

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 (H₂O₂ and HO₂⁻), 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 (NH₄Cl), and on the applied electrode potential. Pure magnetite was obtained due to the simultaneous action of H₂O₂ and the buffer capacity of the added NH₄Cl. Magnetite and goethite were identified as products under different operational conditions. The presence of NH₄Cl 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 H₂O₂ 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

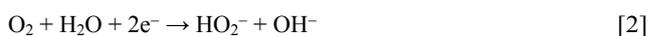
Nanoparticle production methods that are economical, clean, safe, easy-to-implement, and upscalable are an active research subject.^(1–3) A key disadvantage of most alternatives ^(4–7) is the use of non-aqueous molecular solvents, reducing, and capping-agents, which are often environmentally hazardous 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 (Fe²⁺). A gas diffusion cathode is used for the electroreduction of oxygen (O₂) 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 O₂ to H₂O₂ or hydroperoxide ion (HO₂⁻), ⁽⁴¹⁾ which occur at acidic and alkaline conditions, respectively. Besides, in alkaline conditions, HO₂⁻ can be reduced to OH⁻ via reaction [3].



Throughout this work, both chemical species, i.e., H₂O₂ and HO₂⁻, will be referred to as H₂O₂, granting that at more alkaline

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