Electrochemical synthesis of magnetic iron oxide nanoparticles with controlled size

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Abstract We present a novel and facile method enabling synthesis of iron oxide nanoparticles, which are composed mainly of maghemite according to X-ray diffraction (XRD) and Mössbauer spectroscopy studies. The proposed process is realized by anodic iron polarization in deaerated LiCl solutions containing both water and ethanol. Water seems to play an important role in the synthesis. Morphology of the product was studied by means of transmission electron microscopy and XRD. In the solution containing almost 100% of water a black suspension of round shaped maghemite nanoparticles of 20–40 nm size is obtained. Regulating water concentration allows to control nanoparticle size, which is reduced to 4–6 nm for 5% of water with a possibility to reach intermediate sizes. For 3% or lower water concentration

nanoparticles are of a needle-like shape and form a reddish suspension. In this case phase determination is problematic due to a small particle size with the thickness of roughly 3 nm. However, XRD studies indicate the presence of ferrihydrite. Coercivities of the materials are similar to those reported for nanoparticle magnetite powders, whereas the saturation magnetization values are considerably smaller.

Keywords Magnetic nanoparticles · Iron oxide · Maghemite · Magnetite · Electrochemical synthesis

Introduction

Synthesis of magnetic nanoparticles with specific size and shape attracts attention of many researchers due to promising current and prospective applications (Cornell and Schwertmann 1996; Teja and Koh 2009). The popular magnetic iron oxides; magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which are in fact ferrimagnets, exhibit a particular property of superparamagnetism if their particles are small enough (Cornell and Schwertmann 1996; Teja and Koh 2009). Magnetite, which is chemically less stable, oxidizes or rather weathers to more stable maghemite. However, maghemite may be transformed into hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is a very weak ferromagnet. The last process occurs at elevated temperatures but may be inhibited if maghemite is doped with other metal ions (Teja and Koh 2009).

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The nanoparticles of magnetic iron oxides (magnetite and maghemite) are known for their low toxicity and biocompatibility and therefore can be used in medicine (Teja and Koh 2009; Jun et al. 2006). The particles may be dispersed in water to form a ferrofluid. The possible medical applications include magnetic fluid hyperthermia bringing certain positive results in alternative cancer therapy (Neuberger et al. 2005), drug targeting transport directed by magnetic field (Neuberger et al. 2005; Lübke et al. 1996; Voltairas et al. 2002) and application as contrast agents in nuclear magnetic resonance imaging (Wang et al. 2001; Cheng et al. 2005). Magnetic nanoparticles may also be used in magnetic data storage devices-like video or audio tapes (Cornell and Schwertmann 1996; Sharrock and Bodnar 1985) to produce pigments (Cornell and Schwertmann 1996), for water purification (Mayo et al. 2007; Cumbal et al. 2003; Uheida et al. 2006; Hu et al. 2005; Tuutijärvi et al. 2009; Park et al. 2009; Afkhami and Moosavi 2010) in magnetic seals and inks or for other numerous applications (Teja and Koh 2009).

Various methods applied to synthesize magnetite or maghemite nanoparticles have been reported so far. Gas phase methods, sol–gel technique, high-pressure hydrothermal or liquid phase methods have been developed. Among the gas phase methods one should mention laser pyrolysis on organometallic systems, which is able to yield magnetite, maghemite, or hematite nanoparticles of good quality (Martelli et al. 2000; Morjan et al. 2003; Morales et al. 1999) but requires sophisticated and expensive equipment. Sol–gel methods based on hydrolysis of metal alkoxides or their precursors can deliver magnetic nanoparticles with the desired size, which is controlled by the process rate, solution content, temperature, and pH (Tavakoli et al. 2007). Good control over particle size and morphology is offered by the continuous hydrothermal technique (Teja and Koh 2009). The liquid phase methods are relatively easy and inexpensive. One of the commonly used methods is coprecipitation of ferrous and ferric ions with a specific ratio in aqueous media (Massart 1981; Kim et al. 2001; Tartaj et al. 2005). Thermal decomposition method is able to deliver magnetic iron oxide with various sizes depending on chemical environment and used organometallic precursor (Kwon et al. 2007; Sun et al. 2004). Magnetite has also been obtained electrochemically by means of electrolysis performed in $\text{Fe}(\text{NO}_3)_3$

solution in ethanol using two carbon electrodes (Marques et al. 2008) or by oxidation of metallic iron in hydrous solution of Me_4NCl (Cabrera et al. 2008).

This article proposes and describes a novel electrochemical method, which enables a synthesis of maghemite nanoparticles. The described process is realized in LiCl solution in deaerated mixture of water and ethanol. The average size of nanoparticles, which is controlled by water-to-ethanol ratio, can be set between 5 and 40 nm, what is a relatively broad range for a single method. Although, a presence of $\text{Fe}(\text{OH})_n$ as an intermediate product can be a common point with the cited electrochemical reports (Marques et al. 2008; Cabrera et al. 2008), pH level does not rise considerably during the reaction indicating that the process is based on another mechanism, which may be related to anaerobic corrosion of iron.

Experimental

The reagents used in the experiment were LiCl (99%+, Merck), unhydrous ethanol (99.8%, Eurochem BGD), iron (99.999%, Goodfellow), and distilled water. The polarization process was carried out in a solution of 0.1 mol of LiCl in a mixture of water and ethanol. The starting solutions were 0.1 mol solution of LiCl in water (0.1 M LiCl– H_2O) and 0.1 M LiCl solution in ethanol (0.1 M LiCl– $\text{C}_2\text{H}_5\text{OH}$). These were mixed subsequently to obtain different concentrations of water (different ratio of water to ethanol) while LiCl concentration was maintained constant.

The electrochemical process was conducted in a glass electrochemical cell with a setup of three electrodes. The reference electrode was Ag/AgCl, counter-electrode was a platinum plate and a working electrode was spectrally pure iron in a form of cylinder with a diameter of 5 mm and a height of 10 mm. The cylinder was sealed in Teflon with remaining uncovered area of 0.5 cm^2 for the polarization studies but in order to produce larger quantity of nanoparticles the full surface was used.

Both cyclic voltammetry studies and a synthesis of magnetite were realized by means of the AUTOLAB 301 station. Voltammetric curves were recorded in a range from -1.5 to 1.5 V . For each solution three measurement cycles were performed and only the third cycle is presented in the publication without the

reverse curve which is less relevant for our considerations.

The process was performed at room temperature (25 °C) in the deoxygenated atmosphere. Argon gas was flowing through the 100 mL solution for 10 min before the working Fe electrode was introduced in the electrochemical cell and during the time of the electrochemical process. Time of synthesis was 4 h in all solutions except for the non-alcoholic solution of LiCl–H₂O where synthesis lasted only 30 min because of the fast rate of the process.

The determination of the chemical composition of the deposit was realized by X-ray diffraction (XRD) with Philips PW-3710 X'PERT diffractometer using Cu-K_α radiation. The Mössbauer studies were performed in the transmission geometry with the Co⁵⁷(Rh) source and the velocity range of ± 12 mm/s. Morphology of the deposit was studied by means of the transmission electron microscopy (TEM) using a Phillips CM20 TWIN microscope operating at 200 kV.

Magnetic characterization has been carried out with vibrating sample magnetometry (VSM). A Quantum Design Physical Property Measurement System was used. Hysteresis loops have been measured at selected temperatures from the range 10–300 K and at the magnetic field varying between +89 and –89 kOe.

Results and discussion

Properties of anodic polarization of iron in deaerated mixtures of C₂H₅OH and H₂O-based solutions of LiCl were investigated by means of cyclic voltammetry. Figure 1 presents the anodic curves corresponding to the solutions described by the formula $x \cdot (0.1 \text{ M LiCl-H}_2\text{O}) + (1-x) \cdot (0.1 \text{ M LiCl-C}_2\text{H}_5\text{OH})$, where x denotes percentage of water–LiCl solution. In fact, x is approximate water concentration. The cathodic curves are not discussed, as they would represent a process of reduction. The anodic curve for the water solution ($x = 100\%$) exhibits a peak near –1.0 V, which should be associated to oxidation of Fe to Fe²⁺. Next, for higher potential values a flat and short passive region is observed. In this region, an oxidized, passive layer, which is formed on the electrode, inhibits further oxidation. For the potential above –0.7 V a transpassive region related to a fast oxidation and dissolution of iron is visible in the anodic

curve as a steep increase of the current as a function of potential. When water concentration is decreased the oxidation peak becomes blurred and probably shifted to higher potential, the passive region is extended and the transpassive region is also shifted to higher potential.

The process of iron dissolution in 0.1 M LiCl in water–ethanol solutions was carried out typically at the potential of 400 mV. According to the curves shown in the Fig. 1 this potential corresponds to the transpassive region. The process of iron polarization lasted usually for 4 h, and resulted in a formation of nanoparticle suspension. For $x = 0\%$ and $x = 3\%$ of water-based solution a color of the suspension was reddish and it took about 1 day for $x = 3\%$ or even 1 week for $x = 0\%$ before the sediment precipitated. For the x values higher than 3% the solution had initially dark greenish-blue color, next a suspension of black or dark brown color was formed and the time needed for a sediment to precipitate decreased to a few hours with increasing x . In the case of water-based solution ($x = 100\%$) the rate of the dissolution process was very high therefore, the polarization duration was reduced to 30 min.

The sediment obtained in a course of polarization was rinsed in ethanol, dried and subjected to TEM studies, results of which are shown in the Fig. 2. The deposits obtained at low concentration of water ($x = 3\%$) consist of very small needle-like nanoparticles shown in the Fig. 2a. Width of the particles estimated from high-resolution TEM images (not shown) can be estimated as about 3 nm with some

Fig. 1 Anodic curves from the cyclic voltammetry studies of $x \cdot (0.1 \text{ M LiCl-H}_2\text{O}) + (1-x) \cdot (0.1 \text{ M LiCl-C}_2\text{H}_5\text{OH})$ solution

Fig. 2 TEM images of the deposit obtained in a course of Fe polarization in the solution: $x \cdot (0.1 \text{ M LiCl-H}_2\text{O}) + (1 - x) \cdot (0.1 \text{ M LiCl-C}_2\text{H}_5\text{OH})$ for **a** $x = 3\%$, **b** $x = 5\%$, **c** $x = 15\%$, **d** $x = 50\%$, **e** $x = 100\%$

distribution. The morphology of the smallest particles obtained at $x = 0\%$ could not be determined.

Higher water concentration leads to a formation of round-shaped nanoparticles of the size which can be controlled just by water content in the solution. This is presented in Fig. 2b–e with insets showing the size distribution of the produced nanoparticles. The HRTEM studies on the obtained nanoparticles visualized atomic rows forming crystallographic order. The exemplary HRTEM images are shown in the Fig. 3 for the content of water based solution of $x = 15\%$ and $x = 100\%$. The HRTEM images proved that every detected nanoparticle has one crystallographic orientation and hence is a single crystal. This is the case even for 40 nm large particles. The less clear HRTEM images for needle-like deposits obtained with low water concentration ($x \leq 3\%$) do not reveal long range crystallographic order and are not discussed in this article. These needles forming the deposit are just a couple of atoms wide, which corresponds to roughly 3 nm.

XRD on a dried deposit was performed to determine the crystallographic structure of the obtained particles. The diffractograms from Fig. 4 show that the nanoparticles are composed of a phase exhibiting inverse spinel structure, which is either magnetite or maghemite. This can be a mixture of both as well.

The diffraction peaks originating from the structures of magnetite and maghemite are almost at the same positions and due to the large peak widths XRD studies were not able to distinguish between these two phases. For the lowest concentration of water ($x = 0, 3\%$) no clear diffraction peaks are present in the diffractograms but one can notice humps at the angles of 35° and 62.5° for the Cu-K_α radiation. This is a characteristic spectrum of ferrihydrite (Drits et al. 1993), nanoparticle material composed of highly defected Fe_2O_3 and water.

One of the analytical methods, which could identify the iron oxide species present in the deposit is Mössbauer spectroscopy. It was used to study the nanoparticles produced in the solutions with $x = 50\%$ and $x = 100\%$. The spectra recorded for these samples are shown in the Fig. 5 together with the fitted curves. They are compared to the reference spectra measured for magnetite and maghemite standards. The corresponding fit parameters are shown in the Table 1.

Low temperature ($T = 80 \text{ K}$) spectrum for the sample obtained at $x = 100\%$ consists of three sextets, two of them, with hyperfine magnetic fields of 524.2 and 506.4 kGs, match well the values obtained for the maghemite reference. These results reveal that maghemite is the dominating phase in the obtained

Fig. 3 High-resolution transmission electron microscopy (HRTEM) images of the deposit obtained in a course of Fe polarization in the solution: $x \cdot (0.1 \text{ M LiCl-H}_2\text{O}) + (1 - x) \cdot (0.1 \text{ M LiCl-C}_2\text{H}_5\text{OH})$ for **a** $x = 15\%$, **b** $x = 100\%$

nanoparticles. However, one can notice that the intensity ratio of the sextets indicate larger contribution from the sextet of 506.4 kGs if compared to a maghemite reference. This indicates a possible contribution of magnetite which has the hyperfine fields of its most intense sextets at about 505 kGs. Moreover, the third sextet with the lowest hyperfine magnetic field of 475.1 kGs has no its counterpart in the reference maghemite spectrum. However, low value of the magnetic field should be expected and explained as an effect of the small particle size, which may be understood in terms of large surface contribution (Papaefthymiou 2009) or just as a direct effect of the small size, which can weaken the magnetism in the smallest objects.

Fig. 4 XRD patterns of the nanoparticles obtained by means of Fe polarization in $x \cdot (0.1 \text{ M LiCl-H}_2\text{O}) + (1 - x) \cdot (0.1 \text{ M LiCl-C}_2\text{H}_5\text{OH})$ solution

The room temperature ($T = 300 \text{ K}$) spectrum for $x = 100\%$ (Fig. 5b) is fitted with large intensity broad sextet with hyperfine magnetic field of 485 kGs which incorporates contributions from maghemite, however, with slightly lower field values. It is noteworthy that a relatively well-resolved sextet with hyperfine magnetic field of 452 kGs is present, which is characteristic of the Fe at octahedral sites in magnetite. The sextet with low magnetic field of 410.6 kGs can be interpreted as a contribution from the surface or a particle size effect. A clear presence of a doublet denotes that a part of Fe atoms may be in a superparamagnetic or nonmagnetic state. The spectrum obtained for $x = 50\%$ (Fig. 5b) is compatible with that for $x = 100\%$ and confirms that the same phase or phases are formed for lower H_2O content, although in this case the data were collected with a lower statistics. The spectrum for smaller particles ($x = 50\%$) has a larger contribution from superparamagnetic or non-magnetic regions of the product.

Magnetisation measurements have been carried out for the samples obtained at a water content of $x = 50\%$ and $x = 100\%$. The VSM option of a Quantum Design Physical Property Measurement System was used. Hysteresis loops measured at four temperatures from the range 10–300 K and at the magnetic field varying between +89 and −89 kOe are presented in Figs. 6 and 7. The saturation magnetisation measured at 10 K and 89 kOe amounts to 50.9 emu/g for the sample obtained at $x = 100\%$

Fig. 5 Mössbauer spectra of the synthesized iron oxide nanoparticles set together with Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ standards at the temperature of **a** 80 K and **b** 300 K

Table 1 Parameters of the fitted curves to the Mössbauer spectra of the nanoparticles and used Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ standards

Sample	Temperature (K)	Component	G/2 (mm/s)	Rel. int. (%)	IS (mm/s)	H (kGs)	QS (mm/s)
Magnetite $\gamma\text{-Fe}_2\text{O}_3$	80	1	0.22	62	0.359 (6)	524.2 (5)	−0.000
		2		38	0.27 (1)	508 (1)	−0.027
	300	1	0.23	62	0.217 (9)	499.4 (9)	0.009
		2		38	0.22 (1)	483 (2)	−0.033
Magnetite Fe_3O_4	80	1	0.13	22	0.543 (7)	506.3 (5)	−0.140
		2		22	0.950 (7)	503.1 (4)	−0.265
		3		44	0.258 (3)	504.5 (2)	−0.049
		4		11	0.69 (1)	376.1 (9)	−0.829
	300	1	0.14	34	0.124 (4)	483.3 (3)	−0.032
		2	0.18	66	0.571 (2)	458.6 (2)	0.016
Nanoparticles $x = 100\%$	80	1	0.23	29	0.390 (5)	524.2 (4)	−0.001
		2	0.23	35	0.308 (4)	506.3 (4)	0.009
		3	0.47	36	0.48 (1)	475 (1)	−0.045
		4	0.25	11	0.42 (1)	412 (1)	0.040
	300	1	0.40	12	0.24 (1)	0.000	0.384
		2	0.30	51	0.215 (4)	484.6 (3)	−0.004
		3	0.26	26	0.486 (8)	451.9 (7)	0.015
		4	0.39	19	0.38 (4)	406 (4)	0.06
Nanoparticles $x = 50\%$	300	1	0.40	25	0.25 (2)	0.000	0.37
		2	0.48	35	0.17 (15)	483 (12)	−0.02
		3	0.35	21	0.52 (26)	457 (20)	0.04
		4	0.39	19	0.38 (4)	406 (4)	0.06

Isomer shift (IS) is expressed with respect to Co^{57} in Rh. Errors are given in parentheses

Fig. 6 Magnetization curves (magnetization vs. applied field) for the sample obtained at $x = 100\%$. The inset shows hysteresis loops

Fig. 7 Magnetization curves (magnetization vs. applied field) for the sample obtained at $x = 50\%$. The inset shows hysteresis loops

(particle size of 20–40 nm) and 35.5 emu/g for the sample obtained at $x = 50\%$ (particle size 10–20 nm). This is much smaller than 91.5 emu/g reported for nanocrystalline magnetite of 37 nm particle size (Ozdemir et al. 2002). For bulk magnetite it amounts to 98 emu/g and for maghemite is of 84 emu/g (Cullity 1972). That considerable discrepancy can be attributed to a possible nonparallel coupling of the magnetisation in the surface regions of grains, which are likely to be oxidized, maghemite-like. The other simple explanation of this discrepancy is a presence of impurities, which might have appeared during synthesis. The saturation magnetisation is smaller for the sample with smaller particles ($x = 50\%$) which is

Fig. 8 Normalized magnetization curves in the enlarged region showing approach to saturation for the samples synthesized at $x = 100\%$ (squares) and at $x = 50\%$ (triangles). Black color corresponds to the temperature 10 K and green color corresponds to 300 K. (Color figure online)

consistent with a larger relative contribution of the surface regions in this sample. A closer inspection of the enlarged region of magnetization versus applied field showing the approach to saturation, Fig. 8, indicates that the sample with larger grains ($x = 100\%$) saturates faster than the sample which consists of smaller grains. The ratio of the remanence-to-the saturation magnetisation at 10 K amounts to 0.27 and 0.32 for the particles synthesized at $x = 100\%$ and $x = 50\%$, respectively. At 300 K it equals 0.13 for both samples. Considering the nanocrystalline magnetite (Ozdemir et al. 2002), these values would correspond to a pseudo-single domain state of the particles.

Both samples exhibit a relatively large coercive force at 10 K which amounts to 528 Oe for the sample synthesized at $x = 100\%$ and 397 Oe for the sample obtained at $x = 50\%$. It drops by a factor more than two on increasing the temperature to 100 K for both samples but then decreases less rapidly upon warming to 300 K, where it equals 88 and 13 Oe for the samples with $x = 100\%$ and $x = 50\%$, respectively.

To understand the mechanism of nanoparticle synthesis, one should analyze the processes, which occur on both electrodes and in the solution taking into account all the known experimental facts. First of all, it is known that the size of nanoparticles systematically grows with increasing content of water in the solution, which is shown in the Fig. 9. Both analyses

Fig. 9 Size of iron oxide nanoparticles determined by means of TEM and XRD versus H₂O concentration in 0.1 M LiCl–H₂O–C₂H₅OH solution

of size population in the regions recorded by TEM and the nanoparticle size obtained from X-ray peak widths by means of the Williamson–Hall method (Williamson and Hall 1953) reveal the same tendency with an agreement within the experimental error (Fig. 9). It can be concluded that the average nanoparticle size can be between 5 and 40 nm but these values may not be the limits if the method is further developed. It is likely that water is necessary for the process to proceed and alcohol seems to inhibit this process.

Important characteristic indicators are the pH value, which is slightly above 7 and the color of the solution soon after the beginning of the reaction, which is dark greenish-blue. Taking into account that the environment is deaerated, one may expect that Fe(OH)₂ is formed, which is a typical intermediate product in anaerobic corrosion of metallic iron. In fact, this compound is easily oxidized to green rust having the color similar to that observed in the solution. The important factors in the described process are the electrode polarization enabling electrolysis and the presence of LiCl, which is highly dissociated assuring good electrical conductivity of the solution. This conductivity amounts to 1.651 mS in the case of 0.1 M LiCl–ethanol, while for pure ethanol it would be 0.77 μS. It is possible that LiCl is not the unique choice of the electrolyte, which helps to initiate the electrolysis.

The process of electrolysis introduces iron ions on the anode and OH[−] groups on the cathode, what apparently leads to the efficient production of Fe(OH)₂.

The next step should be the well known Schikorr reaction $3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2$ (Schikorr 1933), which takes place as a further stage of anaerobic iron corrosion and leads to a formation of magnetite. Indeed, it was observed that hydrogen bubbles volatilize from the solution, what lasts even for some minutes after the electrolysis have been stopped.

According to the described scenario, water is an active medium playing a dominant role in the formation of Fe(OH)₂. For the water-based solution the process proceeds with the highest rate. The principal role of ethanol is to regulate water concentration. Hence, lowering the content of water reduces the rate of the process what leads to a synthesis of smaller particles.

In addition, one should be aware of oxygen formation as a result of water electrolysis on the anode. Therefore, the environment is not strictly oxygen free and magnetite is likely to oxidize partially or completely to maghemite.

Conclusions

The anodic polarization of iron was studied in the solution of 0.1 M LiCl in water and ethanol mixed at different proportions. The polarization in the trans-passive range of the potential may be used to synthesize magnetic nanoparticles consisting mainly of maghemite with certain addition of magnetite. The process is carried out at rather neutral pH, which is slightly above 7. The nanoparticles are of a round shape and their average size can be controlled between 5 and 40 nm by a ratio of water-to-ethanol concentration. The largest particles are formed in water solution and addition of alcohol reduces their size. A reddish product of the polarization is obtained for very low concentration of water, approximately below 3%. It is identified as ferrihydrite and consists of very small needle-like particles. For the particles of 10–20 and 20–40 nm size the saturation magnetization is of 40–56% of that reported for nanocrystalline magnetite materials of similar particle sizes, which is consistent with their pseudo-single domain state concluded from the remanence-to-saturation magnetization ratios.

The proposed new and simple method of iron oxide nanoparticle synthesis can be further developed in order to gain a better control over the maghemite and magnetite content. Next, a more detailed study of the

smallest particles may contribute to our knowledge of ultra small magnetic systems. Finally, embedding the nanoparticles in a protective coating would increase their stability and enable potential applications.

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