Sr−Fe oxides is presented in this work. It consists of the electrolysis of nitrate or chloride solutions with Sr^{2+} and Fe^{3+} salts using commercial Fe electrodes. Magnetic materials are collected as precipitates from nitrate media in the pH range 1−3 and from chloride media within the pH range 1−12. The presence of 100−300 ppm aniline in acidic nitrate media yields a decrease in energy cost and particle size. Inductively coupled plasma analysis of materials and energy-dispersive X-ray spectrometry of single particles confirm that they are composed of mixed oxides of Sr and Fe. All synthesized materials crystallize as inverse cubic spinels, usually with intermediate structures between magnetite and maghemite. They are formed by nanoparticles with average sizes from 2 nm to ∼50 nm, as observed by scanning electron microscopy. The electrogenerated mixed oxides have higher saturation magnetization, but lower remanent magnetization and coercive field, than commercial strontium hexaferrite with micrometric particle size.

I. Introduction

There is great interest in the synthesis and characterization of nanostructured materials with particle sizes from 1 to 100 nm for technological application.[1−15] The fascinating electronic, optical, and magnetic properties of these materials are attractive prospects for information storage, bioprocessing, color imaging, magnetic refrigeration, ferrofluids, and gas sensors. In these fields of application, metal oxide nanoparticles are important. While the chemical synthesis of these materials has been well-established for different methods involving oxidation in micellar media or in polymer or mineral matrixes,[16] oxyhydrogen flame pyrolysis,[17] and sol−gel processes,[18] less is known about their possible preparation from electrochemical routes. Recently, Pascal et al.[19] have developed an electrochemical method to synthesize magnetic nanoparticles of maghemite (γ-Fe_2O_3) with average sizes varying from 3 to 8 nm from a sacrificial iron anode in an organic medium with cationic surfactants as stabilizer. The authors have shown that the particle size can be controlled by the imposed current density, although the resulting particles have amorphous character. Other electrolytic procedures have been proposed for the preparation of magnetite (Fe_3O_4) from different aqueous media,[20−23]

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but no information about the size of the particles formed is given.

Mixed-metal oxides, such as strontium hexaferrite ($SrFe_{12}O_{19}$) and barium hexaferrite ($BaFe_{12}O_{19}$), are also magnetic materials widely used in television, telephone, and automobile industries, and for the production of electromechanical devices, magnetic recording, electronic toys, door holders, etc.[24] The commercial demand of strontium hexaferrite increases continuously, because it is the Sr−Fe oxide with most significant magnetic properties and has higher coercitivity than that of barium hexaferrite. However, no nanostructured Sr−Fe oxides have been previously reported in the literature. Strontium hexaferrite, as well as more than 20 Sr−Fe oxides known, are usually prepared at high temperature (1100−1200 °C) by an expensive method involving powder preparation, shaping, firing, and finishing.[24,25] The procedure is accompanied by homogenization on a local scale, and for the shaping stage the material has to be milled down to particles of micrometic size.

In this paper, we present an alternative and cheap electrochemical method for the preparation of new magnetic Sr−Fe oxides with nanometric particle sizes. Since our purpose is to design a process which can be scaled and industrialized, commercial iron has been employed for both the sacrificial anode and the cathode. The mixed oxides have been obtained as precipitates from aqueous solutions containing mixtures of Fe^{3+} and Sr^{2+} salts in the form either of nitrates or chlorides using a one-compartment cell of 100-mL capacity. Some experiments with a stirring batch tank of 700-mL capacity are also reported. Different salt compositions, solution pH's, temperatures, and current densities have been tested. We have also estimated the energy cost for the materials obtained. In nitrate medium, the effect of an organic additive, such as aniline, on particle size has been studied. The composition, microstructure, and magnetic properties for the materials produced have been determined by inductively coupled plasma (ICP), energy-dispersive X-ray spectrometry (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), and SQUID magnetometry.

II. Experimental Section

The Sr−Fe oxides were synthesized from the following electrolytes: (a) $Sr(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, and concentrated HNO_3; (b) $Sr(NO_3)_2$ and KOH; (c) $SrCl_2 \cdot 6\ H_2O$, $FeCl_3 \cdot 6\ H_2O$, and concentrated HCl; (d) $SrCl_2 \cdot 6\ H_2O$, $FeCl_3 \cdot 6\ H_2O$, and KOH in neutral and alkaline medium. These chemicals were analytical or puriss. grade from Panreac and Merck. Aniline (Probus) was distilled at 178−180 °C under atmospheric pressure before use. All solutions were prepared with twice distilled water. The composition in weight of the commercial iron used as electrode was analyzed by ICP-MS using a Perkin-Elmer Elan 6000 spectroscope, yielding Fe, 99.5%; Mn, 0.4%; Cu, 0.1%.

Electrolyses were performed with a Hewlett-Packard 6554A dc power supply. The solution pH was measured with a Crison 2002 pH meter. The morphology of precipitates was examined by SEM with a JEOL JSM840 scanning electron microscopy. This instrument was also used to study the composition of the single particles by EDX (energy-dispersive X-ray microanalysis). The Sr and Fe content in the mixed oxides was obtained by ICP using a Jobin Yvon JY38VHR inductively coupled argon plasma spectroscope. The XRD spectra were recorded on a Siemens D-500 Bragg−Brentano $\theta/2\theta$ geometry powder diffractometer for $\lambda = 1.5418$ Œ (the wavelength of the Kα band for Cu).The remanent magnetization M_r, saturation magnetization M_s, and coercive field H_c for each material were determined at room temperature from the hysteresis cycles by using a Quantum Design MPMS5.5 SQUID magnetometer.

Electrochemical experiments were conducted in two different cells. In nitrate medium, the anode was a commercial iron and the cathode was a porous graphite from Sofacell; while in chloride medium, electrodes of commercial iron were used as both the anode and the cathode. Iron electrodes were polished before use to eliminate surface oxides. Most of trials were carried out with a one-compartment cell consisting of a cylindrical vessel of 100-mL capacity with a jacket to be thermostated with an external circuit of water. For this cell, the electrodes were sheets or foils of 50 × 40 × 3 mm in dimension with 20 cm^2 of area immersed in the solution andseparated a distance of ∼4 cm, and the electrolytic solution was stirred with a magnetic bar. Some electrolyses were performed with a batch tank of 120 × 120 × 80 mm in dimension and 700 mL capacity, which was immersed in a thermostated water bath. The electrodes for this batch tank were plates of 110 × 100 × 3 mm in dimension, which were suspended in parallel into the reactor at a gap of ∼2 cm, yielding 110 cm^2 of area immersed in the solution. The electrolyte bulk was mechanically stirred with a PTFE-coated steel shaft coupled to a Heidolph RZR1 stirrer.

All electrolyses were carried out by applying a constant current density j. The cell voltage V was directly read on the power supply. The solution pH was adjusted each 15 min by adding small volumes of concentrated (a) KOH or HNO_3 for nitrate medium and (b) KOH or HCl for chloride medium. The temperature was maintained in the range between 25 and 80 °C. In each trial, large amounts of magnetic mixed oxides were produced, precipitating the major part of them in the solution. Smaller amounts of mixed oxides were also collected at the electrodes, mainly at the cathode and, in much lower proportion, at the anode. Each magnetic material was extracted with the help of a permanent $Nd_2Fe_{14}B$ magnet, rinsed with bidistilled water, diluted hydrochloric acid, and bidistilled water again, and finally, dried in an oven at 80 °C before its analysis. The energy cost for each process was determined as the consumed kilowatt hour per kilogram (kW h kg^{-1}) of total collected magnetic material.

III. Results and Discussion

The proposed electrochemical procedure for the synthesis of Sr−Fe oxides is based on the coprecipitation of oxides of Sr^{2+}, Fe^{3+}, and Fe^{2+} in the solution and electrodes under the action of the applied electrical field. Sr^{2+} and Fe^{3+} ions are initially present in the medium, while soluble Fe^{2+} ion is continuously supplied to it from the two-electron oxidation of the Fe anode:[26]

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

In the cathode, the main reaction corresponds to water reduction to H_2 gas

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

although a partial reduction of Fe^{3+} to $Fe^{2+}$and Fe^{2+} to

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Table 1. Weights of Magnetic Sr−Fe Oxides and Energy Costs Obtained after 6 h of Electrolysis from Nitrate Medium with *x* M $Sr(NO_3)_2$ + *y* M $Fe(NO_3)_3$ under Different Experimental Conditions

exp.	medium, M x	 y	[aniline], ppm	pH[a]	*T*,°C	applied density, mA cm^{-2}	cell voltage, V	weight lost by the anode, g	total Sr−Fe oxide weight, g[b]	energy cost, kWh kg^{-1}
						Cell of 100 mL				
1	0.1	0.1		1.2	80	25	1.9	6.397	2.076	2.7
2	0.1	0.15	200	1.5	80	35	1.9	5.986	0.318	24.4
3	0.2	0.1	300	3.0	65	25	4.5	5.148	1.423	9.5
4	0.5	0.1	100	1.5	30	25	2.1	3.035	1.865	3.4
5	0.5	0.1	100	1.5	60	5	0.9	1.054	0.149	3.6
6	0.5	0.1	100	1.5	60	25	1.8	4.243	3.594	1.5
7	1.5	0.1	300	3.0	60	25	2.6	1.299	0.158	49.4
						Batch tank of 700 mL				
8	0.3	0.1		1.5	40	50	5.5	46.56	6.138	26.9
9	0.1	0.1	300	1.5	40	30	3.2	21.91	18.74	3.1

[a] The solution pH was regulated each 15 min. [b] Total magnetic material weight collected from the solution, cathode, and anode.

Table 2. Weights of Magnetic Sr−Fe Oxides and Energy Costs Obtained from Chloride Medium with *x* M $SrCl_2$ + *y* M $FeCl_3$ under Different Experimental Conditions

exp.	medium, M *x*	 *y*	pH[a]	*T*,°C	applied density, mA cm^{-2}	cell voltage, V	electrolysis time,h	weight lost by the anode,g	total Sr−Fe oxide weight,g[b]	energy cost, kWh kg^{-1}
						Cell of 100 mL				
10	0.3	0.1	1.0	40	25	1.1	6	3.733	0.263	12.5
11	0.3	0.1	1.5	40	25	1.3	6	3.124	0.553	7.6
12	0.3	0.1	1.9	40	25	1.4	6	3.208	1.469	2.8
13	0.3	0.1	1.9	40	50	2.4	6	5.928	4.718	3.0
14	0.3	0.1	3.0	40	50	3.3	6	5.671	4.783	4.1
15	0.3	0.1	7.0	40	150	9.1	4	12.87	18.38	5.9
16	0.3	0.1	12.0	40	50	3.7	6	6.235	13.15	1.7
17	0.6	0.2	5.0	80	50	1.2	6	6.687	5.461	1.4
18	0.6	0.3	4.0	80	50	1.2	6	6.401	4.576	1.4
						Batch tank of 700 mL				
19	0.3	0.1	1.5	40	50	4.3	3.5	20.34	4.027	18.7
20	0.3	0.1	4.0	40	50	3.5	3.5	19.46	14.33	4.3

[a] The solution pH was regulated each 15 min. [b] Overall magnetic material weight collected from the solution, cathode and anode.

metallic Fe can also occur

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (3)$$

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad (4)$$

Equation 4 can then explain the presence of Fe particles in some of precipitates formed.

To regulate the entrance flow of Fe^{2+} in the medium, different current densities were applied. The effect of solution pH upon the process was studied as it does play an important role in the production of magnetic materials. Preliminary results showed that only at pH > 1, Sr−Fe precipitates were obtained. Since insoluble hydrated Fe oxides are formed from pH 1.9,[27] it can be concluded that coprecipitation of iron ions with Sr^{2+} to yield Sr−Fe oxides occurs at more acidic media. However, a surprising effect was found using different electrolyte compositions. While magnetic materials always precipitated from chloride media within the pH range 1−12, nonmagnetic mixed oxides were collected from nitrate media at pH > 3, even in the presence of an organic additive, such as aniline. For this reason, the study of this last media was limited to pH between 1 and 3. The influence of temperature on the above processes was also investigated.

The following experiment (exp. *1* in Table 1) illustrates the proposed electrochemical procedure. An aqueous solution (100 mL) of 0.1 M $Sr(NO_3)_2$ + 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$, was prepared and heated to 80 °C and its pH was adjusted to 1.2 with a small volume of concentrated HNO_3. The solution was then introduced in the one-compartment cell thermostated at 80 °C, and it was stirred with a magnetic bar at 1000 rpm. An iron foil as the anode and a porous graphite foil as the cathode, both with an working area of 20 cm^2, were immersed in the solution, and a constant current density of 25 mA cm^{-2} was applied through them for 6 h. The average cell voltage was 1.9 V. During electrolysis, a black precipitate was continuously formed in the solution while its pH gradually increased, reason for which it was adjusted to initial pH 1.2 each 15 min by addition of HNO_3. The final solution volume was ~110 mL. After electrolysis, the magnetic precipitate suspended in the solution was extracted with a permanent magnet. The precipitates retained at the anode and cathode were separated by washing with bidistilled water and further, their magnetic components were extracted with the permanent magnet. Each collected magnetic material was rinsed several times with bidistilled water, hydrochloric acid, and bidistilled water again to eliminate all soluble salts, being finally dried in an oven at 80 °C. The total magnetic material weight thus obtained was 2.076 g with an energy cost of 2.7 kW h kg^{-1}.The weight lost by the iron anode was 6.397 g.

Tables 1 and 2 summarize results for several electrochemical synthesis performed from nitrate and chloride media, respectively, in both, the cell of 100 mL and

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Table 3. Magnetic Properties at 25 °C, Average Particle Size, and Formula Determined by ICP for Several Sr−Fe Oxides Obtained from Nitrate Medium (see experimental conditions in Table 1)

exp.	collected material[a]	M_r, emu g^{-1}	M_s, emu g^{-1}	H_c, Oe	d,[b] nm	formula $SrFe_wO_z$ w	z	O/Fe ratio
1	S	11	57	111	28.2	not determined		
6	A	0.8	14	12	16.5	not determined		
6	C	6.3	33	67	27.7	269	405	1.51
6	S	8.0	34	56	20.9	89	134	1.51
7	S	2.6	17	76	17.5	not determined		
8	C	4.0	23	56	23.4	386	580	1.50
9	A	2.6	35	60	15.9	not determined		
9	C	5.1	28	61	19.8	not determined		
9	S	0.5	21	9	12.3	not determined		
	$SrFe_{12}O_{19}$[c]	30	47	1122	49.4	12	19	1.58

[a] Sr−Fe oxide collected from the solution (S), anode (A), or cathode (C) [b] Estimated by applying the Scherrer equation to the maximum peak of the corresponding XRD spectrum related to an inverse cubic spinel structure [c] Sample supplied by Galvarplast. Its XRD spectrum corresponds to the hexagonal structure

the batch tank reactor. As can be seen, electrolytes with different $[Sr^{2+}]/[Fe^{3+}]$ (x/y) composition were tested. Note that most of precipitates were collected from the solution (~60−65%), and lower proportions were obtained from the cathode (30−35%) and anode (<5%). For chloride media, the weight lost by the anode in all trials agrees with the value calculated if only reaction 1 takes place. For example, a loss of 3.125 g of Fe is theoretically expected after 6 h of electrolysis at 25 mA cm^{-2} in the cell of 100 mL, in agreement with data of Table 2. In contrast, more Fe is usually dissolved using a nitrate medium (see Table 1), suggesting that other anodic reactions different from eq 1 with lower number of electrons are also involved. This anomalous behavior in nitrate medium, along with the formation of nonmagnetic materials at pH > 3, are possibly related to the existence of complex equilibria between the electrolyte cations and their oxide precipitates. In this way, it seems plausible to consider that the higher complexant power of Cl^- with metallic cations seems to favor the synthesis of magnetic Sr−Fe oxides in the pH range between 1 and 12 from chloride medium, as experimentally found. In some cases (see exp. *7*, Table 1), less Fe than the theoretically predicted from reaction 1 was dissolved, due to the presence of O_2 evolution from water oxidation.

The existence of complex equilibria in nitrate medium is also reflected in the total weight of magnetic Sr−Fe oxides reported in Table 1. The presence of aniline in the cell of 100 mL at 25 mA cm^{-2} increases the production of magnetic materials when the temperature decreases from 80 °C (exp. *1*) to 60 °C (exp. *6*). At the same j value, similar Sr−Fe oxide weights were found operating at a x/y ratio between 5 and 1 (exps. *3* and *4*). For $x/y < 1$ (exp. *2*) and $x/y = 15$ (exp. *7*), much smaller amounts of material were collected, reason for which their energy costs were very high (see last column in Table 1). The use of low j values (e. g., 5 mA cm^{-2} in exp. *5*) also causes the formation of smaller proportions of magnetic materials. These findings allow us to conclude that magnetic Sr−Fe oxides can be adequately produced from nitrate medium in the pH range 1−3, operating with a x/y ratio between 5 and 1 at 25 mA cm^{-2}, independent of temperature. Under these conditions, an energy cost as low as 1.5 kW h kg^{-1} is found in the presence of 100 ppm aniline (exp. *6*). Several trials were then carried out in similar conditions using the batch tank reactor at pH 1.5 and 40 °C. Comparison of results of exps. *8* and *9* allows us to conclude that the presence of 300 ppm aniline favors the formation of more mixed oxides, along with the reduction of theirenergy cost to 3.1 kW h kg^{-1} at 30 mA cm^{-2}.

On the other hand, results of Table 2 for chloride media with 0.3 M $SrCl_2$ + 0.1 M $FeCl_3$ in the cell of 100 mL (exps. *13*−*16*) show an increasing total Sr−Fe oxide weight with increasing pH from 1.9 to 12 at 50 mA cm^{-2} and at 40 °C. The lowest energy cost is 1.7 kW h kg^{-1} after 6 h of electrolysis at pH 12. Similar costs were obtained by applying 50 and 25 mA cm^{-2}, as can be deduced by comparing exps. *12* and *13* at pH 1.9. However, much higher costs were found either at lower pH's (exps. *10* and *11*) or increasing the current density until 150 mA cm^{-2} (exp. *15*). The positive effect of increasing temperature to 80 °C on this parameter was confirmed by working at 50 mA cm^{-2} in acidic media of pH 5 (exp. *17*) and pH 4 (exp. *18*) with different x/y ratios of 3 and 2, respectively. In both cases, a low cell voltage was applied due to the decrease in ohmic drop (current x resistance product) of solution, giving rise to energy costs as low as 1.4 kWh kg^{-1}. A similar behavior was observed using the batch tank reactor. The exp. *20* at pH 4.0 performed under the same conditions as exp. *19* at pH 1.5 yielded more magnetic materials with a cost of 4.3 kW h kg^{-1}. All these findings indicate that large amounts of magnetic Sr−Fe oxides can be synthesized from chloride media, especially in alkaline solutions and at high temperatures. Acceptable energy costs lower than 4.3 kW h kg^{-1} can then be achieved operating between 25 and 50 mA cm^{-2} within the pH range 1.9−12 at 40−80 °C.

The electrochemical synthesis of Sr−Fe oxides was confirmed by ICP analysis of precipitates. The resulting formula expressed in the form $SrFe_wO_z$ for several selected samples is given in Tables 3 and 4. In acidic nitrate media, mixed oxides with poor Sr contents were generated. In contrast, magnetic materials from chloride media showed higher proportions of Sr, especially those obtained in alkaline medium with formulas even richer in Sr than the proper strontium hexaferrite (see exp. *16* in Table 4). Thus, the anodic sample has a large proportion of Sr with an average formula $SrFe_{0.28}O_{1.43}$ and an O/Fe ratio of 5.11. This experimental fact is difficult to explain, because Sr was not found in the cathodic precipitate where it could be generated from a

Table 4. Magnetic Properties at 25 °C, Average Particle Size, and Formula Determined by ICP for Several Fe−Sr Oxides Obtained from Chloride Medium (see experimental conditions in Table 2)

exp.	collected material[a]	M_r, emu g^{-1}	M_s, emu g^{-1}	H_c, Oe	d,[b] nm	formula as $SrFe_wO_z$ w	z	O/Fe ratio
11	C	1.9	140	23	20.5	117	176	1.50
12	A	1.9	13	107	17.4	not determined		
12	C	2.7	103	25	29.7	1305	1960	1.50
16	A	0.8	8.0	70	25.6	0.28	1.43	5.11
16	C	5.1	23	94	25.5	39	61	1.56
16	S	5.7	24	119	29.0	10	16	1.60
19	A	3.0	33	86	28.6	not determined		
19	C	4.0	170	30	28.2	not determined		
19	S	5.0	75	66	31.6	not determined		
20	A	6.0	38	124	25.7	839	1260	1.50
20	C	2.9	98	23	24.9	56	85	1.52
20	S	12	74	99	30.7	1691	2537	1.50

[a] Sr−Fe oxide collected from the solution (S), anode (A), or cathode (C). [b] Estimated value by applying the Scherrer equation to the maximum peak of the corresponding XRD spectrum related to an inverse cubic spinel structure.

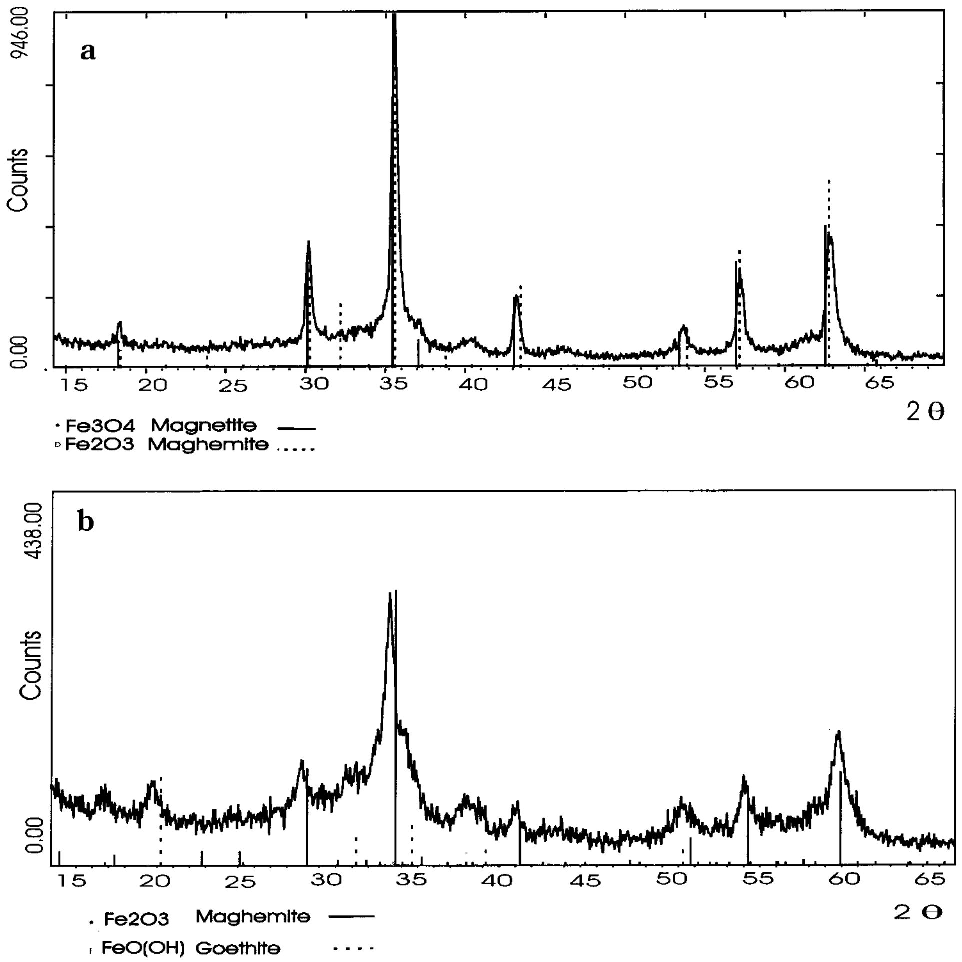

Figure 1. XRD spectra corresponding to the magnetic materials collected from the solution in nitrate medium: (a) exp. *6* and (b) exp. *8*.

two-electron reduction of Sr^{2+}. Further co-deposition of this metal with Sr−Fe oxides yields the stable precipitate collected at the anode.

Typical XRD spectra determined for several Sr−Fe oxides generated from nitrate and chloride media are shown in Figures 1 and 2, respectively. These materials have an inverse cubic spinel structure, very different from the hexagonal crystalline structure of $SrFe_{12}O_{19}$. The binary oxides obtained from nitrate medium own structures similar to magnetite or intermediates between magnetite and maghemite (Figure 1a), and magnetite with a fraction of goethite (Figure 1b). Materials collected from chloride medium show structures intermediates between magnetite and maghemite. In these acidic solutions the samples from the cathode and solution contain a proportion of metallic Fe due to the existence of reaction 4 (Figure 2a). The percentage in weight of Fe determined by the method of Chung[28] was always lower than 5%. In contrast, the oxides with larger content of Sr formed at pH 12 did not show the presence of metallic Fe (Figure 2b). The lattice constants (*a*) were calculated from the XRD results. For example,

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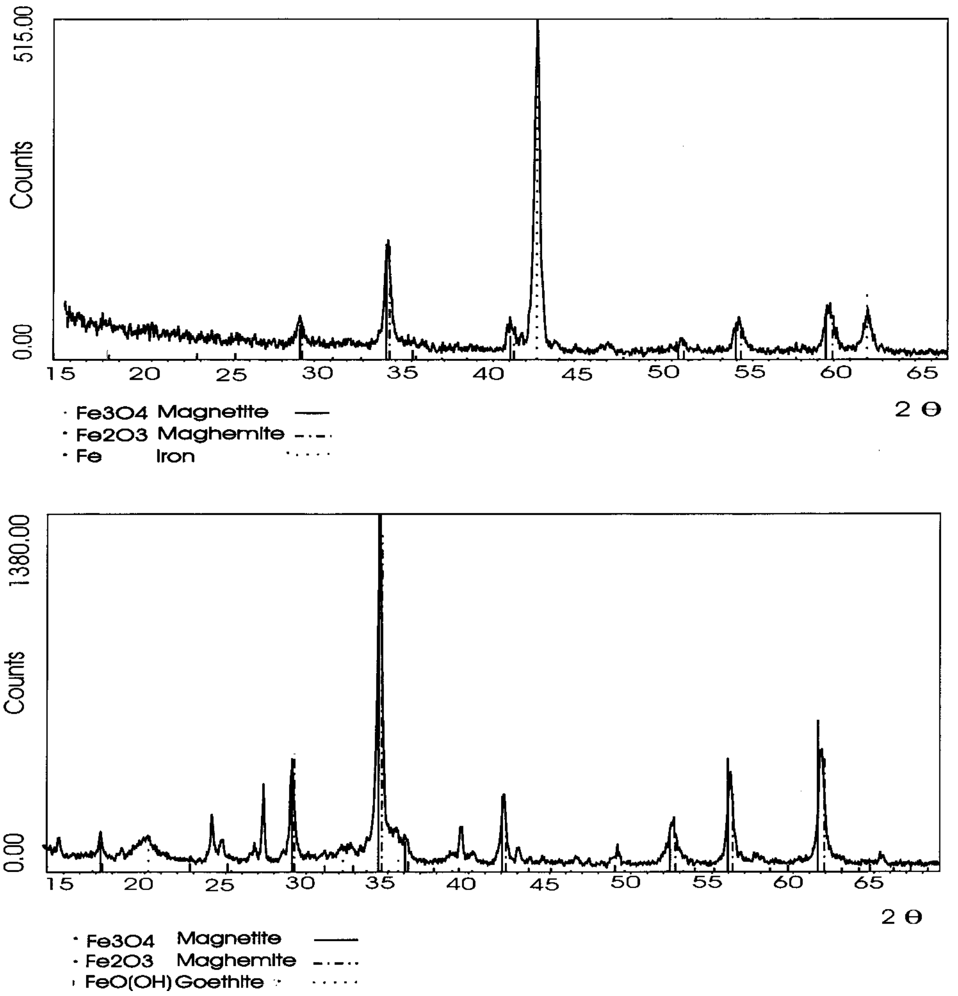

Figure 2. XRD spectra related to the magnetic Sr−Fe oxide produced in chloride medium: (a) exp. *11*, cathodic precipitate; (b) exp. *16*, precipitate collected from the solution.

values of $a = 8.363 \pm 0.002$ Å and $a = 8.378 \pm 0.002$ Å. were found for the materials collected from the solution in exps. *6* (Figure 1a) and *16* (Figure 2b), respectively. These are intermediate values to those of magnetite ($a = 8.396$ Å) and maghemite ($a = 8.351$ Å).

The last column of Tables 3 and 4 shows the O/Fe ratio for the Sr−Fe compounds obtained. This value usually oscillates between 1.50 and 1.60, close to that of the maghemite (1.50) or hexaferrite (1.58), but very far from that of magnetite (1.33). By taking into account the low Sr content found in oxides, it can be established that they are mainly composed by Fe^{3+}, with a very low presence of Fe^{2+}.

These results allow us to propose that the magnetic materials obtained are solid solutions of Sr−Fe oxides. Probably, the coprecipitation of the materials starts with the formation of a solid solution of maghemite with a small proportion of magnetite near to the electrodes during the electrolysis. Under the action of the applied electrical field, this compound is then doped by Sr^{2+} in more or less extension. The overall reaction for the formation of maghemite can be written as

$$2Fe^{3+} + 6OH^- \rightarrow \gamma\text{-}Fe_2O_3 + 3H_2O \qquad (5)$$

whereas magnetite is generated from the coprecipitation of Fe^{2+} formed by eq 1 and Fe^{3+} present in solution:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \qquad (6)$$

The further doping of the mixture of these oxides is due to the partial substitution of Fe^{2+} of magnetite by Sr^{2+}. This process can be expressed as follows:

$$Sr^{2+} + [\,(\gamma\text{-}Fe_2O_3)_\xi(Fe_3O_4)_\zeta] \rightarrow [(\gamma\text{-}Fe_2O_3)_\xi(Fe_3O_4)_{\zeta-1}(SrFe_2O_4)] + Fe^{2+} \qquad (7)$$

where ξ/ζ represents the proportion of maghemite/magnetite mixture doped by one Sr^{2+} ion. In accordance with the O/Fe ratio near to 1.50, $\xi/\zeta \gg 1$, that means that the major part of the mixture is maghemite. The final product formula may be written also as $SrFe_wO_z$, as reported in Tables 3 and 4. Therefore, the following equations can be written:

$$w = 2\xi + 3\zeta - 1$$
$$z = 3\xi + 4\zeta \qquad (8)$$

It is clear that if $\xi/\zeta \gg 1$, the O/Fe ratio ($= z/w$) is 1.50.

To corroborate if Sr−Fe oxides are formed during electrolysis, the composition of single particles was analyzed by EDX. Two examples are shown in parts a and b of Figure 3 for samples obtained from nitrate and chloride media, respectively. From these spectra, it is clear that the particles are composed of binary oxides

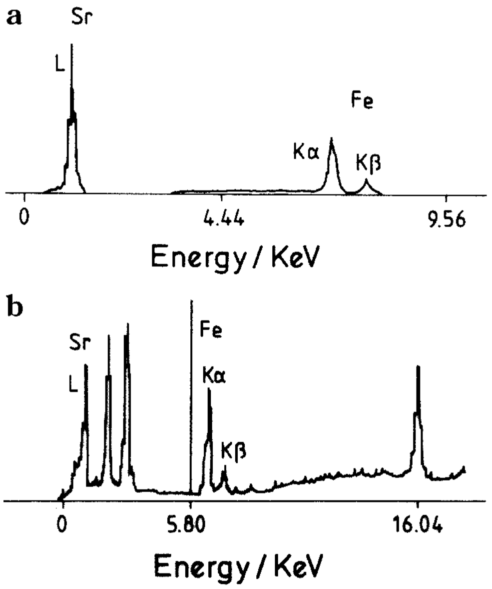

Figure 3. EDX spectra of a single particle of the magnetic material synthesized in (a) exp. *7*, precipitate collected from the solution; and (b) exp. *16*, anodic precipitate.

of Sr and Fe. These materials are, therefore, new magnetic Sr−Fe oxides, not described previously in the literature. Note that all the samples collected were rinsed with bidistilled water, further with hydrochloric acid solution, and finally, with bidistilled water in excess to eliminate all soluble compounds of Sr. Following this method, compounds such as $SrCl_2$ or $Sr(NO_3)_2$ were not detected in the XRD spectra.

The average particle size *d* for synthesized materials was estimated from their XRD spectra by applying the Scherrer equation to the maximum peaks, usually at a 2 Å angle ∼33° (see Figures 1 and 2). Several data obtained are listed in Tables 3 and 4. The mixed oxides collected from acidic nitrate media undergo a decrease in *d* when aniline is present in solution. This beneficial effect for the preparation of more nanostructured materials can be easily deduced if *d* values found for exps. *6*, *7*, and *9* with aniline are compared with those of exps. *1* and *8* without aniline (see Table 3). For chloride media, similar *d* values were found for each kind of magnetic material (see Table 4). It is noteworthy that all Sr−Fe oxides have much lower average particle sizes than 49.4 nm determined for commercial hexaferrite with the same method, suggesting that they contain a much higher number of nanoparticles. In general, nanoparticles with an average size from 2−3 nm to ∼50 nm were detected by SEM, depending on the experimental conditions. A decrease in average particle size with increasing current density and decreasing temperature was observed in all media. The presence of aniline for nitrate media results in the same effect.

The above results indicate that the proposed electrolytic method allows the preparation of nanostructured Sr−Fe oxides with potential application in different technological fields. The specific applicability will be determined by their magnetic properties, which are reported in Tables 3 and 4 for several selected samples. The saturation magnetization for these materials can achieve values as high as 140 or 170 emu g^{-1} (see Table 4). These values are much higher than those corresponding to magnetite (65 emu g^{-1}), maghemite (72 emu g^{-1}), and commercial hexaferrite (72 emu g^{-1})[25].

On the other hand, results of Tables 3 and 4 show that synthesized mixed oxides have low remanent magnetizations (until 11 emu g^{-1}) and coercive fields (until 124 Oe), in comparison with commercial $SrFe_{12}O_{19}$ with $M_r = 30$ emu g^{-1} and $H_c = 1122$ Oe, respectively. This behavior may be easily associated with the existence of particles with a broad range of volumes.[29,30]

IV. Conclusions

It is demonstrated that magnetic nanoparticles of new Sr−Fe oxides can be electrochemically synthesized in a cell of 100 mL and a batch tank of 700 mL using commercial Fe electrodes and nitrate and chloride media with Sr^{2+} and Fe^{3+} salts. These materials can be adequately obtained as precipitates from nitrate media in the pH range 1−3 with a $[Sr^{2+}]/[Fe^{3+}]$ ratio between 5 and 1, yielding a minimum energy cost of 1.5 kW h kg^{-1} at 25 mA cm^{-2}. The presence of 100−300 ppm aniline in this medium, as additive organic, causes a decrease in energy cost and particle size. In contrast, magnetic Sr−Fe oxides are always collected from chloride media within the pH range 1−12, although at pH ≥ 1.9 acceptable energy costs lower than 4.3 kW h kg^{-1} are achieved working between 25 and 50 mA cm^{-2} and at 40−80 °C. ICP analysis shows poor Sr contents in mixed oxides produced from acidic nitrate media, and higher contents of this element in materials collected from chloride media, especially at pH 12 where a large proportion of Sr is detected in the anodic precipitate. For acidic chloride media, less than 5% of metallic Fe is found in the materials produced at the cathode and in the solution. EDX analysis of single particles confirms that materials are solid solutions of oxides of Fe and Sr. All compounds crystallize in the form of inverse cubic spinels, usually with intermediate structures between magnetite and maghemite. This structure differs from the hexagonal one found for $SrFe_{12}O_{19}$. A large fraction of nanoparticles with an average size from 2−3 nm to ∼50 nm are observed by SEM, decreasing the size when increasing the current density and decreasing temperature. The saturation magnetization for these oxides is higher than that of commercial strontium hexaferrite. They have, however, lower remanent magnetizations and coercive fields.

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