Influence of Base Electrolytes on the Electrodeposition of Iron onto a Silicon Surface

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Comparative electrodeposition of iron onto the surface of silicon was investigated at large overpotential in the presence of some base electrolytes. The nanostructure of the iron electrodeposits was analyzed with SEM and FE-SEM measurements. The results highlight the influences of ion specificity on the rate of hydrogen evolution and of selective ion adsorption on the morphology of the iron electrodeposits.

1. Introduction

Both the size and the shape of metal or semiconductor colloidal particles have received much attention in recent years because of their strong influence on the physical and chemical properties of materials. The properties and applications of metal nanoparticles with various morphologies can be used in a variety of areas including catalysis, electronics, and optics.^{1–3} The preparation of many monodisperse inorganic colloids of various shapes (spheres, rods, cubes, triangles, disks) by precipitation and/or reduction reactions from homogeneous solutions has been reported in the literature.^{4–7} The use of a soft template or capping agent (polymers, surfactants) is often required in these reaction pathways. The control of the shape of the nanoparticles was found to be related to that of the templates, and this allows the generation of various morphologies in different experimental conditions.^{8,9}

In parallel, the presence of metal nanoparticles directly deposited onto a substrate is also required in some technological applications (catalysts for the synthesis of carbon nanotubes, electrochemical sensors). In this sense, the electrochemical synthesis of metal nanoparticles through the electrocrystallization process has gained renewed attention and is considered to be a promising way because of its simplicity, convenience, and use of inexpensive equipment.^{10,11} Metal electrocrystallization takes place at an electrode-electrolyte interface under the influence of an electric field and is directly related to nucleation and crystal growth processes.^{12,13} On the basis of energetic considerations, general trends can be expected. When the interfacial bonding between the foreign substrate and the deposited metal is weaker than the bonding in the metallic deposit itself, the surface concentration of adsorbed metal, Me_{ads}, is low, and the growth of isolated 3D islands is more favored.14 Recent fundamental studies have been directed toward identifying and understanding the modulation of the key parameters allowing control of the dimensions and the narrowing of the size distribution of many metal nanoparticles without the use of any additives or template.^{10,15,16} Moreover, various surface analytical techniques, such as SEM and TEM (scanning and transmission electron microscopies, respectively), EXAFS (extended X-ray absorption fine structure) analysis, and AFM (atomic force microscopy), have allowed important information on the

structure of substrates and the morphology of metal electrodeposits to be obtained. It was inferred from these studies that the nucleation of the new metallic phase and its growing form play a dominant role in the size distribution and structure of the metallic deposit.

Although the electrolyte phase was assumed to affect the characteristics of the substrate-electrolyte interface and probably the properties of the metallic deposits, very few studies have been focused on investigating the influence of the nature of the background electrolyte in the electrocrystallization process. Very often, the metal is deposited by using an electrolyte having the same anion as the metallic salt. However, it has been known for some time that some components can have a pronounced effect on the resulting crystal shape because of their specific adsorption onto a particular crystallographic plane.¹⁷ Moreover, the nature of an ion can have a significant influence on the behavior of a colloidal system, particularly at concentrations exceeding 0.10 M, where the range of electrostatic interactions is greatly reduced.¹⁸ These ion-specific effects, related to the Hofmeister series, are relevant to many systems and processes, implying colloidal interactions where short-range hydration contributions were shown to play a crucial role.¹⁸⁻²¹ Both ions and substrate surfaces change the solvent properties around them, and this can have an influence on solvent-surface, surface-ion, and solvent-ion interactions during the electrocrystallization process.

In this study, the influence of the nature of some base electrolytes on the electrodeposition of iron onto the hydrophobic surface of silicon without any capping agent or template was investigated. The experiments were performed with the same imposed overpotential (-670 mV). The base electrolyte concentration was taken as 0.6 M to avoid any migration current in the electrochemical system and to ensure the eventual manifestation of ionic specificity. Iron electrodeposits were analyzed through SEM and FE-SEM measurements.

2. Experimental Section

The iron sulfate salt FeSO₄·7H₂O and the base electrolytes (NH₄)₂SO₄ (ammonium sulfate), NH₄SCN (ammonium thiocyanate), NH₄ClO₄ (ammonium perchlorate), NH₄Br (ammonium bromide), and NH₄CH₃CO₂ (ammonium acetate) were obtained from Sigma-Aldrich (France) and were used as received. The electrolytic baths (50 mL) were prepared by dissolving the required amount of iron salt and base electrolyte in distilled

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and deionized water. It should be noted that the electrolytic solution composed of ammonium thiocyanate and iron sulfate salts exhibited the characteristic red color corresponding to the formation of the soluble iron(III) thiocyanate complex Fe-(SCN)²⁺ originating from the rapid oxidation of iron(II) by dissolved oxygen in water²² (0.26×10^{-3} M maximum solubility at 25 °C). The concentration of the iron(III) thiocyanate complex was determined spectroscopically (466.7-nm maximum absorption wavelength) and was found to correspond to 1.5×10^{-3} M, a negligible amount with respect to the 0.4 M iron(II) concentration used.

Prior to each experiment, electrolytic baths were degassed by bubbling of nitrogen gas during 10 min. The pH of the various electrolyte solutions was between 3 and 5.2.

The electrochemical setup was a standard three-electrode cell with a silicon plate as the working electrode $(1 \times 2 \text{ cm}^2)$, platinum foil as the counter electrode, and a saturated calomel reference electrode (SCE). The working electrode, n-type Si-(100) single crystals with a resistivity of 0.003 Ω ·cm (Neyco Co.), was first sonicated in trichloroethylene for 10 min to remove dirt and rinsed with acetone. It was then immersed for 1 min in dilute (1/40) hydrofluoric acid (HF) to dissolve the (eventual) hydrophilic superficial silica layer, thoroughly rinsed with distilled water, and finally dried in a stream of nitrogen gas. The electrode was immersed (1-cm depth) in electrolytic bath at 298 K just before experiments. After electrodeposition, the electrode was rinsed with water and then dried by nitrogen gas.

The electrochemical experiments (cyclic voltammetry and chronoamperometry) were executed at ambient (room) illumination with a potentioscan (Radiometer Analytical S.A. Copenhagen, Tacussel DEA 332) coupled with a digital converter (Radiometer Analytical, IMT 102) and controlled by a PC running the electrochemical software (Radiometer Analytical, VoltaMaster 2).

Iron electrodeposits were examined by scanning electron microscopy (SEM) with a LEO 435 VP electron microscope and by field-emission scanning electron microscopy (FE-SEM) with a JEOL JSM 6700F apparatus, using various magnifications to observe the morphology of the deposits. An energy-dispersive X-ray spectroscopy (EDS) apparatus (INCA Energy 250, Oxford Instruments), attached to the SEM instrument, was used to obtain information on the composition of the electrodeposits.

Contact angles of water droplets deposited on the electrode surface were measured with a Digidrop apparatus (GBX, France) to determine the wetting behavior.

3. Results and Discussion

3.1. Comparative Electrodeposition of Iron. The different phases occurring during the electrocrystallization of metals have been described elsewhere.^{12,23} The specificity of the electrocrystallization process comes from the presence of the charged electrode, which generates the well-known electrical double layer. The distribution of ions around the electrode is governed by the balance between electrostatic interactions and thermal agitation.²⁴ Counterions having a charge of opposite sign to that of the surface are attracted, whereas co-ions with a charge of the same sign as the surface are depleted. However, depending on the nature of the substrate surface, interfacial water molecules can exhibit spatial orientations significantly different from that of bulk water.²⁵ When a hydrophilic (polar) surface is immersed in water, a high-density layer of water molecules around it is promoted through an extensive network of hydrogen bonds. In contrast, when a hydrophobic surface is used, there is a local



Figure 1. Water droplet deposited on the silicon surface after hydrofluoric acid treatment.

disruption of the adjacent water network, so that the layer of water molecules is of much lower density. Consequently, the hydrophilic or hydrophobic character of the surface can exert an influence on the surrounding ions because surfaces of different characters do not present the same affinity with water molecules. Ions have been divided into two broad classes (Hofmeister series) according to their ability to structure the water molecules in their vicinity.²⁶ Ions with a large surface electric field that interact more strongly with water molecules than water molecules interact with each other are called structure makers or cosmotropes (Mg²⁺, Li⁺, Na⁺, SO₄²⁻, CH₃CO₂⁻, F⁻), whereas those presenting the opposite effect, with a small surface electric field, are called structure breakers or chaotropes $(NH_4^+, Cs^+, Rb^+, SCN^-, ClO_4^-, Br^-)$. These hydration effects were shown to be more pronounced with anions because anions can bind more strongly with water molecules through hydrogenbond-like interactions.26

The wetting behavior of the studied silicon substrate was determined by measuring the contact angle of a water droplet deposited on the surface. The average value was found to be around 87° after the hydrofluoric acid treatment (see Figure 1), thus reflecting the hydrophobicity of the electrode surface. As chaotropic ions disrupt the water structure around them, it might be suggested that such ions would tend to be embedded more favorably than cosmotropic ions in this interfacial region with a low-density water layer at the contact of the hydrophobic silicon surface. First, comparative iron electrodeposition experiments were carried out by using FeSO₄ salt at 0.4 M and (NH₄)₂-SO₄ or NH₄SCN base electrolyte at 0.6 M to satisfy similar conditions encountered in previous studies11 and to enable easier observation of electrodeposit morphology. The cosmotropic SO₄²⁻ and chaotropic SCN⁻ anions were chosen to investigate the influence of ion specificity because they are in the extreme of the Hofmeister series.²⁶ The ammonium counterion was taken as the same common chaotropic cation.

To determine characteristic electrochemical potentials such as the deposition potential, the onset of cathodic reduction, and the nucleation overpotential, comparative cyclic voltammograms were obtained at the same scanning rate (20 mV/s) for both systems. The results of current-voltage (CV) experiments are shown in Figure 2. The onset of iron deposition is found to occur at essentially the same potential during the direct cathodic scan, namely, -1082 mV/SCE for (NH₄)₂SO₄ (A) and -1072 mV/SCE for NH₄SCN (B), and no cathodic peak is observed because of the high concentration of iron salt. Upon sweep reversal, the cathodic current gradually decreases until it crosses 0 and becomes an anodic current. The beginning of iron oxidation is found to occur at -790 mV/SCE for $(NH_4)_2SO_4$ (A), whereas it corresponds to -870 mV/SCE for NH₄SCN (B), thus indicating a greater nucleation overpotential²⁷ in the presence of (NH₄)₂SO₄. Further sweeping in the positive direction results in a different shape of the anodic peak. In the case of (NH₄)₂SO₄, this peak is sharper and higher. It corre-



Potential vs SCE (mV)

Figure 2. Cyclic voltammogram with (A) 0.4 M FeSO₄ and 0.6 M $(NH_4)_2SO_4$ and (B) 0.6 M NH₄SCN.



Figure 3. Current versus time transients for iron electrodeposition onto silicon at -1500 mV/SCE in the presence of $(NH_4)_2SO_4$ (thin curve) and NH_4SCN (thick curve) base electrolyte.

sponds to a greater current magnitude (1420 mC) than in the case of NH₄SCN (950 mC). Moreover, the current past the peak is nil with $(NH_4)_2SO_4$ (A), whereas this is not the case with NH₄SCN (B). These results suggest hindered and incomplete oxidative dissolution of deposited metallic iron at the electrode surface in the presence of NH₄SCN.

All of the following experiments were performed at -1500 mV/SCE, corresponding to an overpotential η of about 670 mV. Current versus time transients for iron electrodeposition onto the silicon surface for both electrolytic baths are shown in Figure 3. The curve with (NH₄)₂SO₄ starts at a lower value of the current density and begins to level off later than that with NH₄-SCN. Moreover, it should be noted that some bubbles were



Figure 4. Water droplet deposited on the silicon surface after iron electrodeposition.





Figure 5. FE-SEM images of iron electrodeposits obtained with (A) 0.4 M FeSO₄ and 0.6 M (NH₄)₂SO₄ and (B) 0.6 M NH₄SCN, top view.

observed on the electrode surface in the case of NH_4SCN . These aspects will be studied in more detail in section 3.3. After iron electrodeposition, the measurement of a low contact angle for a water droplet on the electrode surface (see Figure 4) reveals the dramatic modification of the wetting behavior due to the presence of the hydrophilic metallic phase, regardless of the electrolytic bath used.

3.2. Comparative Morphology of Iron Deposits. The top view from FE-SEM measurements (see Figure 5) shows that many iron cubes are obtained on the surface in the presence of $(NH_4)_2SO_4$ (A), whereas round-shaped deposits are present when NH₄SCN is used (B). The sizes of the larger cubes and round-shaped deposits are around 200 and 500 nm, respectively, with $(NH_4)_2SO_4$ and NH₄SCN. In the case of NH₄SCN (B), the larger



Figure 6. FE-SEM image of iron electrodeposits obtained with 0.4 M FeSO₄ and 0.6 M (NH₄)₂SO₄, magnification.

particles are located in regions of lower population density (two large particles are observed to "coalesce"), and the size distribution is wider. This observation has already been pointed out,¹⁵ and it was ascribed to interparticle diffusional coupling during the growth phase.¹⁰ Closer inspection shows highly faceted cubic iron deposits (see Figure 6). The side view (Figure 7A) and profile view (Figure 7B) reveal that the electrodeposits with NH₄SCN correspond to hemispheres (domes) protruding toward the aqueous phase, the highest corresponding to about 400 nm. As the applied overpotential is quite large, iron particles are assumed to nucleate instantaneously and to grow through a diffusion-controlled reaction. Under these conditions, the metal deposits are expected to adopt the cubic shape corresponding to the natural crystal habit of iron.²⁸ According to Wulff's rule, the morphology of a crystal depends on the growth rates of the different crystallographic faces, the slow-growing faces having the greater influence.¹⁷ The presence of some ions or additives can have a profound effect on the growth of a crystal and thus modify the crystal habit.^{17,29} Some additives can suppress growth entirely, whereas others can be adsorbed selectively onto different crystal faces and retard their growth rates because adsorption reduces the interfacial tension. The adsorption of thiocyanate ions on large bare and passive iron surfaces has been reported in the literature.^{30,31} The amount adsorbed was found to increase significantly with thiocyanate concentration and electrode potential. It was inferred from these studies that SCN⁻ adsorption should occur with the S-C-N axis normal to the surface, and the standard Gibbs free energy of adsorption was found to correspond to -1.26 and -0.7 kcal/mol for bare and passive iron, respectively. Therefore, energy-dispersive X-ray spectroscopy (EDS) was used to detect the eventual presence of thiocyanate in the composition of electrodeposits. The EDS patterns of electrodeposits on silicon substrate showed only the presence of iron (Fe) when the base electrolyte was $(NH_4)_2SO_4$ (Figure 8A), whereas the presence of iron, sulfur (S), and carbon (C) was systematically detected for various measurements when the NH₄SCN electrolyte was used (Figure 8B). These results thus confirm the presence of thiocyanate ions in iron electrodeposits (even after water rinsing of the electrodeposits). This might justify the previous observed differences in the comparative CV curves (Figure 2A,B) because of SCN⁻ poisoning as soon as iron becomes electrodeposited. As such,





Figure 7. FE-SEM images of iron electrodeposits obtained with 0.4 M FeSO₄ and 0.6 M NH₄SCN: (A) side view and (B) profile view.

adsorption of thiocyanate ions during growth of the iron metallic phase is found to inhibit the formation of the crystal habit, without privileging any face, but rather to generate equal growth rates in all directions with respect to the substrate surface, thus allowing hemispherical electrodeposits to be obtained.

To obtain more information, experiments were performed with the same electrolyte concentration, say, 0.6 M, but with varying proportion of SO42- and SCN- anions such that [SO42-]/ [SCN⁻] ranged from 0.33 to 600 in the electrolytic bath. Only at the lowest thiocyanate proportion ([SCN⁻] = 10^{-3} M and $[SO_4^{2-}] = 0.6 \text{ M}$) were cubic deposits obtained, but yet many of these deposits exhibited a rounded shape (see Figure 9A). As the amount of SCN⁻ increased, the formation of iron domes on the surface was promoted, and cubic deposits were no longer observed (see Figure 9B). Electrodeposition of iron was conducted in the presence of a quite chaotropic electrolyte such as NH₄ClO₄. As can be seen in Figure 10, cubic iron deposits were obtained (the same results were found in the presence of ammonium bromide NH₄Br), thus indicating that the modulation of the particle shape is not correlated with the ion-dependent water structure at the interface. These results thus emphasize the significant impact of SCN⁻ adsorption on the morphology of the electrodeposits. This might offer the opportunity to test



Figure 8. EDS pattern of iron electrodeposits obtained with (A) 0.4 M FeSO₄ and 0.6 M (NH₄)₂SO₄ and (B) 0.6 M NH₄SCN.

the controlled effect of electrodeposit shape on catalytic performance, for instance.

3.3. Effect of Ion Specificity during Iron Electrodeposition. As mentioned previously, the variation of the current as a function of time was found to exhibit different behaviors during iron electrodeposition in the presence of $(NH_4)_2SO_4$ and NH_4 -SCN electrolytes (see Figure 3), and some bubbles were noticed in the latter case. To investigate more deeply the primary instants of electrodeposition, a low iron salt concentration was taken as 5×10^{-4} M in the presence of varying base electrolytes having

the same concentration (say, 0.6 M); the electrodeposition time was increased (30 s) at the same applied overpotential. The results are shown in Figure 11. Two distinct behaviors can be observed depending on the nature of the anions: in the presence of chaotropic anions of the ammonium salt, NH₄SCN, NH₄-ClO₄ and NH₄Br, the current increases (in absolute value) very steeply from the beginning and becomes nearly constant after a few seconds, whereas with cosmotropic anions, (NH₄)₂SO₄ and NH₄CH₃CO₂, the increase is much less pronounced. Moreover, it should be noted that a continuous flow of tiny





Figure 9. SEM images of iron electrodeposits obtained with (A) 0.4 M FeSO₄ + 0.6 M (NH₄)₂SO₄ + 10^{-3} M NH₄SCN and (B) 0.4 M FeSO₄ + 0.55 M (NH₄)₂SO₄ + 0.05 M NH₄SCN.

ascending hydrogen (H₂) bubbles was observed quasispontaneously along the electrode surface in the presence of chaotropic electrolytes. As time proceeds, the association of growing hydrogen bubbles and their screening of the electrode surface resulted in the rapid appearance of a plateau region with chaotropic salts (see Figure 11), whereas bubbling was significantly delayed and fewer hydrogen bubbles were produced in the presence of (NH₄)₂SO₄ and NH₄CH₃CO₂.

For sufficiently high overpotential, hydrogen evolution takes place through the reaction of proton reduction $(2H^+ + 2e^- \rightarrow H_2)$ on the freshly deposited iron particles at the cathode surface. As an indication, hydrogen evolution was checked to be absent when the experiment was performed without any iron electrodeposits on the silicon surface or without any iron salt in solution when the potential was applied. To obtain complementary information, the same experiments were carried out using varying proportions of $(NH_4)_2SO_4$ and NH_4CIO_4 salts in solution, but with the same 0.6 M total concentration. The curves are shown in Figure 12. As the amount of perchlorate anions decreased, bubbling was delayed, and the current intensity



Figure 10. SEM image of iron electrodeposits obtained with 0.4 M $FeSO_4$ and 0.6 M NH_4CIO_4 .



Figure 11. Current as a function of time for iron electrodeposition onto silicon at -1500 mV/SCE in the presence of (NH₄)₂SO₄, NH₄-CH₃CO₂, NH₄SCN, NH₄ClO₄, and NH₄Br base electrolytes.



Figure 12. Current as a function of time for iron electrodeposition onto silicon at -1500 mV/SCE in the presence of varying proportions of $(NH_4)_2SO_4$ and NH_4CIO_4 base electrolytes. The amount indicated corresponds to the perchlorate ion concentration.

increased less strongly. When the perchlorate concentration was lower than 0.1 M, the behavior became similar to that of cosmotropic base electrolytes. These results thus reflect the



Figure 13. Current as a function of time for comparative hydrogen evolution reaction at -1500 mV/SCE in the presence of $(NH_4)_2SO_4$ (thin curve) and NH_4ClO_4 (thick curve) base electrolytes at 0.6 M.

influence of the nature of the base electrolyte on iron electrodeposition occurring concomitantly with hydrogen evolution.

To investigate the separate contribution of hydrogen evolution, the influence of the nature of the base electrolyte on the hydrogen evolution reaction alone was investigated. For that purpose, hydrogen evolution was compared at the same applied potential (-1500 mV/SCE) in the presence of (NH₄)₂SO₄ or NH₄ClO₄ electrolyte (0.6 M concentration) by taking similar silicon plates with sufficient and identical amounts of iron already electrodeposited on the same surface area. As an indication, the pH was 5.2 for both electrolytic solutions (i.e., the amounts of free protons are the same). The results reported in Figure 13 (and also from direct observation of bubbling) clearly show that the intensity of the hydrogen evolution reaction was greater in the presence of NH₄ClO₄ electrolyte. This indicates that the production of hydrogen gas is enhanced when the water network at the interface is significantly disrupted as in the presence of chaotropic electrolytes at 0.6 M. The origin of this behavior is still unclear and merits deeper studies because the release and the motion of hydrogen bubbles near the electrode surface were found to generate a beneficial convective transport of ions and to improve the narrowing of the size distribution of various electrodeposits.10

The effect of salts on bubble formation (stability) has been already studied and was found to be operative at concentrations greater than 0.1 M for some electrolytes.³²⁻³⁴ As reported in the work of Weissenborn et al.,35 electrolytes are known to decrease the dissolved gas concentration, the decrease correlating well with the entropy of hydration of ions (the decrease is greater with the most cosmotropic salts). It was inferred from these studies that highly hydrated ions cause compaction of water molecules and therefore a reduction in the amount of dissolved gas, which, in turn, decreases the strength of the (hydrophobic) attraction between microscopic bubbles and this inhibits coalescence, i.e., the generation of macroscopic bubbles. Craig and al.32 and Pashley36 also reported that degassing a water/oil emulsion resulted in enhanced emulsion stability, suggesting a link between dissolved gas concentration and the hydrophobic attraction between oil droplets.

Although the nature of the base electrolyte was shown to have an influence on the magnitude of the hydrogen evolution reaction, it might also have an effect on iron electrodeposition. It has been recognized that the reaction environment (nature and state of the electrode, electrolyte composition, flow effects) should be very important in electrodeposition processes.²³ In the fundamental aspects of electrocrystallization, ^{12,23} it has been assumed that, once the adatoms are formed on the surface, they should break the bonds with the molecules of solvent before being attached to the nucleus, so that an energy barrier for desolvation must be overcome. Accordingly, it can be expected that dehydration of iron adatoms should be more favored when the network of water molecules is disrupted at the electrode– solution interface, as in the case of a high concentration of chaotropic electrolytes. This might contribute to improving the rate of iron electrodeposition, although it is difficult to find evidence for this experimentally.

4. Conclusions

In this study, the nature of base electrolytes was varied so as to investigate the implication of ion-specific effects on renewed electrochemical approaches for the synthesis of nanoparticles. Two incidences have been highlighted in the process of iron electrodeposition onto hydrophobic silicon surface:

The morphology of electrodeposits can be modulated through the selective adsorption of some ions: the presence of thiocyanate anions was shown to change the shape from cubes to hemispheres, thus allowing further comparative effects of catalyst shape.

The ion-specific character of electrolytes affects the rate of hydrogen evolution near the electrode surface: in the presence of chaotropic species, faster production of hydrogen bubbles occurs, and dehydration of adatoms is presumably enhanced.

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