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Electrochimica Acta 51 (2006) 4393-4404

ELECTROCHIMICA

www.elsevier.com/locate/electacta

EQCM study of the electrodeposition of manganese in the presence of ammonium thiocyanate in chloride-based acidic solutions

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Received 5 October 2005; received in revised form 13 December 2005; accepted 14 December 2005 Available online 24 January 2006

Abstract

The influence of ammonium thiocyanate (NH₄SCN) on the mechanism of manganese electrodeposition from a chloride-based acidic solution was investigated by cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM). The EQCM data were represented as plots $d\Delta m dt^{-1}$ versus *E*, known as massograms. Because massograms are not affected by interference from the hydrogen evolution reaction, they clearly show the manganese reduction and oxidation processes. By comparing the voltammograms with their corresponding massograms, it was possible to differentiate mass changes due to faradaic processes from those due to non-faradaic processes. Morphology, chemical composition and structure of the manganese deposits formed in different potential ranges were analyzed by scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), and X-ray diffraction (XRD). The results showed that in the absence of NH₄SCN, Mn(OH)_{2(s)} is formed in the potential range -1.1 to -0.9 V due to the hydrogen evolution reaction in this region. At more cathodic potentials, the deposition of β -manganese and the inclusion of Mn(OH)_{2(s)} into the deposit occur; both of these species underwent dissolution by non-faradaic processes during the anodic scan. In the presence of NH₄SCN, the formation of α - and γ -manganese was observed. When the potential was ≤ -1.8 V and [NH₄SCN] exceeded 0.3 M, the α -manganese phase was favored.

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Keywords: Electrodeposition; Electrochemical quartz crystal microbalance; Massograms; Manganese

1. Introduction

Metallic manganese (Mn) is used in certain types of steel, particularly low-carbon steels (e.g. 200 series), and in nonferrous alloys. Coatings of Mn [1], Cu–Mn [2,3], Zn–Mn [4–12], Ni–Mn [13] and Co–Mn [14] alloys are potentially useful as sacrificial coatings for protecting ferrous substrates against corrosion. In spite of the potential applications of Mn in coatings, little work has been done on the mechanism of electrodeposition of pure metallic manganese. This lack of previous research is likely due to the difficulty of studying the electrodeposition of Mn. Specifically, due to the very low potential value of the Mn²⁺/Mn(0) couple in aqueous solution ($E_{Mn^{2+}/Mn} = -1.18$ V

0013-4686/\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2005.12.019 versus SCE), reduction of Mn^{2+} to Mn is always accompanied by hydrogen evolution, which makes it difficult to clearly detect the manganese reduction process. The study of manganese reduction is also complicated by the fact that Mn is easily oxidized.

The electrodeposition of manganese has been studied in chloride- and sulfate-based electrolytic solutions, both with and without additives. Using a chloride-based electrolytic solution with ammonium chloride as an additive, Lewis et al. [15] electrodeposited metallic manganese on the cathode, achieving efficiencies between 65% and 70%. Under these conditions, chlorine gas was produced at the anode as a secondary product. In addition, using selenium as an additive, Lewis et al. obtained efficiencies of up to 90% [16]. In other work in this area, Fink and Kolodney [17] electrodeposited manganese from a sulfate-based electrolytic solution containing glycerol as an additive. The manganese coatings obtained were easily oxidized

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when they were exposed to air, forming a dark oxide film on the surface. When the fresh manganese coating was submerged in dichromate solution, the white and shiny appearance of the coating was maintained indefinitely. Bradt et al. [18,19] obtained soft, silver-white manganese deposits from electrolytic solutions containing sulfates and ammonium salts. The efficiency of manganese electrodeposition under these conditions was 77%. In another study, Gong and Zangari [1] found that adding ammonium sulfate to the electrolytic solution increased the reduction of manganese ions while also providing a buffering effect. They obtained two types of manganese coatings, depending on the applied current density: at low current densities, deposits of crystalline manganese in the γ -phase were obtained, whereas at high current densities the formation of amorphous manganese deposits was favored. Recently, above-mentioned authors found that the addition of small amounts of ions Sn²⁺ and Cu²⁺ into the electrolyte for Mn electrodeposition decreases the percentage of oxide codeposited, giving greater metallic character to manganese coatings [20]. In other work, using cyclic voltammetry and potential pulses, Gonsalves and Pletcher [21] found that during the reduction of manganese (II) in solutions containing selenium as an additive, the selenium was adsorbed onto the surface of the cathode and inhibited both the hydrogen evolution reaction and the deposition of manganese. Sulfur containing additives (e.g. ammonium sulfate, sulfur dioxide) are commonly added to the solution from which manganese is electrodeposited, it has been reported [15,16] that the addition of such additives to the electrolytic bath lead to the deposition of manganese in the brittle α -phase, to change the crystal size and structure of the deposit, and to inhibit the oxidation of Mn^{2+} to MnO_2 at the anode. In addition, the use of ammonium salts as additives has been reported to increase the efficiency of Mn(II) reduction [15].

In the present study, we used cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) to investigate the influence of ammonium thiocyanate (NH₄SCN) as an additive on the mechanism of manganese electrodeposition from a chloride-based acidic solution. The EQCM data were represented as graphs of $d\Delta m dt^{-1}$ versus *E*, known as massograms [22,23]. The term $d\Delta m dt^{-1}$ corresponds to the rate of mass transfer. For faradaic processes $d\Delta m dt^{-1}$ can be directly related to the rate of charge transfer at the electrode surface. Moreover, $d\Delta m dt^{-1}$ can be plotted against the electrode potential (E) to generate massograms that are completely analogous to voltammograms. Massograms have certain advantages over the conventional approaches to representing EQCM data. One key advantage is that by comparing a voltammogram with its corresponding massogram, it is possible to distinguish mass changes due to faradaic processes (mass changes that are coupled to charge transfer at the electrode surface) from those due to nonfaradaic processes (mass changes that are not associated with charge transfer processes). In the present work, massograms are presented as an alternative approach to the study of systems in which there is interference from the hydrogen evolution reaction. The morphology, chemical composition, and structure of the manganese deposits formed in different potential ranges of the massograms were analyzed using scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), and X-ray diffraction (XRD).

2. Experimental

The electrochemical and electrogravimetric study of the reduction of Mn(II) in the presence of NH₄SCN as an additive was performed in a conventional three-electrode cell using a base solution (S_0) of composition: 0.6 M MnCl₂·4H₂O + 0.32 M H₃BO₃+2.8 M KCl, pH 5.0, with various concentrations of NH₄SCN. The solutions were prepared immediately prior to each experiment using deionized water $(18 M\Omega cm)$ and analytic-grade reagents (Aldrich). Before each experiment, the solutions were deoxygenated for 30 min with ultrapure nitrogen (Praxair), and a nitrogen atmosphere was maintained during the experiments. A EQCM (Maxtek, Mod. 710) and a potentiostat/galvanostat (PAR, Mod. 263A) controlled by independent computers using the software PM710 and M270, respectively, were used to simultaneously record electrochemical measurements and the resonance frequency of the quartz crystal. An AT-cut quartz crystal ($f_0 = 5 \text{ MHz}$) covered with an iron film (Maxtek) was used as the working electrode (Fe-EQCM) (geometrical area $1.37 \,\mathrm{cm}^2$). Because the manganese deposited during the cathodic scan could not be completely dissolved anodically, a new Fe-EQCM electrode was used for each experiment. Before each experiment, the electrode was cleaned with degreasing solution. A spectroscopy-grade graphite rod, mounted inside a separate compartment, was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode; all potential values cited in the text are referred to SCE. To minimize iR-drop effects, a Luggin capillary was employed to connect the reference electrode compartment to the working electrode one.

The EQCM signal was registered as Δf_{exp} (Hz) (= $f - f_0$), the experimental frequency change, which can be expressed as [24–26]:

$$\Delta f_{\exp} = -C_{\rm f}(\Delta m) + \Delta f_{\eta} + \Delta f_{\rm r} + \cdots$$
 (1)

The first term on the right-hand side of Eq. (1) is the Sauerbrey term [27], which represents the total mass change at the electrode surface; $\Delta m = \Delta m_{dep} + \Delta m^*$. Δm_{dep} is the mass change due to the deposition/dissolution of the metal, and Δm^* includes the contributions from adsorption and from trapped solvent molecules [28]. Other possible contributions to the frequency change include changes in the solution viscosity [29] and the surface roughness [30–32]. In the present work, the use of polished Fe-EQCM electrodes (roughness 1.171 nm, as measured by AFM) should minimize the effects of surface roughness, and the effects of viscosity variations are expected to be negligible. The value of $C_{\rm f}$ (Hz ng⁻¹ cm²), the sensitivity factor of the quartz crystal employed in the measurements, was calculated as $0.056 \,\rm Hz \,ng^{-1} \,cm^2$ using the equation:

$$C_{\rm f} = \frac{2f_0^2}{\sqrt{\mu_{\rm q}\rho_{\rm q}}}\tag{2}$$

where f_0 is the natural frequency of the quartz crystal $(f_0 = 5 \text{ MHz})$, μ_q the shear modulus of the quartz crystal $(\mu_q = 2.94 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2})$ and ρ_q is the density of the quartz crystal ($\rho_q = 2.65 \text{ g cm}^{-3}$).

The surface morphology and chemical composition of the deposits were evaluated using a scanning electron microscopy (SEM) (Jeol, Mod. DSM-5400LV) coupled to an Energy Dispersion Spectrometer (EDS) (Kevex). Crystal structures were determined by X-ray diffraction (XRD) using a Bruker diffractometer (Mod. D8 Advance).

3. Results and discussion

3.1. Thermodynamic study

Before conducting the electrochemical study, we constructed a Pourbaix-type diagram (E = f(pH)) (Fig. 1) for the system Mn(VII)^{///}/Mn(VI)^{///}/Mn(V)^{///}/Mn(III)^{///}/Mn(0)/Cl^{-/} break NH₃/SCN⁻/H₂O using the thermodynamic constants associated with the formation of complexes of manganese with Cl⁻, SCN⁻ and NH₃ reported in the literature [33] (Mn^{'''} indicates the generalized species to third order [34,35] of manganese). In the construction of this diagram, the graphical method of Rojas and González [36] was used and the working concentrations of the following generalized species were maintained at constant values: $pCl' = -log[Cl^-]_{total} = -0.6$, pSCN' $= -\log[SCN^{-}]_{total} = 0.097$, $pNH_{3}' = -\log[NH_{3}]_{total} = 0.097$, and $pMn''' = -log[Mn]_{total} = 0.22$. In the diagram, the soluble complex $Mn(SCN)_4^{2-}$ is the species that predominates in the potential range -1.58 to 0.7 V versus SCE at pH 5.0. For pH values greater than 10.5, $Mn(OH)_{2(s)}$ is the predominant species. Complexes of the type Mn-NH₃ are not observed in the diagram, indicating that these complexes are not the predominant species under the working conditions. On the basis of this analysis, we can therefore assume that in the presence of NH₄SCN and at the working concentrations, the reduction of Mn(II) involves the species $Mn(SCN)_4^{2-}$, in agreement with



Fig. 1. Pourbaix-type diagram for Mn(VII)''/Mn(VI)''/Mn(VI)''/Mn(III)''/Mn(III)''/Mn(III)''/Mn(II)''/Mn(0), constructed for the following conditions: $pCI' = -log[CI^-]_{total} = -0.6$, $pSCN' = -log[SCN^-]_{total} = 0.097$, $pNH_3' = -log[NH_3]_{total} = 0.097$, and $pMn' = -log[Mn(II)]_{total} = 0.22$. The H_2O/H_2 system is also shown.

the following reaction:

$$Mn(SCN)_4^{2-} + 2e^- \rightarrow Mn(0) + 4SCN^-$$
(3)

whose apparent formal potential $(E'_{Mn(SCN)_4^{2-}/Mn})$ can be expressed as a function of the concentrations of thiocyanate (pSCN') and manganese (pMn''') ions by the following equation:

$$E'_{Mn(SCN)_4^{2-}/Mn} = -1.58 - 0.03 pMn''' + 0.12 pSCN' V \text{ versus SCE}$$
(4)

Eq. (4) is only valid in the pH range 0–10 and for all the NH₄SCN concentrations studied. For the working concentrations (pSCN'=0.097, pMn'''=0.22), $E'_{Mn(SCN)4^{2-}/Mn}$ has a value of -1.57 V versus SCE.

A similar thermodynamic study was carried out in the absence of NH₄SCN. Under these conditions, the reduction of Mn(II) involved the species $MnCl_4{}^{2-}$, in agreement with the following reaction:

$$MnCl_4{}^{2-} + 2e^- \to Mn(0) + 4Cl^-$$
(5)

The apparent formal potential is expressed as a function of the concentrations of chloride and manganese ions using the following equation:

$$E_{\text{MnCl}_4^{2-}/\text{Mn}} = -1.42 - 0.03 \text{pMn}' + 0.12 \text{pCl}' \text{V} \text{ versus SCE}$$
(6)

For the working concentrations (pCl' = -0.6, pMn' = 0.22), $E'_{MnCl_4^{2-}/Mn}$ has a value of -1.49 V versus SCE.

In addition, it is necessary to consider the hydrogen evolution reaction:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{7}$$

(E' = -0.54 V versus SCE: pH 5.0).

The above analysis thus indicates that, from a thermodynamic perspective, the hydrogen evolution reaction occurs at more anodic potentials than the reduction of manganese.

3.2. Voltammetric and EQCM study

To determine the effect of NH₄SCN on the reduction of Mn(II) on a Fe-EQCM electrode, we carried out voltammetric and EQCM studies in the potential range -1.9 to -0.7 V using solutions S_0 (0.6 M MnCl₂·4H₂O + 0.32 M H₃BO₃ + 2.8 M KCl, pH 5.0) and S_0 + various concentrations of NH₄SCN. The potential scans were initiated in the cathodic direction from the resting potential (E_{rest}) with a potential scan rate (v) of 50 mV s⁻¹. The manganese deposits obtained in different potential regions were dried in a nitrogen atmosphere for analysis by SEM, EDS and XRD.

3.2.1. Study in the absence of NH₄SCN

Fig. 2 shows a typical voltammogram and its associated mass change (Δm) obtained from solution S_0 . In the voltammogram



Fig. 2. (a) Cyclic voltammogram and (b) Δm vs. *E* plot for a Fe-EQCM electrode in solution S_0 (=0.6 M MnCl₂·4H₂O + 0.32 M H₃BO₃ + 2.8 M KCl, pH 5), v = 50 mV s⁻¹.

(line a) a wave (a) is observed in the range -1.4 to -0.8 V during the potential scan in the cathodic direction. Similar behavior was reported by Casanova et al. [37], who attributed this wave to the hydrogen evolution reaction. At more cathodic potentials, a rapid increase is observed in the cathodic current density, which is associated with two processes, the reduction of Mn²⁺ ions and the reduction of H₂O (hydrogen evolution). On switching the potential scan to the anodic direction from -1.9 V, the absolute value of the current density is greater than was observed during the potential scan in the cathodic direction, leading to a crossover characteristic of the formation of a new phase [38]. It is important to note that no oxidation peak is observed during the potential scan in the anodic direction. Similar behavior has been reported by Sylla et al. [9], who attributed the lack of this peak to the instability of the manganese deposits, which are easily dissolved in acidic media.

The mass response (line b) associated with the voltammogram shows a slight increase in Δm (~1.4 µg cm⁻²) in the potential range -1.6 to -0.8 V (encompassing wave *a* in the voltammogram) during the cathodic potential scan. This increase can be attributed to the formation of the insoluble species Mn(OH)_{2(s)} on the electrode surface due to hydrogen evolution in this potential region and to the resulting increase in pH in the vicinity of the working electrode. At more cathodic potentials (<-1.7 V), a rapid increase in Δm is observed, associated with the reduction of Mn(II) ions. It is possible that the observed increase in Δm contains a contribution from the incorporation of manganese hydroxide (Mn(OH)_{2(s)}) during the growth of the deposit. Previously, Gong and Zangari [1] showed by X-ray photoelectron spectroscopy (XPS) analysis that Mn(OH)_{2(s)} is incorporated into the deposits when high current densities were applied.

On switching the potential scan to the anodic direction, Δm continues to increase until it reaches a maximum value and forms a plateau in the potential range -1.5 to -1.25 V. At more positive potentials, Δm shows a decreasing. This decrease in Δm can be attributed to the dissolution of manganese, which is unstable and tends to dissolve easily in acidic media [9,21]. In addition, dissolution of Mn(OH)_{2(s)} may contribute to the decrease in Δm , given that in this potential region hydrogen evolution does not occur and the pH returns to its value in the bulk solution (pH

5.0). At the end of the scan, the value of Δm does not return to its initial value of zero, indicating that a quantity (12.2 µg cm⁻²) of material remains on the electrode surface.

The decrease in Δm observed during the potential scan in the anodic direction is not accompanied by an oxidation current in the corresponding voltammogram (line a, Fig. 2), suggesting that the dissolution process is non-faradaic (without charge transfer associated). To verify the dissolution of manganese in the potential range -1.2 to -0.7 V, we constructed graphs d Δm dt^{-1} versus E, known as massograms [22,23], where $d\Delta m dt^{-1}$ is the rate of mass change (mass flux) that occurs at the electrode surface. For mass changes that are associated with charge transfer processes at the electrode surface (faradaic processes), $d\Delta m$ dt^{-1} is directly proportional to the current density, and hence a massogram is analogous to a voltammogram. For greater clarity, the sign of the mass flux in the massogram is associated with the sign of the corresponding current density: negative mass flux corresponds to the reduction process (mass gain), and positive mass flux corresponds to the oxidation process (mass loss). In this way, a positive mass flux without a corresponding anodic current density is evidence of non-faradaic dissolution (mass changes without charge transfer associated) of species at the electrode surface.

Fig. 3 shows the massogram (line b) for solution S_0 , along with the corresponding cyclic voltammogram (line a); the behavior of the voltammogram was discussed above in relation to Fig. 2. Note that the contribution of the hydrogen evolution reaction is massive in the voltammogram but minimal in the massogram. This difference highlights fact that the voltammogram, but not the massogram, is affected by interference from the hydrogen evolution reaction, and thus the massogram shows the manganese reduction and oxidation (dissolution) processes with greater clarity. During the potential scan in the cathodic direction, in the potential range -1.50 to -0.8 V, the mass flux varies slightly due to the formation of Mn(OH)2(s) on the electrode surface. At more cathodic potentials, an increase in the reduction mass flux (negative mass flux) is observed, which derives from the formation of the Mn deposit and the inclusion of $Mn(OH)_{2(s)}$ into the deposit.



Fig. 3. (a) Cyclic voltammogram and (b) the corresponding massogram for a Fe-EQCM electrode in solution S_0 . v = 50 mV s⁻¹. (c) The supporting electrolyte: 2.8 M KCl + 0.32 M H₃BO₃, pH 5.0 is also shown.

On switching the potential scan at -1.9 V and scanning in the anodic direction, two cross-overs are observed between the mass fluxes recorded during the cathodic and anodic scans. The potential at which the more anodic cross-over occurs (-1.48 V) is known as the cross-over potential (Eco) [22,39,40]. The appearance of these two cross-overs is characteristic of processes involving the formation of a new phase [38,39]. At potentials more anodic than Eco, two processes of positive mass flux are observed – peak A (-1.2 V) and peak B (-0.8 V) – after which the mass flux diminishes. The observed changes of $d\Delta m$ dt^{-1} according to the potential (peaks A and B), are indicative of the dissolution of two different species. It is important to note, that the processes A and B in the massograms do not have an associated oxidation current density in the voltammograms, indicative of two processes of non-faradaic dissolution. From the above results, it is evident that massograms give better and clearer information than plots of Δm versus E (line b, Fig. 2).

3.2.1.1. Switching potential study in the absence of NH₄SCN. To analyze the anodic processes and the behavior of Eco, we used the switching potential technique [39–42]. In this technique, the potential scan was initiated in the cathodic direction from the rest potential (E_{rest}) and was switched to the anodic direction at different values of the switching potential (E_{λ}). The values of E_{λ} were chosen to fall in different zones of the voltammogram (line a, Fig. 3): in the potential range -1.3 to -0.8 V, which corresponds to wave a; and the range -1.9 to -1.5 V, which corresponds to the reduction of Mn(II) ions.



Fig. 4. (a) Cyclic voltammogram and (b) Δm vs. *E* plot for a Fe-EQCM electrode in solution S_0 , $E_{\lambda} = -1.1$ V vs. SCE, v = 50 mV s⁻¹.

Fig. 4 shows a typical voltammogram obtained at $E_{\lambda} = -1.1$ V (line a) and the corresponding mass variation (Δm) (line b). During the potential scan in the cathodic direction, both the cathodic current density and Δm increase. On switching the potential scan to the anodic direction, no peak corresponding to the oxidation current density is observed, and Δm gently decreases and then remains constant until the end of the potential scan, indicating that the mass accumulated during the cathodic scan remains on the electrode surface (0.213 µg cm⁻²). A manganese deposit was obtained by holding the potential scan at -1.1 V for 180 min. An SEM image of this surface (Fig. 5) shows an amorphous deposit covering some parts of the substrate, EDS analysis (inset) showed the presence of manganese and oxygen.



Fig. 5. An SEM image of manganese deposition onto Fe-EQCM at E = -1.1 V, t = 180 min from solution S₀. Analysis EDS is also shown.



Fig. 6. Series of massograms obtained for solution S_0 with different values of the switching potential (E_{λ}) . (a) $E_{\lambda} = -1.55$ V vs. SCE, (b) $E_{\lambda} = -1.67$ V vs. SCE, (c) $E_{\lambda} = -1.74$ V vs. SCE, and (d) $E_{\lambda} = -1.8$ V vs. SCE. The corresponding voltammograms are shown in the inset, v = 50 mV s⁻¹.

In addition, XRD analysis (not displayed) showed the formation of a broadband in the interval $10 < 2\theta < 25$, characteristic of an amorphous deposit, as well as the signals corresponding to the substrate (Fe). These results indicate that the insoluble species $Mn(OH)_{2(s)}$ is formed on the electrode surface due to hydrogen evolution in this potential region and to the resulting increase in pH in the vicinity of the working electrode.

Fig. 6 shows a series of massograms and their corresponding voltammograms (inset) obtained at different values of E_{λ} in the potential range -1.8 to -1.55 V. In the massogram for the system in which the potential scan was switched at -1.55 V (line a), we observe the formation of peak A and a small peak B. At more cathodic switching potentials ($E_{\lambda} < -1.55$ V), both peaks A and B increase in intensity. Fig. 7a shows an SEM image of the deposit obtained at E = -1.65 V after 180 min. This images shows that the deposit formed under these conditions is uniform and porous (due to the hydrogen evolution under these conditions). EDS analysis of this deposit (inset) shows that it is principally Mn with a small amount of oxygen. Iron, the substrate material, was also detected due to the porosity of the coating. In addition, XRD analysis showed that the deposit was the β -manganese phase (body-cubic (a = 6.31160Å), S.G.: P4132) (Fig. 7b). These results indicate that peaks A and B in the massograms correspond to the non-faradaic dissolution of the species formed during the cathodic scan, that is, β -manganese and $Mn(OH)_{2(s)}$, respectively.

When E_{λ} is successively switched in the potential range -1.85 to -1.55 V (Fig. 6), it is found that the value of the cross-over potential (Eco = -1.47 V) is independent of E_{λ} . By a standard result of nucleation theory [39], in these cases, Eco corresponds to thermodynamic reversible potential of the metallic ion/metal couple in the absence of interference from additional currents. Given that the massogram does not respond to the hydrogen evolution reaction, the value of Eco obtained in the massogram corresponds to thermodynamic reversible potential of the Mn(II)^{'''}/Mn(0) couple. The value of Eco is very

close to the value of the apparent formal potential obtained in the thermodynamic study, $E'_{Mn(Cl)_4^{2-}/Mn} = -1.49$ V. On the basis of this result, it is possible to propose that the manganese reduction reaction in solution S_0 principally involves the species $MnCl_4^{2-}$ as represented in reaction (5) (see Section 3.1), but with slight interference due to the presence of $Mn(OH)_{2(s)}$.

3.2.2. Study in the presence of NH₄SCN

The study of the influence of ammonium thiocyanate (NH₄SCN) was performed in the potential range -2.0 to -0.7 V using the base solution S_0 with various concentrations of NH₄SCN (0.1, 0.2, 0.3, 0.5, and 0.8 M). Fig. 8 (inset) shows the voltammograms obtained. Addition of NH₄SCN to the solution has important effects on the voltammograms obtained. During the cathodic potential scan, the wave a increases in intensity and is displaced in the negative direction as the NH₄SCN concentration is increased. Additional experiments performed using solutions S ($2.8 \text{ M KCl} + 0.32 \text{ M H}_3\text{BO}_3$) and S + 0.8 M NH_4SCN showed that the intensity of wave *a* increases in the presence of NH₄SCN, and thus may be associated with the reduction of the proton of the ammonium ion. A similar displacement was observed in the combined process of Mn(II) discharge and evolution of hydrogen gas. When the potential scan was switched to the anodic direction, an anodic peak (peak Ia) was observed that increased in intensity and was displaced in the positive direction as the additive concentration was increased up to 0.3 M. At additive concentrations of 0.3 M and above, the intensity and potential (-1.16 V) of peak Ia remained constant and the formation and growth of a shoulder (H) (-1.04 V) was observed. As suggested by Jovic et al. [43], the detection of multiple peaks during the electrochemical oxidation of metals can be attributed to the dissolution of different phases. It is important to note that the oxidation processes observed in the presence of NH₄SCN (peak Ia and shoulder H) are not observed in the voltammogram obtained in the absence of additive (line



Fig. 7. (a) An SEM image (analysis EDS is also shown in the inset) and (b) X-ray diffraction (XRD) pattern, of a manganese coating electrodeposited at E = -1.65 V, t = 180 min from solution S_0 .



Fig. 8. Series of massograms obtained for the Fe-EQCM electrode in solutions comprised of S_0 with various concentrations of NH₄SCN. (a) 0.0 M, (b) 0.1 M, (c) 0.2 M, (d) 0.3 M, (e) 0.5 M, and (f) 0.8 M. $v = 50 \text{ mV s}^{-1}$. The corresponding voltammograms are shown in the inset, $v = 50 \text{ mV s}^{-1}$.

a, Fig. 8 (inset)), suggesting that the manganese phases formed during the cathodic scan in the presence of NH₄SCN are stable and permit the electrochemical oxidation of the manganese.

Fig. 8 also shows the massograms corresponding to the voltammograms in inset. As the additive concentration is increased, diverse changes are observed with respect to the massogram obtained in the absence of NH₄SCN (line a). Specifically, the cross-over potential is displaced in the cathodic direction, which is in accord with the prediction of the potential equation obtained in the thermodynamic study (Eq. (4)) and is indicative of the formation of complexes between Mn²⁺ and SCN⁻. The mass flux associated with the reduction of manganese decreases considerably, principally due to the cathodic displacement of the potential required for the discharge of manganese in the presence of the NH₄SCN. In addition, it is important to observe that in the presence of NH₄SCN, the mass flux during the cathodic scan in the potential range -1.4 to -0.8 V, which is associated with the formation and adsorption of $Mn(OH)_{2(s)}$, diminishes considerably with respect to that observed in the absence of additive in the same potential range. This result is contrary to expectations, given that the increase in the intensity of wave a (hydrogen evolution) in the voltammograms (Fig. 8, inset) with increasing NH₄SCN concentration would lead one to predict an increase in the quantity of $Mn(OH)_{2(s)}$ that is adsorbed on the electrode surface. This result raises the possibility that species like: the complex formed between Mn²⁺ and SCN⁻, ions SCN⁻ or NH₃, are adsorbed specifically on the surface and inhibits the adsorption of $Mn(OH)_{2(s)}$.

During the anodic potential scan, the intensities of peaks A and B observed in the absence of additive decrease considerably as the additive concentration is increased up to 0.1 M (line b, Fig. 8). At additive concentrations greater than 0.1 M and cathodic potentials close to peak A, an increase in the positive mass flux is observed, likely due to the dissolution of a manganese phase different from that formed at lower addi-



Fig. 9. (a) Cyclic voltammogram and (b) Δm vs. *E* plot for a Fe-EQCM electrode in solution $S_0 + 0.8$ M NH₄SCN, $E_{\lambda} = -1.15$ V vs. SCE, v = 50 mV s⁻¹.

tive concentrations. In addition, the growth of a new peak, H' (-1.06 V) and the gradual disappearance of peak B are observed. At the highest concentration of NH₄SCN considered (0.8 M) (line f), a shoulder (Ia') is observed at -1.16 V and peak H' (-1.06 V) is observed at more anodic potentials and with greater intensity. At the end of the scan cycle, the mass flux does not return to zero, indicating that an accumulated mass of manganese remains on the surface without reacting. The mass accumulated on the electrode surface decreases from 9.3 to 0.4 μ g cm⁻² when the concentration of NH₄SCN is increased from 0.1 to 0.8 M.

Comparing the voltammograms (Fig. 8 (inset)) with their respective massograms (Fig. 8), we see that the appearance of shoulder H (-1.03 V) in the voltammograms is associated with the appearance of peak H' (-1.06 V) and the disappearance of peak B (-0.8 V) in the massograms.

3.2.2.1. Switching potential study in the presence of NH_4SCN . We next studied the behavior of Eco and the formation of the



Fig. 10. Series of massograms obtained for solution $S_0 + 0.8$ M NH₄SCN with various values of the switching potential (E_λ). (a) $E_\lambda = -1.80$ V vs. SCE, (b) $E_\lambda = -1.85$ V vs. SCE, (c) $E_\lambda = -1.90$ V vs. SCE, and (d) $E_\lambda = -2.0$ V vs. SCE. The corresponding voltammograms are shown in the inset.

oxidation peaks (peak Ia and shoulder H) in the voltammogram using the potential switching technique in various potential ranges: -1.3 to -0.8 V, which corresponds to wave a; -2.0 to -1.8 V, which corresponds to the potential region in which manganese reduction occurs. The solution $S_0 + 0.8$ M NH₄SCN was used in this study.

Fig. 9 shows a typical voltammogram obtained at $E_{\lambda} = -1.15$ V (line a) and its associated mass change (Δm) (line b). During the potential scan in the cathodic direction, an increase in the cathodic current density and a slight increase in Δm are observed. In addition, on switching the scan to the anodic direction, no peak corresponding to the oxidation current density is observed and Δm remains constant until the end of the potential scan. It is important to observe that the value of Δm

(0.137 μ g cm⁻²) at the end of the potential scan is much less than that observed in the absence of additive in this potential region, which is consistent with the additive inhibiting adsorption in this region. SEM, EDS and XRD analysis of the deposit obtained at E = -1.15 V showed that the morphological and chemical characteristics of this deposit were similar to those of the deposit formed in the absence of NH₄SCN (Fig. 5).

Fig. 10 (inset) shows a series of voltammograms obtained at different values of E_{λ} in the potential range -2.0 to -1.8 V. As E_{λ} is made more cathodic, peak Ia increases in intensity and is displaced in a positive direction. In addition, shoulder H shows is appreciable only when $E_{\lambda} \leq -1.9$ V. The massograms corresponding to the voltammograms are also shown, when $E_{\lambda} = -1.80$ V (line a), two processes are observed: shoul-



Fig. 11. (a) An SEM image (analysis EDS is also shown in the inset) and (b) X-ray diffraction (XRD) pattern, of a manganese coating electrodeposited at E = -1.80 V, t = 100 min from solution $S_0 + 0.8$ M NH₄SCN.

der Ia' (-1.17 V) and peak H' (-1.06 V). As E_{λ} was made more cathodic, both processes increased in intensity and were displaced in the anodic direction. At sufficiently cathodic potentials ($E_{\lambda} < -1.9$ V), peak H' was the dominant feature. This may indicate that, in the presence of NH₄SCN and at sufficiently cathodic potentials, the formation of two stable manganese phases is favored, and that these phases are oxidized during the anodic potential scan. Note that the potentials of processes Ia' (-1.16 V) and H' (-1.06 V) in the massogram are very close to the potentials of processes Ia (-1.17 V) and H (-1.04 V) in the voltammogram (inset, Fig. 10), respectively.

Fig. 11a shows an SEM image of the deposit obtained at -1.8 V after 100 min. The image shows a compact coating made up of flakes grouped in clusters. Chemical analysis by EDS (inset) shows that the deposits contain manganese and in

a much lower proportion oxygen, indicating the presence of oxide in the deposit. In addition, analysis of the crystal structure by XRD (Fig. 11b) indicates the presence of two phases, α -manganese (body-centered cubic (a = 8.91210Å), S.G.: I-43m) and γ -manganese (body-centered-tetragonal (a = 2.67200Å, c = 3.55000Å), S.G.: 14/mmm). The XRD data also show features that possibly originate from the β -manganese phase.

The SEM image obtained at E = -1.95 V after 100 min (Fig. 12a) shows a compact coating made up of uniformly sized semicircular clusters. It is important to note that in the presence of NH₄SCN, holes in the obtained manganese coatings were not observed, since in these conditions the generation of bubbles associated to the reaction of hydrogen evolution carried out mainly in the edges of the electrode. Chemical analysis of this coating using EDS (inset) indicated that the deposit contained



Fig. 12. (a) An SEM image (analysis EDS is also shown in the inset) and (b) X-ray diffraction (XRD) pattern, of a manganese coating electrodeposited at E = -1.95 V, t = 100 min from solution $S_0 + 0.8$ M NH₄SCN.

manganese and in a much lower proportion oxygen and sulfur. The presence of sulfur may be associated with solution hidden in the deposit. XRD (Fig. 12b) analysis of the deposit showed that it was principally composed of α -manganese, along with a much smaller proportion of γ -manganese.

The above results suggest that the shoulder I'a in the massograms corresponds to the dissolution of the γ -manganese phase, whereas the peak H' corresponds to the dissolution of the α manganese phase. It is important to note that the peaks of the different phases of manganese (Figs.11b and 12b) are very close and some are superposed to each other, thus that the assignment could be uncertain.

When E_{λ} was successively switched in the potential range -2.0 to -1.8 V (Fig. 10), the value of Eco (=-1.58 V) remained constant with a value very close to the value of the apparent formal potential obtained in the thermodynamic study for the Mn(SCN)₄²⁻/Mn couple ($E'_{Mn(SCN)_4^{2-}/Mn} = -1.57$ V versus SCE), indicating that under these conditions, the reduction of manganese proceeds via reaction (3) obtained in the thermodynamic study. Thus, the cathodic displacement of the discharge potential of Mn(II) observed in the presence of the additive can be attributed to the formation of the complex Mn(SCN)₄²⁻.

4. Conclusions

In this study we used voltammetry and EQCM to examine the effect on the electrodeposition of manganese onto an Fe-EQCM electrode of adding NH₄SCN to the electrolytic solution. The EQCM data were represented as graphs of $d\Delta m dt^{-1}$ versus *E*, known as massograms. Use of the massograms allowed us to eliminate the contribution of the hydrogen evolution reaction and thus to clearly discern aspects of the manganese reduction and oxidation processes, such as the cross-over potential (Eco) and the influence of the NH₄SCN on these processes.

In the absence of the NH₄SCN additive, the formation and adsorption of Mn(OH)_{2(s)} was observed in the potential range -1.1 to -1.7 V. The formation of Mn(OH)_{2(s)} can be attributed to the increase in pH in the vicinity of the electrode caused by the hydrogen evolution reaction in this potential region. At more cathodic potentials, deposition of β -manganese occurred, in conjunction with the inclusion of $Mn(OH)_{2(s)}$ into the deposit. Comparison of the voltammetric response and the corresponding massogram indicated that the dissolution of two different manganese species occurs in the interval -1.1 to -0.7 V during the potential scan in the anodic direction and that it is a non-faradaic process (without charge transfer associated). By analyzing the behavior of Eco in the massograms, and through a thermodynamic study of the reduction of manganese complexes, we determined that the reduction process in the absence of additive occurs via the reduction of the complex $MnCl_4^{2-}$. These findings demonstrate the great value of massograms in the measurement of reversible potentials in systems affected by interference from the hydrogen evolution reaction.

In the presence of NH_4SCN , the discharge potential of manganese was displaced in the cathodic direction. By studying the cross-over potential (Eco) and using the theory proposed by Fletcher [37], we concluded that this displacement is due to the formation of the complex $Mn(SCN)_4^{2-}$. We additionally found that the presence of the additive inhibited the adsorption of $Mn(OH)_{2(s)}$. At concentrations greater than 0.3 M NH₄SCN and sufficiently cathodic potentials, the formation of two stable manganese phases, α - and γ -manganese, was promoted.

Acknowledgments

The authors are grateful for financial assistance provided by CONACyT (Consejo Nacional de Ciencia y Tecnología), México, Proyects: 48440 and 48335. P. Díaz-Arista, also acknowledge CONACyT for scholarship support.

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