



Influence of electrode material and roughness on iron electrodeposits dispersion by ultrasonification



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ABSTRACT

This study relates the sonoelectrochemical production of metallic particles and nanoparticles. The emphasis is on the influence of electrode material and roughness on the morphology of iron electrodeposits and their dispersion from the electrode by ultrasonification. Ultrasonification is either applied during cyclic voltammetries with solution stirring or after galvanostatic iron electrodeposition; no dispersion was observed when using a gold electrode, whereas dispersion was always observed when using vitreous carbon (VC) substrates. Scanning Electron Microscopy (SEM) imaging of the electrodeposits shows higher iron coverage on gold than on VC electrodes. Iron spreads more on gold than on VC. The values of both the interfacial energy of the iron/electrode interface and the work of adhesion of iron on the electrode are in agreement with the previous observations. Dispersion kinetics on VC were found to be dependent on the electrode surface roughness. Results suggest that dispersion follows a first order kinetics, which is coherent with the constant action of cavitation bubbles in the vicinity of the electrode surface. Enhancement of mass-transfer by ultrasound has also been observed.

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1. Introduction

Iron-based nanoparticles (Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, nickel-cobalt-iron alloy) exhibit interesting magnetic properties in the medical field, such as contrast agents for Magnetic Resonance Imaging [1,2] and for treatment of tumors by hyperthermia [3,2]. Recent studies [4] indicate that zero-valent iron nanoparticles (ZVI-nP) show better magnetic performance than iron oxides for medical applications. ZVI-nP can also be used for various other applications such as an effective reducing agent: i) in water treatment [5], ii) for dechlorination [6,7], iii) nitrate removal [7–9], and iv) for destruction of various other pollutants (see [5] for an extensive review).

ZVI-nP can be synthesized by several techniques (see [10] and [5] for an exhaustive list): ball milling [11], thermal reduction (reduction of iron salts [12] and reduction of oxide [13]), iron salts wet-chemical reduction [6,14] (using borohydride salt as a

reducing agent) and direct electrochemical reduction [15,16,9]. The most widely used technique is the wet-chemical method.

Scaling-up of wet-chemical method, in order to produce large quantities of ZVI-nP, requires expensive reagents and specific security conditions because of the gaseous hydrogen production [12].

Direct electrochemical ZVI-nP synthesis appears as a promising technique for economic and safe production processes, especially at a large scale; the reducing reagent is replaced by electricity and under controlled conditions hydrogen production is avoided. Nevertheless, metallic iron, produced at the cathodic surface, must be removed from the electrode and dispersed in the liquid at the required size. Various works involve ultrasonic dispersion of electrodeposited iron, simultaneously or sequentially with iron-precursors reduction, allowing the renewal of the cathode surface. Generally, power ultrasounds (~ 20 kHz, using an ultrasonic horn or bath) are used to generate cavitation bubbles that, during their violent collapses, create fluid motion which removes solid deposits from the electrode surface. During iron electrodeposition, under sequential pulses of the applied current, Delplancke et al. [15] apply shifted pulses of ultrasounds, using a titanium ultrasonic horn (20 kHz, 50 W/cm^2), also used as the polarized cathode. Nanoparticles (6 nm–100 nm) of pure Fe and alloys of Fe/Ni/Co have been successfully synthesized in aqueous solutions; partial ‘chemical oxidation’ of pure iron particles has been observed. In

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Nomenclature

A	geometric surface area (m^2)
A_{elect}	Hamaker constant of electrode material, $elect = Au$ or VC (J)
$A_{elect/L/Fe}$	Hamaker constant for electrode material ($elect = Au$ or VC) and iron interacting across the liquid (J)
Ar	Argon
A_{Fe}, A_L	Hamaker constants of the iron and the liquid (J)
C_{H^+}	Protons concentration (mol/m^3)
d	Separation distance (m)
D	Diffusion coefficient (m^2/s)
e	Thickness of the deposit (m)
E_{adh}	Adhesion energy of iron on VC electrode = $W_{Fe/VC}S_{Fe/VC}$ (J)
E	Electrode potential (V)
F	Faraday constant (96,500 C/mol)
h	Local surface height (m)
j_{lim}	Limiting current density (A/m^2)
$I, I_{applied}, I_{lim}$	Current, applied current and limiting current (A)
M_{Fe}	Molecular weight of iron (kg/mol)
n	Electrons number
Q_c, Q_a , and $Q_{a_{ref}}$	Respectively the cathodic, the anodic and the anodic reference amount of charges (C)
r	Potential scan rate (mV/s)
r_a	Arithmetic roughness (m)
r_w	Wenzel's roughness = ratio between actual surface and geometrical surface
s	Dispersion rate constant (s^{-1})
S_{disk}	Surface area of the disk electrode (m^2)
t	Time (s)
t_{US}	Ultrasonification duration (s)
$W_{Fe/elect}$	Work of adhesion of iron on the electrode, $elect = Au$ or VC (J/m^2)
x, y	Cartesian coordinates (m)
Greek letters	
γ_a	Surface tension of medium a (J/m^2)
$\gamma_{a/b}$	Interfacial tension between both media a and b (J/m^2)
γ_{elect}	Surface energy of the electrode, $elect = Au$ or $VC1$ or $VC2$ (J/m^2)
γ_d and γ_p	Respectively the dispersive and the polar components of the surface energy (J/m^2)
η	Overpotential (V)
ρ_{Fe}	Volumetric mass of iron (kg/m^3)
ν	Kinematic viscosity (m^2/s)
$\Phi_{a/b}$	Adjustment parameter which depends on interactions between both interacting media a and b
ω	Angular velocity (rpm)

another study [16], cathode is assembled both with a high (0.2–2 MHz, 5 W/cm²) and a low (20 kHz, 100 W/cm²) frequency ultrasonic transducers who irradiate the cathodic area; constant current electrolyses were carried out in tetrahydrofuran, under ultrasonification, and 10 nm sized ZVI-nP are produced when the low and the high frequency transducers are used simultaneously. Chen et al. [9], claim that ZVI-nP ranging between 1–20 nm were synthesized using aqueous 1 M FeCl₃ in the presence of

cetylpyridinium chloride as a dispersing agent; a two platinum electrodes 'classical electrochemical cell', 'entirely' immersed into an ultrasonic bath (20 kHz), was used and galvanostatic electrolyses were carried out under ultrasonification. Other metallic nanoparticles (silver, palladium, platinum, zinc, nickel, gold) have been synthesized by the sonoelectrochemical method, see [17] for a review. Previous studies were generally devoted to determining the best operating parameters (pulse times, current, temperature, ultrasounds intensity, stabilizers, etc.) for a given set-up allowing the synthesis of desired nanoparticles.

Effects of power ultrasound on various electrochemical systems have also been extensively studied. Ultrasounds are generally applied using a titanium ultrasonic horn acting as the ultrasound generator placed in front of the working electrode ('face-on' configuration); the working electrode can also be directly integrated on the ultrasonic horn ([18]). Another possibility is to immerse the electrochemical cell in an ultrasonic bath [19]. Among other effects and regardless of the experimental configuration, ultrasounds induce cavitation bubbles and acoustic streaming which enhance mass-transfer leading to an increase of the current [20–25,19]. Current fluctuations are also observed due to violent bubble collapses [21,26,27].

The ability of the fluid motion and also the shocks induced by ultrasound to 'clean' the electrode surface has been investigated in several works. Cavitation bubble collapses induced by ultrasound were found to be able to activate electrodes avoiding passivation by 'eroding/roughening' the electrode material [28,19]. Coupling mercury electrodeposition and ultrasonification simultaneously on a vitreous carbon electrode has led to a 'steady state' regime where the quantity of electrodeposited Hg on the electrode remains constant (electrodeposition flux = ablation flux) [29]. Under ultrasonification, the electrodeposition of metals such as Zn, Co, Pb, and Hg, was investigated on a vitreous carbon substrate by cyclic voltammetry in [30] (see also [31]). The authors analyzed the ratio of anodic to cathodic charges as a function of the ultrasound intensity, for their particular experimental conditions (potential scan rate, sonoelectrochemical system, electrode material . . .), and showed that it depends on both the ultrasound intensity and the metal used. This suggests the importance of metal/substrate affinity on the electrodeposits dispersion. Considering the case of a particle lying on a substrate and submitted to ultrasonification in [32], the authors discussed the competition between the hydrodynamic forces and the adhesion force as a function of the particle size; they showed that ultrasounds should be able to remove submicrometer particles but not smaller particles such as molecular adsorbates (adhesion outweighs hydrodynamics forces).

These previous studies show that the efficiency of ultrasound to remove/disperse electrodeposited metals should depend on:

- the ultrasound intensity (and the experimental configuration used) [30,31]
- the size/morphology and the spatial distribution of deposited metallic particles [32]
- the adhesion energy of electrodeposited metal on the electrode material

Note that, to date, the effect of the adhesion energy of the electrodeposited metal on the electrode substrate, has not been directly investigated.

In the present work, the dispersion by ultrasound of iron electrodeposits is studied for various electrode materials (gold and vitreous carbons) which allows to vary the adhesion energy. The effect of the electrode material on the morphology of the electrodeposited iron is also studied by SEM imaging. The influence of the electrode surface roughness is investigated using VC electrodes having different levels of polishing.

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