



Controlling the diameter and magnetic properties of carbon-encapsulated iron nanoparticles produced by carbon arc discharge



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ABSTRACT

The systematic studies on synthesis of carbon-encapsulated iron nanoparticles by a carbon arc route are presented. The influence of several operational parameters (Fe content in the anode (7.5–65.0 at.%), discharge current (30–80 A), and preparation procedure of the anode) on the yield, selectivity, morphology, diameter distribution, phase composition, graphitization degree and magnetic properties of the products is investigated. It is found that Fe content in the anode is a parameter that *entirely* controls the yield, diameter distribution, graphitization degree and magnetic properties of carbon-encapsulated iron nanoparticles. This parameter also influences the process selectivity. Two other factors, i.e. the discharge current and preparation procedure of the anode, slightly affect the product morphology, diameter distribution and graphitization degree. The phase composition neither depends on the Fe content in the anode nor the discharge current. It is also found that the studied synthesis process has high reproducibility and has a potential to be scaled up.

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1. Introduction

The unique size-dependent properties of magnetic nanoparticles attract the attention of physicists, chemists and engineers. This is reflected in their numerous applications, which include data storage [1], magnetic sensors [2], mobile platforms for catalysts [3], environment protection [4] and various biomedical purposes (drug delivery, hyperthermia, and targeted molecular imaging) [5,6]. The nanoparticles of non-oxide magnetic phases (e.g. transition metals) have substantially better magnetic characteristics in comparison to their oxide counterparts. It is especially expressed in the values of saturation magnetization, which achieves 220 emu/g and 80–90 emu/g for metallic iron and iron oxide, respectively [7]. The magnetic nanoparticles made of pure metallic phases, despite better magnetic performance, may undergo spontaneous unwanted and uncontrollable reactions: (i) surface oxidation, (ii) agglomeration, and (iii) corrosion. The specific properties of magnetic nanoparticles (that are made of pure metallic phases) can be preserved by encapsulating them in thin protective coatings. Several encapsulation agents were proposed to enhance their stability, e.g. silica, polymers, boron nitride, gold and carbon [8]. Polymer-coated nanoparticles have limited stability at elevated temperature and may become permeable. Silica shells frequently possess a porous structure and are easily etched in alkaline solutions. Boron-nitride and carbon coatings are free of these drawbacks. These coating agents are resistant to acids, bases, greases, oils and remain stable at high temperature (up to 650 K under a pure oxygen atmosphere) [9]. They also have a low density which is 6–9 times lower in comparison to

gold. Carbon coatings, unlike their BN counterparts, are readily susceptible to chemical functionalization [10–12].

Carbon-encapsulated magnetic nanoparticles can be synthesized using various techniques. The carbon arc route was historically the first method, which was used to synthesize magnetic carbon encapsulates [13]. This route has high selectivity and high encapsulation yield. Moreover this method can be easily adapted to synthesize carbon encapsulates containing complex magnetic phases, e.g. Fe–Co [14], Fe–Nd–B [15]. Carbon-encapsulated magnetic nanoparticles can also be obtained using thermal plasma [16], chemical vapour deposition [17], combustion synthesis [18], flame synthesis [19], hydrothermal reactions [20], pyrolysis metalloorganic compounds [21] and explosive reactions [22]. So far, a significant progress has been achieved in the development and optimization of efficient and low-cost techniques of fabrication of carbon-encapsulated magnetic nanoparticles. Nevertheless, there is a large gap in the literature, which concerns the problem of controlling the diameter distribution of carbon-encapsulated magnetic nanoparticles. There are few reports devoted to this problem only. Bonard et al. showed that the mean diameter of carbon-encapsulated cobalt nanoparticles synthesized in carbon arc discharge can be varied by changing the buffer gas pressure and the flow rate of the additional quenching gas [23]. The mean diameter can also be controlled in the case of chemical vapour deposition route [24]. However, this is a multi-step and time consuming approach, because it requires first the pristine magnetic nanoparticles with the desired diameter distribution. Then the carbon coatings are grown during thermal decomposition of a carbon precursor.

In this work, the attention is focused on carbon arc discharge route. Contrary to the mentioned paper authored by Bonard, this work concerns the experiments which are conducted at constant pressure, but

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with the wide range of Fe contents in the anode. Moreover, systematic studies of the encapsulation yield, magnetic properties, morphology, phase composition and graphitization degree are additionally included.

2. Materials and methods

The experiments were conducted in a carbon arc discharge chamber equipped with a vacuum system and an automatic system, which allows the precise movement of electrodes. The reactor chamber is described in details elsewhere [25]. All experiments were carried out at the constant pressure of 60.0 kPa under Ar–H₂ (50% vol.: 50% vol.) atmosphere. Graphite rods (8 mm in diameter) were used as cathodes. For the sake of comparison two types of anodes were prepared: homo- and heterogeneous. The homogeneous anodes containing 7.5–65.0 at.% Fe were fabricated of fine graphite powder (1–2 μm), fine Fe powder (10 μm) and pitch (detailed amounts of the precursors are listed in Table S1 in Supplementary data). The as-prepared mixture of graphite, iron and pitch was pressed at 2 MPa in a cylindrical form. Then, the pressed rolls were annealed in a tube furnace under Ar at 1273 K (heating rate of 3 K/min). In the case of heterogeneous anodes (which contained 7.5–22.5 at.% Fe), the graphite rods (8 mm in diameter) were drilled and the cavity (6 mm in diameter) was filled with a mixture of graphite and Fe powder. The Fe content in the heterogeneous anodes could not be greater than 22.5 at.% (in this case the filling mixture contained 90 wt.% of Fe). The densities of the homo- and heterogeneous anodes are shown in Supplementary data (Table S1).

Three discharge currents (30, 40 and 50 A) were used for arcing in experiments with the homogeneous anodes. There were no observable sublimation of the anode containing 7.5 at.% Fe in the experiment performed at 30 A. A typical arcing time was between 5 and 10 min for other runs. The heterogeneous anodes required higher currents (70 and 80 A) in order to maintain comparable sublimation rates. The raw products were collected from the inner walls and the lid of the reactor chamber. In all tests the erosion rate and the product formation rate were monitored. The erosion rate is defined as the ratio of the difference between the starting and final mass of the anode, and the total discharge time. The product formation rate is calculated as the ratio between the total mass of the collected product and the total discharge time. The raw products were subjected to a purification procedure, which included the 24 h boiling process in 3 M HNO₃, followed by washing with excess water and ethanol. This purification was necessary to remove the non-encapsulated Fe nanoparticles.

The physical and chemical properties of raw and purified products were thoroughly examined. The Fe content was evaluated by a thermogravimetric analysis (TA Instruments Q-50). The thermogravimetric measurements were conducted under oxygen atmosphere in the temperature range of 300–1273 K. The Fe content was calculated from the ratio between the initial and final mass of the analysed sample. The morphology was studied by transmission electron microscopy (TEM, Zeiss Libra 120 operated at 120 kV). TEM analyses were carried out using standard Cu grids (300 mesh). Phase composition studies were conducted on a Bruker D8 diffractometer using a Cu K-α radiation in a 2θ range between 10 and 70 with a step of 0.02. Raman spectra were measured using a dispersive Raman spectrometer (Jobin Ivon T-64000) equipped with a 514.5 nm excitation laser. Magnetic measurements were carried out at 298 K using a vibrating magnetometer (Lake Shore 668).

3. Results and discussion

3.1. Operational parameters and encapsulation yield

Fig. 1a shows the dependence of Fe content in the anode on the erosion rate (for selected arc currents). The erosion rate rises with Fe content for each current. To explain this effect, one has to refer to the heat of sublimation, which is 716 kJ/mol and 340 kJ/mol for graphite and iron, respectively. These values show that the evaporation of iron requires a

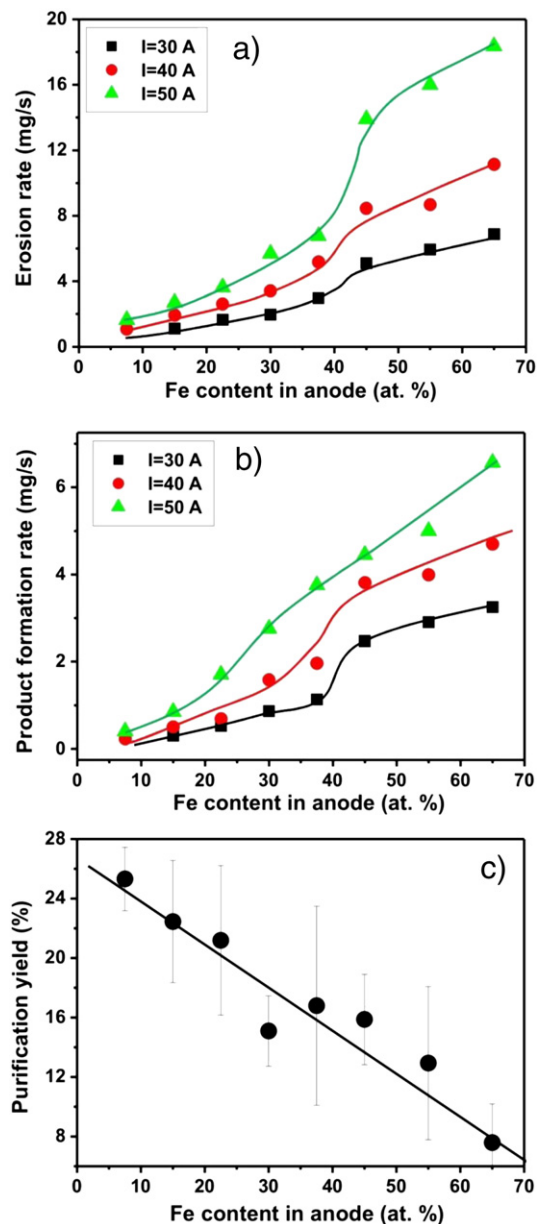


Fig. 1. Erosion rate, product formation rate and purification yield in a series of tests with homogeneous anodes.

half of energy, which is required for sublimation the same amount of graphite. This finding explains the observed increase of the erosion rate. The erosion rate further increases with an increase of the discharge current. This is an expected result, because under these conditions the higher amount of energy is introduced into the plasma. The relation between the normalized erosion rate and the anode composition is the same for each discharge current (Fig. S1). This observation undoubtedly demonstrates, that the arc plasma sublimation of Fe-doped homogeneous anodes is a reproducible and controllable process. In the case of heterogeneous anodes the observed trend in the erosion rate does not mimic the behaviour of homogeneous electrodes (Fig. 2). For the discharge current of 70 A there is no correlation between the erosion rate and Fe content in the anode. The erosion rate at 80 A increases 3–5 times, however, there is no correlation with Fe content. One has to be aware that the heterogeneous anodes are composed of compact graphite shell and “soft” Fe–C core. Obviously, the core has higher porosity and may sublimate faster.

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