Electro-precipitation of magnetite nanoparticles: An electrochemical study

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\textbf{ABSTRACT}

Nanoparticles of magnetite (\(\text{Fe}_3\text{O}_4\)) are synthesized with a new process based on electro-precipitation in ethanol medium. A mechanism pathway is proposed consisting of a \(\text{Fe(OH)}_3\) precipitation followed by the reduction of iron hydroxide to magnetite in the presence of hydroxyl ions which are generated at the cathode.

\section{1. Introduction}

The prospect of a new generation of materials and devices based on nanoparticles (NPs) is a major driving force in the rapidly emerging field of nanoscale research. Magnetic NPs, and more particularly magnetite (\(\text{Fe}_3\text{O}_4\)) and maghemite (\(\gamma\text{Fe}_2\text{O}_3\)), have been widely used for biomedical applications such as cell targeting, cell separation, drug delivery, hyperthermia [1–5], or in environmental sciences, for metal separation from wastewater [6,7]. Due to their magnetic moment, magnetic NPs can be driven by an applied magnetic field into specific regions of the human body for in vivo applications. For in vitro diagnosis or for metal separation, magnetic separation and selection can be done. For these applications, magnetic NPs have to become magnetized at low magnetic field. However, in order to avoid any agglomeration phenomenon, the magnetic NPs must not present magnetic remanence, i.e. must have a zero magnetization in the absence of an applied magnetic field. This particular behavior is achieved with superparamagnetic NPs. Typically, magnetite nanoparticles become superparamagnetic at sizes below 15 nm [8].

Chemical synthesis of colloidal magnetite has been known for a long time: aqueous mixture of ferric and ferrous salts are mixed with an alkali in order to induce the precipitation of magnetite particles (maghemite can then be obtained by soft oxidation of magnetite) [9]. The average diameter of particles can be tuned between 5 and 100 nm by varying experimental conditions (concentration, temperature, nature of alkali, ionic strength, agitation . . .) but the system is always polydispersed in size [9–11] due to the Oswald ripening mechanism (the large particles will grow at the cost of the small ones) [12]. Organized assemblies or complex structures have been used as nanoreactors (microemulsion, vesicle, polymer matrix media synthesis) in order to obtain nearly monodispersed ultratine iron oxide NPs. Some interesting reviews summarize all these techniques [13,14].

In practice, even if better control can actually be done over the size and the size distribution of NPs, progress in the use of superparamagnetic NPs depends on the improvement of synthetic methods. Though electrocoagulation in aqueous media of magnetite has been first reported in 2001 by Tsouris and colleagues [15,16], then by other researchers [17,18], these first studies reported only on supramicronic aggregates [15–17] or thin film [18] elaboration. It was only very recently (2008) that new processes were carried out, based on electro-precipitation of magnetite [19] or maghemite [20] in aqueous media, that yields nanoparticles with a controlled size distribution. In this study [19], the process allows to elaborate particles in the range size of 20–30 nm in the presence of surfactant. At the same time, we presented [21] a new process consisting of a cathodic electro-precipitation in an ethanol–water media, that yields very fine nanoparticles with a controlled size distribution (4–9 nm; std#15%) without the use of surfactant. This first paper concerned the first results with empirical data showing the influence of experimental conditions, particularly current density on the size distribution of the magnetite particles.

The aim of this article is to report an electrochemical study in order to propose a mechanism pathway for the elaboration of magnetite by electro-precipitation.
2. Experimental

Cyclic voltammograms were carried out in a conventional three-electrode cell using a computer controlled Voltalab potentiostat PGZ 100 model. A vitreous carbon disk (0.07 cm²) was used as working electrode, an Ag/AgCl/Cl⁻ (1 M) as a reference separated with an agar-agar junction and a platinum rod as counter electrode.

Electrolysis were performed in a cell containing 90 cm³ of Fe(NO₃)₃·9H₂O solutions in ethanol (absolute commercial 99.5% ethanol, water = 0.5% max) in the concentration range (0.01–0.16 M). During the experiment, the solution was stirred using a magnetic bar. The anode and cathode were graphite rods (0.01–0.16 M). During the experiment, the solution was stirred with a geometric area of 4.7 cm². Electrical current was provided by an ISO-Tech Laboratory DC Power Supply model IPS-1630D. The range of potential between the anode and the cathode to produce Fe₃O₄ nanoparticles is 20–60 V. Magnetite particles were collected on the cathode as black magnetic macroscopic platelets and washed with ethanol before being dried under air at room temperature.

Iron (III) concentration evolution in the electrolyte during the electro-precipitation process is followed using a UV–visible–NIR spectroscopic platelets and washed with ethanol before being dried under air at room temperature.

3. Results and discussion

Typical Fe₃O₄ nanoparticles elaborated by the electro-precipitation procedure are shown in Fig. 1. As shown on the picture, those particles have an average mean size centered on 6.2 nm with a quite narrow distribution (standard deviation = 18%). Because the nanoparticles produced are free of any surfactant, they show a strong tendency to be agglomerated and form a solid powder. However, after the electrosynthesis, one can disperse them in a given matrix by choosing the appropriate surfactant. Producing nanoparticles free of any surfactant is a true advantage, ensuring interesting handling possibilities. The characterization of these particles was reported in a previous paper.[21]

3.1. On the Fe³⁺ reduction

Fig. 2 shows the evolution of Fe³⁺ concentration versus the electrical charge and the variation of the instantaneous current efficiency Y₁ corresponding to the Fe³⁺ disappearance with time during the electrochemical process for two initial concentrations of iron nitrate (10⁻² and 2 × 10⁻² M). Y₁ is calculated considering the global reaction (1) which will be discussed at the end of the paper:

\[3\text{Fe}^{3+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} + 9\text{e}^- \rightarrow \text{Fe}_3\text{O}_4 + 2\text{NO}_2^- + 2\text{H}_2\] (1)

Elaboration of one mole of magnetite needs three moles of Fe³⁺ ions and nine moles of electrons. Consequently the instantaneous current efficiency Y₁, can be expressed by the relation (2):

\[Y_1(\%) = \frac{(n_{\text{Fe}^{3+}} - n_{\text{Fe}^{2+}})3\text{F}}{3It} \times 100 \] (2)

where \(n_{\text{Fe}^{3+}}\) and \(n_{\text{Fe}^{2+}}\) are respectively the number of Fe³⁺ moles at initial time and at time \(t\) (s). Fig. 2 shows clearly, for both initial concentrations (10⁻² and 2 × 10⁻² M), that the current efficiency Y₁ is higher than 80% at the beginning of the process. However, it decreases quickly during the electrolysis. Note that a low Y₁ is not directly correlated to a weak Fe³⁺ concentration. Indeed, even for the lowest initial concentration experiment (10⁻² M), the Y₁ values versus time are very close for both concentrations. The efficiency decreases continuously even if addition of iron nitrate in ethanol is carried out during the process. These results seem to show that an inhibition phenomenon has occurred on the cathode. This inhibition results probably from the very low electrical conductivity of magnetite deposited on the cathode, since, the ratio of electrical conductivity between graphite and magnetite is higher than 10⁵ [22–24].

3.2. On the magnetite production

In order to study the influence of the concentration of the precursor Fe(III) on the magnetite production, series of galvanostatic electrolysis were carried out at different concentrations. Up to 4 × 10⁻² M, a pure black magnetite is obtained. However, beyond this value, the collected product is polluted by brownish pollution. Beyond 8 × 10⁻² M only a non-magnetic amorphous precipitate is collected (iron III hydroxide [21]). This behavior is explained by the excess of water molecules at high nitrate concentration which causes the iron hydroxide production. An electrolysis was carried out with FeCl₃ (anhydrous) as iron precur-

![Fig. 1. Transmission electron microscopy photograph for typical Fe₃O₄ nanoparticles. Experimental conditions: Fe(NO₃)₃·9H₂O = 2 × 10⁻² M in ethanol, 30 mA cm⁻². Size: \(\varnothing = 6.2\) nm [std = 18%].](image-url)
sor instead of Fe(NO\textsubscript{3})\textsubscript{3} 9H\textsubscript{2}O. No particles were produced and the Fe\textsuperscript{3+} concentration fluctuated slightly around the initial concentration \((2 \times 10^{-2} \text{ M} \pm 0.02)\) and remained almost constant even after a long electrolysis time (not shown). Fe\textsuperscript{3+} ions are reduced into Fe\textsuperscript{2+} at the cathode but those ferrous ions migrate to the anode to be oxidized into Fe\textsuperscript{3+} again. We conclude that nitrate and also little water must be present to produce Fe\textsubscript{3}O\textsubscript{4} particles on the cathode.

Preliminary results reported elsewhere [21] have shown that current density is an important parameter. Fig. 3 reports the evolution of Fe\textsuperscript{3+} concentration with charge at four current densities \((2.3, 6.4, 12.7, 25.5 \text{ mA cm}^{-2})\) during electrolyses performed at initial Fe\textsuperscript{3+} concentration equal to \(2 \times 10^{-2} \text{ M}\). Fig. 3 highlights that the Fe\textsuperscript{3+} reduction/precipitation phenomenon is more efficient using high current density. Moreover at the lowest current density, the Fe\textsuperscript{3+} concentration is constant, there is no formation of magnetite.

After each electrolysis, corresponding to 1200 As, the particles were collected, dried and weighted, the efficiency of the process is evaluated following two equations:

- On one hand, by comparison of the quantity of Fe\textsubscript{3}O\textsubscript{4} particles produced with the number of Fe\textsuperscript{3+} ions disappearing into the bath considering Eq. (1):

\[
Y_2(\%) = \frac{3n_{\text{Fe}_3\text{O}_4}}{n_{\text{Fe}^{3+}} - n_{\text{Fe}^{3+}}} \times 100
\]

- On the other hand, the evolution of the faradic efficiency for magnetite production is calculated following Eq. (4):

\[
Y_3(\%) = \frac{9n_{\text{Fe}_3\text{O}_4}}{I} \times 100
\]

For current densities higher than, or equal to \(13 \text{ mA cm}^{-2}\), 100% of Fe\textsuperscript{3+} ions reduced at the cathode are used to produce magnetite but it collapses dramatically (52%) for \(6.4 \text{ mA cm}^{-2}\) and becomes 0% at \(2.3 \text{ mA cm}^{-2}\) confirming that magnetic production needs a minimum current density. One can note that \(Y_3 > 100\%\) is due to mass incertitude: Fe\textsubscript{3}O\textsubscript{4} nanopowders were not dried at high temperature to avoid Fe\textsubscript{2}O\textsubscript{3} formation. The maximum current efficiency for magnetite production is close to 30%. This weak value can be explained by the inactivation of the cathode resulting from the formation of magnetite particles during the process.

### 3.3. Cyclic voltamperometric study

Fig. 4 shows cyclic voltamograms of Fe(NO\textsubscript{3})\textsubscript{3} 9H\textsubscript{2}O \((10^{-2} \text{ mol L}^{-1})\) in pure ethanol. Four reduction peaks appear during the reduction process at respectively 0.5, 0.07, −1.15 and −2.35 V/ref. (see peaks I–IV, Fig. 5). The anodic peaks I’ and III’ are associated with peaks I and III respectively. To identify the reduction processes which occur at these potentials, addition of LiNO\textsubscript{3}, FeCl\textsubscript{3} salts and water were carried out. The inset panels in Fig. 5 present the intensity of peaks variation with addition of compounds.

The addition of FeCl\textsubscript{3} anhydrous salts provokes a proportional increasing of the peak I intensity. Thus, peak I corresponds to the reduction of iron III (Fe\textsuperscript{3+} + e\textsuperscript{−} → Fe\textsuperscript{II}). Similarly, the reduction peak IV varies proportionally with the concentration of nitrate ions. Thus we conclude that nitrate reduction occurs at very low potential \((\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- → \text{NO}_2^- + 2\text{OH}^-)\). Nitrite generation has been detected during electrolysis of Fe(NO\textsubscript{3})\textsubscript{3} 9H\textsubscript{2}O solutions in previous study [21].

The intensity of peak III increases proportionally with addition of water, peaks I and IV are not affected. These peaks are directly correlated to water reduction:

\[
\text{H}_2\text{O} + \text{e}^- → (1/2)\text{H}_2 + \text{OH}^-
\]
Peak II (0.07 V/ref.) which decreases under argon atmosphere seems to correspond to the reduction of dissolved oxygen \((1/2)\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}\) in water.

4. Conclusions

After this work we can summarize main results and we can establish some rules to electro-precipitate \(\text{Fe}_3\text{O}_4\) NPs in ethanol bath:

- A \(\text{Fe}^{3+}\) source is necessary. \(\text{Fe}^{3+}\) ions are reduced at the cathode into \(\text{Fe}^{2+}\) at a potential between 0 and 1 V/ref.
- These \(\text{Fe}^{2+}\) ions precipitate at the cathode under \(\text{Fe}_3\text{O}_4\) NPs only if the ethanolic bath contains water and nitrates. However, too much water leads to hydroxide production and not magnetite NPs.
- Reduction waves of water and nitrates occur at much more negative potential than iron reduction and produce \(\text{OH}^-\) ions.
- Only high current density produces \(\text{Fe}^{3+}\) ions are well reduced into \(\text{Fe}^{2+}\), but the local pH at the cathode vicinity is not basic enough to precipitate \(\text{Fe}_3\text{O}_4\) NPs. Consequently, \(\text{Fe}^{2+}\) migrates to the anode to be reoxidized.
- In a solution including \(\text{Fe}^{3+}\) and nitrate ions, traces of water and using high current density, 100% of the current is used for \(\text{Fe}^{3+}\) reduction at the beginning of the electro-precipitation process but decreases gradually during the process as \(\text{Fe}_3\text{O}_4\) NPs are formed whatever the initial concentration of \(\text{Fe}^{3+}\). Probably \(\text{Fe}_3\text{O}_4\) NPs are inhibited further by a passivation electrode phenomenon.

The experimental results allowed us to propose the following reactional mechanism for \(\text{Fe}_3\text{O}_4\) NPs electro-precipitation in an ethanolic/water bath (Eqs. (5)–(7)).

- \(\text{OH}^-\) ions are generated at the cathode during the water and nitrates reduction:
  \[\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-\] (5)
  \[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-\] (6)
- The pH increase at the vicinity of cathode causes \(\text{Fe}({\text{OH}})_3\) precipitation.
- Then, the iron (III) hydroxide is reduced to magnetite (\(\text{Fe}_3\text{O}_4\)) following the reaction:
  \[3\text{Fe}({\text{OH}})_3 + e^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + \text{OH}^-\] (7)

Note that this last reaction regenerates the water consumed in nitrate and water reduction. Remark also, that this last reaction is an equilibrium. Consequently in presence of an excess of water in the solution, \(\text{Fe}_3\text{O}_4\) NPs are not formed and \(\text{Fe}({\text{OH}})_3\) remains stable.

Finally, the process can be written more globally following this last equation:

\[3\text{Fe}^{3+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} + 9\text{e}^- \rightarrow \text{Fe}_3\text{O}_4 + 2\text{NO}_2^- + 2\text{H}_2\]

References