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pH Transitions and electrochemical behavior during the synthesis of iron oxide nanoparticles with gas-diffusion electrodes†

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Gas diffusion electrocrystallization (GDEx), was explored for the synthesis of iron oxide nanoparticles (IONPs). A gas-diffusion cathode was employed to reduce oxygen, producing hydroxyl ions (OH^-) and oxidants (H_2O_2 and HO_2^-), which acted as reactive intermediaries for the formation of stable IONPs. The IONPs were mainly composed of pure magnetite. However, their composition strongly depended on the presence of a weak acid, i.e., ammonium chloride (NH_4Cl), and on the applied electrode potential. Pure magnetite was obtained due to the simultaneous action of H_2O_2 and the buffer capacity of the added NH_4Cl. Magnetite and goethite were identified as products under different operational conditions. The presence of NH_4Cl facilitated an acid-base reaction, and in some cases, led to cathodic deprotonation, forming a surplus of hydrogen peroxide while adding the weak acid promoted gradual changes in the pH by slightly enhancing H_2O_2 production when increasing the applied potential. This also resulted in smaller average crystallite sizes as following: 20.3 ± 0.6 at -0.350 V, 14.7 ± 2.1 at -0.550 and 12.0 ± 2.0 at -0.750 V. GDEx is also demonstrated as a green, effective, and efficient cathodic process to recover soluble iron into IONPs, being capable of removing >99% of the iron initially present in solution.

Introduction

Nanoparticle production methods that are economical, clean, safe, easy-to-implement, and upscalable are an active research subject.(1–3) A key disadvantage of most alternatives (4–7) is the use of non-aqueous molecular solvents, reducing, and capping-agents, which are often environmentally hazardous and added in excess.(8,9) Moreover, most methods involve several processing steps, often including different upstream and downstream units, which can appear to be suitable at lab scale but are challenging to implement industrially.(5,10–12)

The development of environmentally-friendly synthesis methods has gained particular attention, (13–17) intensifying the interest in electrochemistry as a synthetic platform under mild conditions.(18–25) In most instances, the known electrochemical approaches to synthesize nanoparticles (26–28) render the growth of films onto inert substrates, mostly by one-step electrodeposition, at working temperatures between 70° and 90° C. A compilation of pathways and methods for the electrochemical formation of magnetite nanoparticles is available in scientific literature.(23,26,29–32)

In the present study, a new electrochemical method, called gas-diffusion electrocrystallization (GDEx) (14), is employed for the formation of iron oxide nanoparticles (IONPs), (33) from a soluble iron precursor (Fe^{2+}). A gas diffusion cathode is used for the electroreduction of oxygen (O_2) contained in a gas phase (air), which, in turn, drives the precipitation of crystalline IONPs at the electrochemical interface.

The oxygen reduction reaction (ORR) using carbon-based gas-diffusion electrodes has been thoroughly investigated and well demonstrated in acidic and alkaline media. Reactions [1] and [2] show the two-electron ORR of O_2 to H_2O_2 or hydroperoxide ion (HO_2^-), (41) which occur at acidic and alkaline conditions, respectively. Besides, in alkaline conditions, HO_2^- can be reduced to OH^- via reaction [3].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad [1]$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad [2]$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad [3]$$

Throughout this work, both chemical species, *i.e.,* H_2O_2 and HO_2^-, will be referred to as H_2O_2, granting that at more alkaline

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