Electrochemical and AFM study of cobalt nucleation mechanisms on glassy carbon from ammonium sulfate solutions

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Abstract

Nucleation mechanisms of cobalt on a glassy carbon electrode (gce) from aqueous ammonium sulfate solutions were investigated through the electrochemical techniques of cyclic voltammetry (cv) and chronoamperometry (ca), coupled with atomic force microscopy (AFM) studies. The studied parameters were pH, cobalt concentration, temperature, scanning rate, and deposition potential. It was found that scanning in the cathodic direction produced two peaks, corresponding to cobalt and hydrogen reduction, respectively. Scanning in the anodic direction was characterized by cobalt dissolution, which was interrupted by formation of cobalt hydroxide, causing a second anodic peak. The amperometric study found progressive nucleation mechanisms, in contrast to the instantaneous nucleation mechanisms determined by the AFM study. An explanation for the contradictory nucleation mechanisms shown in the two studies is provided.

Keywords: Cobalt nucleation; Glassy carbon electrode; Ammonia; Cyclic voltammetry; Chronoamperometry; Atomic force microscopy

1. Introduction

According to recent advances in the theory and production of nanomagnets [1,2] as memory storage units, the morphology of deposited magnetic materials greatly influences the magnetic properties of thin films. Cobalt (and its alloys) is one of the important ferromagnetic components of such magnetic thin film materials. Electrochemical deposition is the most often used technique for its incorporation into the structures of, for example, GMR heads and spin valve devices [3–6] (and references therein).

Cobalt electrodeposition studies can be categorized according to the working electrode and the type of solution systems used. Most studies have been performed with glassy carbon electrodes [4,7–11], others being gold [10,12], nickel [13] and copper [4,11]. Chloride solutions have been the preferred systems for studying the electrochemistry of cobalt [8–13], rather than sulfate systems [7,14]. Regarding the reaction mechanisms, it has been found that cobalt electrodeposition initiates predominantly via progressive nucleation, which can change to instantaneous nucleation mechanisms by enhancing mass transfer, by using ultrasound [7], or by increasing cobalt concentration [10], for example.

It is surprising that the electrodeposition of cobalt from ammoniacal solutions has not received greater attention considering that the complexing property of ammonia can be utilized to modulate the properties of deposited cobalt via solution speciation. Soto et al. [9] and Palomar-Pardave et al. [11] investigated cobalt electrodeposition onto glassy carbon from ammonium chloride solutions. They found that cobalt nucleation on glassy carbon follows either a progressive nucleation mechanism or a combination of several nucleation mechanisms. However, their results were not accompanied by a morphological study, so the proposed nucleation models could not be verified. In another study using ammonium chloride solutions Mendoza-Huizar et al. [12] found evidence of underpotential deposition of cobalt on gold.

This paper presents a study of cobalt nucleation mechanisms from ammonium sulfate solutions on glassy carbon
electrode which combines the electrochemical methods of cyclic voltammetry and chronoamperometry with atomic force microscopy.

2. Experimental

Reagent grade CoSO₄·7H₂O was used to prepare 0.005, 0.01 and 0.05 M Co(II) solutions. All solutions (Type I purity water, Barnstead NANOpure II) contained 1 M reagent grade (NH₄)₂SO₄ that served as a buffering agent and a supporting electrolyte, unless stated otherwise in the text. Solution pH was adjusted by adding dilute NH₄OH (pH 6) or concentrated NH₄OH (pH 9).

The electrochemical setup was a standard three-electrode cell with glassy carbon as a working electrode, platinum foil as a counter electrode, and silver–silver chloride as a reference electrode (Cypress Systems microelectrode, E₀Ag/AgCl = +0.222 V). The glassy carbon working electrode (0.442 cm²) was a non-porous disk (Sigri), RMS about 1nm upon polishing. Electrochemical experiments were controlled with a potentiostat/galvanostat (Ametek, PAR 283) under computerized control (PAR, M270 Software).

Surface morphology was characterized by atomic force microscopy (VEECO, Digital Instruments, Model Nanoscope IIIa-MultiMode) by using the tapping mode technique under fluid. A Digital Instruments computer program was also used for the cross-section and nuclei population density analyses of AFM images.

Thermodynamic calculations were performed by thermochromical software (Stabcal) [15].

3. Results and discussion

3.1. Cobalt–ammonia chemistry

In aqueous solutions, cobalt is present in the form of divalent cobaltous ion with octahedral coordination, having four equatorial and two axial coordination sites [16], each occupied by water molecules. When ammonia is added, water molecules are displaced from octahedral sites, occupied by water molecules. When ammonia is added, four equatorial and two axial coordination sites [16], each divalent cobaltous ion with octahedral coordination, having 3.1. Cobalt–ammonia chemistry

3.2. Cyclic voltammetry

3.2.1. Cathodic branch

Cyclic voltammetry was studied as a function of scanning rate, number of cycles, concentration of reacting species and solution pH. All cv experiments were performed in the potential range from an initial potential of 0 mV to a vertex potential of −1300 mV.

![Fig. 1. Eₜh/acet–pH diagram for the cobalt–ammonia solution containing 0.01 M Co²⁺ and 1.0 M (NH₄)₂SO₄.](image-url)
3.2.1.1. Effect of scanning rate

Fig. 3a and b shows the effect of scanning rate on cvs at pH 6 and 9, respectively. The presence of zero current from the beginning of the scan to about $-1100$ mV indicated no reaction in this potential range. Below $-1100$ mV (the exact potential depends on the pH and scanning rate) the cathodic current began to increase, resulting in the formation of the first cathodic peak, $I_c$, which corresponds to cobalt reduction according to reaction (1) at pH 6, and reaction (2) at pH 9:

$$\text{Co(H}_2\text{O)}_{6}^{2+} + 2e = \text{Co}^0 + 6\text{H}_2\text{O};$$

$$E^0_n = -0.277 \text{ V } (E^0_{\text{Ag/AgCl}} = -0.499 \text{ V}) \quad (1)$$

$$\text{Co(NH}_3)^{2+} + 2e = \text{Co}^0 + 5\text{NH}_3,$$

$$E^0 = -0.440 \text{ V } (E^0_{\text{Ag/AgCl}} = -0.662 \text{ V}) \quad (2)$$

The difference between the equilibrium cobalt redox potential and the onset of cobalt deposition was due to the nucleation overpotential on glassy carbon [17] resulting from the crystallographic misfit between cobalt (hexagonal closely packed lattice) and glassy carbon (interlocked, twisted and entangled microfibrils [18]). The peak that corresponded to reaction (1) at pH 6 and reaction (2) at pH 9 was denoted $I_c$ on the cvs. Further increase of negative potential resulted in peak $I_{lc}$, which corresponded to the hydrogen ion reduction reaction. At pH 6, peak $I_c$ was observed only as a change of slope of the cathodic trace because of the significant contribution of current from hydrogen ion reduction during electroreduction of cobalt.

As the scan was reversed at $-1300$ mV, the current decayed but remained cathodic up to around $-700$ mV, indicating further reduction of cobalt species. As the potential became more positive, the current crossed over the forward current trace, became anodic, increased and formed peak $I_a$, which was immediately followed by peak $II_a$. After peak $II_a$, the current decayed to zero and remained zero, or slightly anodic, until the end of the scan.

3.2.1.2. Effect of cycling

In order to investigate the reversibility of reactions in the systems under study, three cycle cvs in 0.05 M Co$^{2+}$ solutions at pH 6 and 9 were run, Fig. 4. At pH 6, the current at the end of the first cycle was anodic, indicating that an oxidation reaction was still present. At the beginning of the second cycle, the current remained anodic up to $-620$ mV. Peak $I_c$ in the second cycle was smaller and at a more positive potential than peak $I_c$ in the first cycle, indicating a reduced concentration of reacting cobaltous species. Anodic peaks $I_a$ and $II_a$ were also smaller than the corresponding peaks in the first cycle. The same trend continued for the third cv cycle, in which cathodic peak $I_c$ as well as anodic peaks $I_a$ and $II_a$ were the smallest peaks of all three cycles.

At pH 9, the current was also anodic at the beginning of the second cv cycle. As the potential sweep proceeded in the negative direction in the second cycle, the current decayed and became zero at $-670$ mV. With further increase in negative potential, the current became cathodic and formed one additional cathodic peak, before peak $I_c$. This peak corresponded to the reduction of new species formed during the first cycle, residual Co(OH)$_2$. It should be noted that the peak that corresponded to cobalt hydroxide reduction was not present for lower cobalt concentrations, 0.005 and 0.01 M. As the potential swept toward the positive direction, the same two anodic peaks appeared as in the first cycle. Unlike the results at pH 6, the magnitudes of anodic peaks remained the same for all three cycles, while the cathodic peaks and their magnitudes stayed the same for the second and third cycle.

3.2.1.3. Effect of cobalt concentration

Fig. 5a and b presents the effect of Co(II) concentration on cvs at pH 6 and 9, respectively.

The magnitude of the current peaks increased proportionally to the increase of Co(II) concentration, as expected. The concentration of cobalt ions in solution affected the
position of peak Ic, which became more positive as the concentration of Co(II) increased. The shift of peak Ic potential is probably related to concentration overpotential, as the higher concentration of reacting species reduced the concentration overpotential for cobalt reduction [19]. The significance of the shift of peak Ic is obvious at pH 6. At the lowest cobalt concentration of 0.005 M peak Ic overlaps with hydrogen ion reduction, represented by peak IIc. At the highest cobalt concentration of 0.05 M, peaks Ic and IIc are separated due to the shift in peak Ic. This implies that at higher cobalt concentrations, deposition initially proceeds in the absence of hydrogen ion reduction, an important fact for the following chronoamperometric study.

3.2.1.4. Morphological study

In order to establish the effect of cv parameters on the morphology of deposited cobalt, a series of AFM images was taken at the cv crossover potentials. A crossover potential, defined as the potential at which the reverse current trace crosses over the forward current trace, is characteristic for a cv in which a metal is being deposited and dissolved [17]. In an ideal case, when there are no background currents during a cv, the crossover potential should be located on an x-axis, with no net current; i.e., when cathodic current changes to anodic.

The results of the morphological AFM study are presented in Fig. 6a–h. The most characteristic feature of cobalt nucleation was that each nucleus had a hexagonal plane, with a multidirectional 3D-growth (best seen in Fig. 6e). Nakano et al. [14], who performed a study of electrolysis factors affecting the crystal orientation and morphology of deposited cobalt, found by X-ray diffraction that cobalt nucleates in a closely packed hexagonal form with several crystal orientations. The flat hexagonal plane seen on the nuclei in this study corresponds to the (0 0 0 2) plane of densest packing.

According to the present AFM study, the nuclei sizes were a function of scanning rate and pH. The nuclei sizes were the largest at the slowest scanning rate, 5 mV s$^{-1}$. Nuclei population density, on the other hand, increased when the scanning rate was increased from 5 to 100 mV s$^{-1}$. This effect was more pronounced at pH 6 than at pH 9.

The difference in the nuclei population densities observed at pH 6 and 9 was probably due to hydrogen evolution at pH 6 and its absence at pH 9. The overlap of peak Ic with peak IIc shown in the cyclic voltammograms in Fig. 3a suggests that at lower cobalt concentrations hydrogen evolution coincided with the formation of cobalt nuclei. Control cvs of glassy carbon electrode in 1 M ammonium sulfate solutions at pH 6 and 9 in the absence of cobalt (not presented) showed that there was no hydrogen evolution on gce in the entire potential range studied. Therefore, the only viable substrates for hydrogen gas evolution reaction were...
the newly formed cobalt nuclei. As soon as metallic cobalt appeared on the surface of the electrode, it served as a reaction site for hydrogen evolution. The products of the hydrogen reduction were hydrogen gas bubbles that formed on the surface of cobalt nuclei, grew, and eventually prevented further cobalt reduction from taking place on the cobalt nuclei surface. Because cobalt ions could not be reduced on the surface of metallic cobalt, they had to be reduced elsewhere on glassy carbon, leading to the formation of new cobalt nuclei. Overall, the size of nuclei decreased, but the population density increased.

Due to much lower hydrogen ion concentration at pH 9 than at pH 6, a near-absence of hydrogen gas evolution allowed unhindered growth of cobalt nuclei, resulting in nuclei larger than those deposited at pH 6.

3.2.2. Anodic branch
The mechanism of cobalt oxidation in neutral and basic media has been a subject of previous studies [20–23]. Although there are differences in the interpretation of the overall oxidation mechanism, these studies show that cobaltous hydroxide forms either as an intermediate or as a final product of oxidation.

According to Pourbaix [24], cobalt is passivated in aqueous solutions by forming a hydrated cobalt oxide layer, \( \text{Co(OH)}_2 \), according to a hydrolytic reaction (3):

\[
\text{Co} + 2\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2 + \text{H}_2 \quad (3)
\]

In order to relate the presence of ammonia to two anodic peaks, an additional set of experiments was performed in oxygen-free solutions under argon atmosphere. Cobalt films,
120-nm-thick, were deposited from 0.05 M CoSO₄ + 1 M (NH₄)₂SO₄ solutions at pH 6 and pH 9 by applying a constant potential of $-1150$ mV for 60 s. The deposited cobalt was then oxidized in a linear sweep voltammetry experiment in a positive direction, either immediately after deposition, or after the film was conditioned in a cobalt-ammonia solution for some time. The expectation was that the surface cobalt hydroxide layer would be dissolved by the ammonia solution, freeing metallic cobalt below for further reaction. The effect of conditioning time on linear sweep voltammetry is given in Fig. 7a and b.

Linear sweeps at pH 6, Fig. 7a, which started immediately after the electrode was re-immersed in the electrolyte, contained both anodic peaks. As the conditioning time increased, peak Ia diminished, so that after 10 min only peak IIa was present. At pH 9, Fig. 7b, the anodic reactions of cobalt were not as strong as at pH 6.0. Peaks Ia and IIa had much smaller current densities, peak Ia being barely present even in the first potential sweep.

Examinations of the electrode after potential sweeps at pH 6 and 9 revealed that at the end of every sweep at pH 6 the electrode surface was barren, while after every sweep at pH 9 there was still a film on the electrode. The film left after the anodic sweep at pH 9 was imaged using a CCD camera, the inset in Fig. 7b. The deposit observed on the surface of the electrode was cobalt film covered with the formed layer of cobalt hydroxide. The image shows breakage and curling of the film. Dark curls revealed the pristine unoxidized metallic cobalt that was on a side toward the electrode. These surfaces were smooth because of their conformation to the smooth glassy carbon surface, unlike the side of the film covered with the hydroxide layer.

### 3.2.2.1. Effect of anions

The effect of anions on the electrodeposition of cobalt was examined by running cyclic voltammetry experiments in two additional ammonium solutions, ammonium carbonate and ammonium chloride. The results (not presented) were very similar to those with ammonium sulfate.

### 3.2.2.2. Reaction mechanisms of anodic cobalt oxidation

Based on cyclic voltammetry and linear sweep data, anodic oxidation occurred according to reactions ((4)-(11)):

<table>
<thead>
<tr>
<th>Anodic peak</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6</td>
<td></td>
</tr>
<tr>
<td>Ia and IIa</td>
<td>Co + 2OH⁻ $\rightarrow$ Co(OH)₂ + 2e (4)</td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>Co(OH)₂ + (NH₄)₂SO₄ $\rightarrow$ CoSO₄ + 2NH₃ - H₂O (5)</td>
</tr>
<tr>
<td>Overall chemical reaction:</td>
<td>Co(OH)₂ + (NH₄)₂SO₄ $\rightarrow$ Co(NH₃)₂²⁺ + SO₄²⁻ + 2H₂O (6)</td>
</tr>
<tr>
<td>pH 9</td>
<td></td>
</tr>
<tr>
<td>Ia and IIa</td>
<td>Co + 2OH⁻ $\rightarrow$ Co(OH)₂ + 2e (8)</td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>Co(OH)₂ + (NH₄)₂SO₄ + NH₃ - H₂O $\rightarrow$ CoSO₄ + 3NH₃ - H₂O (9)</td>
</tr>
<tr>
<td>Overall chemical reaction:</td>
<td>Co(OH)₂ + (NH₄)₂SO₄ + NH₃ - H₂O $\rightarrow$ Co(NH₃)₂²⁺ + SO₄²⁻ + 3H₂O (10)</td>
</tr>
</tbody>
</table>

Fig. 7. (a and b) Effect of conditioning time on linear sweep voltammetry in the potential range corresponding to anodic dissolution of cobalt for solutions at (a) pH 6 and (b) pH 9. Conditioning is defined as the time of cobalt film exposure to the solution prior to initiation of linear sweep voltammetry. Inset in (b) is the optical microscope image of a broken and curled cobalt film after 5 min of conditioning at pH 9.
According to the proposed reaction mechanisms, the first step at pH 6 was the oxidation of cobalt and formation of passivating cobalt hydroxide film, reaction (4). This reaction corresponded to peak Ia. Cobalt hydroxide in the surface film and ammonium ions from ammonium sulfate reacted to produce soluble cobalt sulfate and ammonia, reaction (5). The resulting cobaltous ions and ammonia formed a cobalt-ammonia complex according to reaction (6). Complexation of cobaltous ion was the last step in the removal of passivating hydroxide film, which exposes metallic cobalt to solution, thus enabling reaction (4) to continue, producing the second anodic peak, IIa. Not all of the cobalt hydroxide was removed, resulting in its accumulation in the subsequent cycles, enhancing the passivation. As a result, the subsequent anodic (and cathodic) currents were smaller, as seen in Fig. 4. The reaction mechanisms at pH 9 were similar to the mechanism at pH 6, the only difference being the presence of free ammonia for reactions (9) and (11). At pH 6, however, the independence from cycling after the first cycle (see Fig. 4) can be explained by the absence of cobalt hydroxide film buildup beyond that which was formed in the first cycle, or by the nature of passive film, which at pH 9 had become porous, thus predefining the available area for anodic (and cathodic) reactions. The anodic cobalt reactions definitely require further study toward the determination of exact mechanisms.

A review of the literature points out that the anodic branch of cobalt cyclic voltammograms has either one peak [7,8,10,13] or two peaks [9,11,12], depending on pH, two peaks being the property of solutions with higher pH. No explanation has been given for the presence of two anodic peaks, except the suggestion that the two peaks could be due to dissolution of cobalt as different ionic species and different cobalt phases [9], or that they represent different allotropic forms of cobalt [11].

3.3. Chronoamperometry

Chronoamperometry was used as a supporting experimental technique to further elucidate the nucleation mechanisms of cobalt on glassy carbon. By stepping up the potential from open circuit to a potential at which reduction of cobaltous ions proceeds under diffusion control, the cobalt nuclei formed will each have a diffusion zone that controls further supply of cobaltous ions. The overlap of these zones results in a peak that is characteristic for nucleation. After the peak, the current is limited by the mass transfer of cobaltous ion to the electrode surface, as described by the Cottrell equation [17]. Within the diffusion zone, the growth of already established cobalt nuclei can continue, or additional nucleation can be initiated on other sites.

![Fig. 8. (a–f) Effect of deposition potential on chronoamperometry of cobalt in pH 6 and 9 solutions. The study was performed for three different cobalt concentrations, 0.005, 0.01 and 0.05 M, all with 1 M (NH₄)₂SO₄ as a supporting electrolyte.](image)
The parameters of interest that were varied in chronoamperometric experiments were deposition potential, concentration of cobaltous ions, solution pH and temperature.

3.3.1. Effect of deposition potential

The deposition potentials studied, $-1150$, $-1200$, $-1250$ and $-1300$ mV, were selected from the more negative side of an $i_c$ peak in Fig. 3a–f. The results for the effect of deposition potential for three studied cobalt concentrations at pH 6 and 9 are summarized in Fig. 8a–f.

Peaks corresponding to the overlap of diffusion zones are clearly seen in most of the cases, except for the conditions at $-1150$ mV in 0.005 M and 0.01 M Co$^{2+}$ pH 6 solutions, for which the duration of the ca was too short for peak expression. Regarding the pH effect, the important difference is (a) slower diffusion current decay, and (b) smaller peak currents at pH 6 than at pH 9. Slower decay of diffusion current was the result of the significant contribution of hydrogen reduction current to the overall current. Smaller peak currents were the result of the shielding effect of hydrogen evolved on the surface of cobalt, reducing the nuclei area available for continuation of cobalt deposition. Due to hydrogen shielding, reduction of cobalt ions to ad-atoms [25] had to take place elsewhere on the electrode surface, resulting in new nucleation sites. The net effect was a higher nuclei population density and smaller nuclei at pH 6 than at pH 9, as verified by the AFM images in Fig. 9a–h, and quantified in Fig. 10.

One way to estimate the contribution of the hydrogen ion reduction current to the overall current during a ca experiment would be to compare the cathodic (cobalt deposition) with anodic (cobalt dissolution) charge. The difference would represent the current due to hydrogen ion reduction. Because cobalt hydroxide film formation could interfere with the total anodic current, another method was chosen instead. Accordingly, the quantity of electrodeposited cobalt was measured from AFM images by using the bearing routine in the Nanoscope™ software. When total volume of scanned nuclei was multiplied by the density of cobalt (8.92 g cm$^{-3}$) the weight of deposited cobalt, per scanned area, was obtained. The electrode area divided by scanned area was used as a multiplication factor to determine the total weight of deposited cobalt. This result was then compared with the weight of cobalt calculated by cathodic current integration and Faraday’s law, Fig. 11.

According to Fig. 11, the amount of deposited cobalt measured by AFM was very close to the calculated amount for all deposition potentials at pH 9 (open and closed circles in Fig. 11). At pH 6, there was a significant discrepancy as a function of deposition potential between measured and calculated amount of deposited cobalt. While the calculated
amount of cobalt increased almost linearly with the more negative potentials (closed squares), the corresponding measured amount of cobalt was significantly lower (open squares). The difference represents the contribution of hydrogen current during electrodeposition of cobalt, which can be as high as 45%, at $/C0$ 1300 mV. At pH 9, the fraction of current spent on hydrogen reduction was between 5 and 10%.

It should be expected that at the more negative deposition potentials the electrode surface would be characterized by higher nuclei population density. However, according to Fig. 10, the nuclei population density decreased as the potential became more negative, especially for pH 6 conditions. The decrease of nuclei population density at more negative deposition potentials has also been observed in the study of copper deposition from ammoniacal solutions [26].

To explain how the nucleation population density would be characterized by higher nuclei population density. However, according to Fig. 10, the nuclei population density decreased as the potential became more negative, especially for pH 6 conditions. The decrease of nuclei population density at more negative deposition potentials has also been observed in the study of copper deposition from ammoniacal solutions [26].

Fig. 12. (a’–c”) Schematic representation of the physical role of hydrogen gas bubbles on the final destination of cobalt nuclei, for two different deposition potentials (a’, b’, c’) $-1150$ mV, and (a”, b”, c”) $-1250$ mV. The number of nuclei and their size after 1 second (a’ and a”) was compared with the number and size of nuclei on the electrode surface after 10 s of electrodeposition. Surface movement of cobalt nuclei was influenced by the size (a function of deposition potential) of formed and affixed hydrogen gas bubbles, b’ and b”.

At $-1250$ mV, Fig. 12b”, cobalt nuclei also continued to grow, but the extent of hydrogen ion reduction was much larger than at $-1150$ mV, resulting in larger hydrogen gas bubbles. The hydrogen bubbles affixed to cobalt nuclei can produce two effects, either physically pushing a nucleus away from its original position until it collides with neighboring nucleus, or providing buoyancy to a nucleus so it can move more easily across the surface. These two physical effects would be more pronounced with an increasing volume of hydrogen gas bubbles, at prolonged depositions. The AFM results after 10 s of deposition at $-1250$ mV, Fig. 12c”, tended to confirm this postulate. Accordingly, the number of cobalt nuclei decreased to 58 $\mu$m $^{-2}$, from 144 $\mu$m $^{-2}$ (after 1 s). Correspondingly, at $-1150$ mV, the hydrogen bubbles were too small to produce the described effects, allowing the growth of existing nuclei and the formation of new ones. Thus, after 10 s, the nuclei population density increased from 98 to 140 $\mu$m $^{-2}$, Fig. 12c”.

A decrease in nuclei population with time has also been observed by Gomez et al. [8], who suggested that surface diffusion of the smaller toward the larger nuclei increased the resulting nuclei size and decreased the overall population...
density. They provided no explanation for the driving force of diffusion.

Although our study provides evidence that cobalt population density is a function of hydrogen ion reduction, this is not the exclusive mechanism for integration of small cobalt nuclei. Being ferromagnetic, cobalt nuclei can travel across the surface under the influence of micromagnetic forces between neighboring nuclei. Again, the buoyancy provided to the nuclei by hydrogen gas bubbles can make such forces more effective. The effect of micromagnetic forces on the surface diffusion of cobalt atoms and nuclei warrants a separate study.

3.3.2. Effect of cobalt concentration

The effect of cobalt concentration on the morphology of cobalt nuclei was studied at pH 6 and 9, by using a deposition voltage of −1250 mV and a deposition time of 10 s. The results are presented in Fig. 13a–f. In general, the increase of

Fig. 13. (a–f) Effect of cobalt concentration on the morphology of cobalt electrodeposited at −1250 mV from solutions at pH 6 and 9.
cobalt concentration increased the surface coverage of cobalt nuclei. Full coverage was achieved in 0.05 M Co²⁺ solutions for both pH levels.

3.3.3. Effect of temperature

The effect of temperature on electrodeposition of cobalt was studied in the temperature range of 5–55 °C. The experimental conditions were 0.01 M Co²⁺ concentration, deposition potential −1250 mV, solution pH 6 and 9. No significant effect was found for either pH.

3.3.4. Nucleation models

Scharifker and Hills [27] used current transients to model nucleation according to both instantaneous and progressive mechanisms. Instantaneous nucleation corresponds to a slow growth of nuclei on a small number of active sites, all activated in the same time. Progressive nucleation corresponds to fast growth of nuclei on many active sites, all activated during the course of electroreduction [28].

The models for instantaneous and progressive nucleation are given by Eqs. (12) and (13), respectively,

\[
\frac{i^2}{i_m^2} = \frac{1}{t/t_m} \left[ 1 - \exp \left( \frac{-1.2564 \left( \frac{t}{t_m} \right)}{1} \right) \right]^2 \quad (12)
\]

\[
\frac{i^2}{i_m^2} = \frac{1}{t/t_m} \left[ 1 - \exp \left( \frac{-2.3367 \left( \frac{t}{t_m} \right)^2}{1} \right) \right]^2 \quad (13)
\]

where \(i_m\) is the current and \(t_m\) is the time coordinate of a chronoamperometric peak. In the following graphs, the instantaneous and the progressive mechanisms will be represented by solid and dashed lines, respectively.

The experimental data from Fig. 8 were used to obtain reduced currents versus reduced time plots, according to Eqs. (12) and (13). The results given in Fig. 14a–f represent the effect of pH, cobalt concentration, and deposition potential. The inspection of graphs in Fig. 14 reveals that in the initial stages cobalt nucleation occurred according to the progressive nucleation mechanisms, regardless of cobalt concentration, pH and deposition potential.

At pH 6 for 0.005 M and 0.01 M Co²⁺ solutions, Fig. 14a–b, the reduced current plots followed the progressive nucleation model (dashed line) from the beginning to the maximum on the curve. After the maximum the reduced current plots started to deviate from both instantaneous and progressive model plots. It was already stated that in 0.005 and 0.01 M Co²⁺ solutions the contribution from the hydrogen ion reduction to the total current is not negligible and cobalt nuclei serve as suitable sites for hydrogen ion reduction. While the total surface area of cobalt nuclei is still relatively small (before the maximum on the reduced current plot) the contribution from the hydrogen reduction will be small. However, once the surface area of cobalt becomes larger, the contribution from the hydrogen ion reduction to the overall current will become significant, causing the deviation observed in Fig. 14a and b.

Fig. 14. (a–f) Reduced current versus reduced time plots, generated by using the data in Fig. 10a–f, represent the effect of deposition potential, cobalt concentration and pH on the mechanism of cobalt nucleation. Theoretical models for instantaneous and progressive nucleation mechanisms are shown as solid and dashed lines, respectively.
Based on Scharifker–Hills equations, nucleation of cobalt on glassy carbon follows progressive mechanisms, meaning that new nuclei are formed during the course of an experiment. In that case, the surface of glassy carbon should be covered with cobalt nuclei of various sizes. However, the AFM images in Fig. 9a–h, which represent the status of the electrode surface at the end of chronoamperograms used for modeling, show otherwise; that is, approximately the same size of nuclei. The AFM examination clearly suggests instantaneous nucleation mechanisms. An explanation for the obvious contradiction between the theoretical models and experimental findings is provided below.

A closer examination of AFM images revealed three types of cobalt nuclei, schematically presented in Fig. 15. The three types differ by their crystallographic orientation on the surface; more precisely, by the angle between the hexagonal plane and the electrode surface. The A-type nuclei are flat hexagonal nuclei with (0 0 0 2) basal plane, B-type are pyramidal nuclei with (1 0 1 1) basal plane, and C-type are nuclei with (1 1 2 0) or (1 0 1 0) basal planes. The hexagonal plane, or its part, represents the plane of closest packing (0 0 0 2), which consequently is the plane with the least favorable conditions for incorporation of cobalt atoms. Favorable planes for incorporation of atoms are schematically indicated by the arrows around each nucleus type. In addition, the A-type nuclei have a small available surface for incorporation of atoms, resulting in slower nucleus growth. The surface available for incorporation of atoms is the largest in type-B nuclei. The C-type nuclei have the smallest area, but their protrusion toward the bulk of the solution improves the conditions for reduction and incorporation of cobalt atoms. Cobalt nuclei of C-type cannot be found as a single nucleus, but always as several nuclei stacked along their closely packed sides. The last column on the right of Fig. 15, labeled as top view, schematically demonstrates the resulting morphology for each nucleation type when profiling from the top, as done in atomic force microscopy.

Each of the proposed nuclei types is identified in an actual 1.5 μm × 1.5 μm AFM image in Fig. 16a. Because the third dimension, the height of nuclei, is not obvious from a planar AFM image, a separate analytical routine was used for its estimation by sectioning across each type of nuclei, as indicated by black arrows and a corresponding letter.

Cross-sectioning lines are numerically labeled 1-1 for type A, 2-2 for type B and 3-3 for type C nuclei. The measured height along the cross-sectioning lines is given in Fig. 16b. It was found that the nucleus parallel to the surface, the A-type, was 14.5 nm high. The B-type nucleus was inclined 45° with a height of 56 nm. The C-type nucleus, 75 nm high, was perpendicular to the electrode surface.

The growth rate of each nucleus will be determined by the area of less densely packed planes available for cobalt incorporation. According to Fig. 13c, the C-type nuclei will prevail at the end of electrodeposition. Obviously, during the growth of nuclei there will be a distribution of nuclei type, with consequent distribution of (a) planes and (b) surface area available for deposition. In the Scharifker and Hills model [27], which was derived for hemispherical geometry, the growth of nuclei is controlled by the growing surface area of idealized hemispheres. For the reasons discussed above, the nucleation of cobalt is characterized by a surface area larger than that which would be provided by the same size hemispheres. A larger surface area for a fixed number of nuclei has the same effect as if the number of nuclei increased during electrodeposition. In other words, the nucleation mechanisms should follow the Scharifker–Hills model for progressive nucleation, which was indeed shown in Fig. 14.
The need to verify, through additional experimental methods, the heterogeneous reaction mechanisms determined by mathematical models, is demonstrated by this study, which clearly shows that although the experimental transients fit the progressive nucleation model, cobalt nucleation is actually instantaneous.

4. Conclusions

Electrochemical deposition of cobalt on glassy carbon from ammonium sulfate solutions was studied by cyclic voltammetry and chronoamperometry. The corresponding electrode morphology was examined by atomic force microscopy. The effect of each parameter was studied at pH 6 and 9:

1. The cyclic voltammograms were characterized by two cathodic and two anodic peaks. The first cathodic peak (scanning in the negative direction) represents the reduction of cobaltous ion to metallic cobalt. The second cathodic peak is due to a hydrogen evolution reaction.

2. The first anodic peak (scanning on return in the positive direction) is a result of cobalt metal oxidation to cobalt hydroxide. Dissolution of cobalt hydroxide with ammonia results in resumption of cobalt oxidation underneath the removed film.

3. An increase of cv scanning rate resulted in an increase of nuclei population density at pH 6, but not at pH 9.

4. An increase of cobalt concentration in solutions reduced the concentration overpotential for cobalt deposition, shifting it to a more positive potential.

5. Hydrogen reduction, which takes place on the cobalt nuclei, and not on the bare glassy carbon surface, plays an important role during the growth of nuclei. Hydrogen gas bubbles enable cobalt ad-atoms to move across the surface toward growing nuclei. At higher cathodic potentials, larger hydrogen gas bubbles contribute more to coarsening of cobalt nuclei than the smaller hydrogen gas bubbles produced at lower cathodic potentials.

6. The Scharifker–Hills models suggested progressive cobalt nucleation mechanisms; i.e., the production of nuclei of variable size. However, the AFM study indicated instantaneous nucleation; i.e., production of nuclei of the same size. The discrepancy between the mechanisms can be explained by the presence of three different types of cobalt nuclei, each with its own rate of growth and reaction surface area.

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