Journal of Electroanalytical Chemistry 803 (2017) 65–71

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Selenium reaction mechanism in manganese electrodeposition process

J.C. Rojas-Montes, R. Pérez-Garibay*, A. Uribe-Salas, S. Bello-Teodoro

Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Unidad Saltillo, Av. Industria metalúrgica 1062, Parque Industrial Saltillo-Ramos Arizpe, CP 25900 Ramos Arizpe, Coahuila, Mexico

ARTICLE INFO

Keywords:
Manganese electrodeposition
Selenium reaction mechanism
Manganese recovery
Selenium electrodeposition

ABSTRACT

A difficulty for the electrochemical deposition is the high negative electrolytic potential of the Mn^{+2}/Mn° pair in aqueous solutions producing water reduction at any pH value; to resolve this problem it is necessary to use selenium dioxide (SeO_2) as additive. However, there is little information about the selenium mechanism presenting discrepancies. Founded on linear voltammetry, cyclic voltammetry, chronoamperometry test, and impulses of constant potential and thermodynamic analysis, are experimental evidences of the reaction mechanism to explain the selenium action; from here the originality of this work. It is demonstrated that two reactions that occur in the selenium mechanism at -0.3 and -0.6 V, the first for the selenium deposition and the second for the selenium dissolution. On the active sites of the cathode the specie of selenium reduced at -0.3 V is the ion hydrogen selenite ($H_2SeO_3^-$), while at -0.6 V the deposited selenium is reduced to selenide.

1. Introduction

Manganese is an important metal used for steel [1,2] and non-ferric alloys of aluminum, copper, nickel and zinc [3,4]. The electrolytic manganese dioxide (EMD) is used in modern alkaline, lithium and sodium batteries, including electrochemical capacitors and hydrogen production [5,6]. Manganese is also employed for manufacturing of chemical reagents and electronic components [7]. Electrolytic grade manganese represents 9% of the treated manganese minerals. Due to the fast expansion of Chinese industry, between the years 2000 and 2012 the annual production of electrolytic manganese increased from 180,000 to1,700,000 t. It has been also predicted that in 2021 the world demand for manganese will increase by 83% due to the growth in the production of articles containing this metal [8,9].

When producing high-purity manganese by an electrochemical process, some technical difficulties are encountered. The high negative electrolytic potential of the Mn^{+2}/Mn° pair in aqueous solutions ($-1.18\ V_{SHE}$) easily produces water reduction at any pH value [10], which represents a problem for process efficiency. Under these conditions, the following reactions take place at the cathode:

$$Mn^{+2} + 2e^- = Mn \qquad E_{25}^{\circ} = -1.182\ V \tag{1}$$

$$H_2O + 2\,e^- = H_2 + 2\,OH^- \qquad E_{25}^{\circ} = -0.67\ V \tag{2}$$

The presence of the latter reaction (2) produces an inefficient consumption of current and makes necessary to add chemical additives to attenuate this problem, with selenium dioxide (SeO_2) being the most commonly used [11,12]. Even though the role of the selenium as an additive is not well known, it is generally accepted that this element is deposited on the active sites of the cathode at the beginning of the electrodeposition process, hampering the gas hydrogen evolution and making manganese electrodeposition possible [13,14]. However, there is no experimental evidence that this additive is only active at the beginning of the electrodeposition process.

There is little information about the selenium acting mechanism, and reports of the literature consulted have discrepancies in their explanations; but the more remarkable fact is the lack of experimental evidences of the proposed mechanisms. To this regard, Wei et al. [15] state that in electrolytes containing 20 mg/l of SeO_2, two reactions can occur at -0.9 and -1.2 V, but they do not specify which of the two reaction occurs. Although Radhakrishnamurthy and Reddy [16] do not propose a reaction mechanism, they report the presence of species such as Se $(+4)$, H_2SeO_3, $HSeO_3^-$, and SeO_3^{-2} in the catholyte, when the SeO_2 is initially dissolved in water. They also pointed out that when different electric potentials are applied, the Se $(+4)$ species is reduced from Se(0) to Se (-2) on the cathode. Xu et al. [11] also report the occurrence of the following reactions between -0.56 and -1.36 V, due to the effect of selenium addition: firstly, $Se^{+4} + 4e^- \rightarrow Se$, and secondly, $Se + 2e^- \rightarrow Se^{-2}$, without specifying all the chemical species involved in the reactions.

Fan et al. [17] and Sun et al. [18] conducted studies focused on identifying the selenium reaction mechanism. In the first study, Fan et al. [17] proposed the following chain of reactions:

---

* Corresponding author.
E-mail address: roberto.perez@cinvestav.edu.mx (R. Pérez-Garibay).

http://dx.doi.org/10.1016/j.jelechem.2017.09.012
Received 4 May 2017; Received in revised form 12 August 2017; Accepted 7 September 2017

$$SeO_2 + H_2O = H_2SeO_3 \qquad (3)$$

$$H_2SeO_3 = HSeO_3^{-} + H^{+} = SeO_3^{-2} + 2H^{+} \qquad (4)$$

$$HSeO_3^{-} + 2H_2O + 4e^{-} = Se^{\circ} + 5OH^{-} \qquad (5)$$

$$Se^{\circ} + 2e^{-} = Se^{-2} \qquad (6)$$

$$Se^{-2} + 2H_2O = HSe^{-} + OH^{-} + H_2O = H_2Se + 2OH^{-} \qquad (7)$$

$$Se^{-2} + Mn^{+2} = MnSe\downarrow \qquad (8)$$

$$MnSe + 2e - = Mn^{\circ} + Se - 2 \qquad (9)$$

Sun et al. [18] proposed a mechanism based on voltammetry, chronopotentiometry, and cross-potential electrolysis observations. In their study, it is reported that the reduction process is conducted in two steps: a) the reduction of the SeO_3^{-2} species to Se° and selenide ions (Se^{-2}), b) adsorption of the selenide ions as elemental selenium at cathodic potential. These authors propose the following reaction mechanism:

$$3H^{+} + SeO_3^{-2} + 4e^{-} = Se^{\circ} + 3OH^{-} \qquad (10)$$

$$3H^{+} + SeO_3^{-2} + 6e^{-} = Se^{-2} + 3OH^{-}$$

$$Se^{-2} = Se^{\circ} + 2e^{-} \qquad (11)$$

Jiao et al. [19] also analyzed the inhibitory effect of selenium dioxide on the hydrogen evolution, reporting the presence of a reaction at $-0.4\ V_{SHE}$, which is associated with the following stoichiometry:

$$SeO_3^{-2} + 3H_2O + 4e^{-} = Se + 6\ OH^{-} \quad E^{\circ} = -0.366\ V_{SHE} \qquad (12)$$

Based on thermodynamic analysis and experimental tests (linear voltammetry, cyclic voltammetry, chronoamperometry, and impulses of constant potential), this study shows experimental results of the reaction mechanism to explain the role of selenium in manganese electrodeposition. Some of the instrumental techniques used are atomic absorption spectrometry (AAS; SpectraAA 220 MS), and hydride generation coupled with atomic absorption (GH-AA; VGA-77, Varian) to determine the manganese and selenite ion concentrations. For the chemical analysis of the electrode surface, scanning electron microscopy (SEM, model XL30, Philips) was used.

2. Experimental method

2.1. Electrolysis tests

The experimental electrolysis tests were conducted in a laboratory cell of 250 ml of catholyte solution capacity (Fig. 1). A 304-stainless steel cathode and a lead–silver alloy (1% Ag) anode, both 9.5 × 8 cm in size, were used. The current was supplied by a power supply (Tektronix PWS4305), and for the experiments involving mixing, a peristaltic pump was used to recirculate the catholyte. In general, the experiments were conducted in the presence of an anionic membrane (CMI-7001, obtained from Membranes International, Inc.). This membrane is manufactured from polystyrene cross-linked with divinylbenzene, has a thickness of 0.45 ± 0.025 mm and electrical resistivity of $< 40\ \Omega{\cdot}cm^2$. The use of such a membrane is critical in preventing the massive transport of protons to the cathode and manganese ions to the anode compartments.

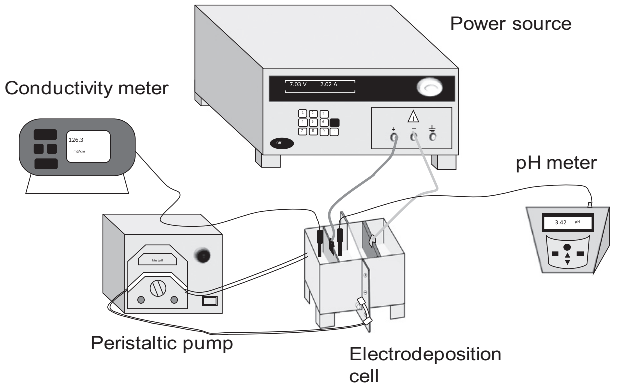

Fig. 1. Schematic of the experimental rig used for the electrolysis tests.

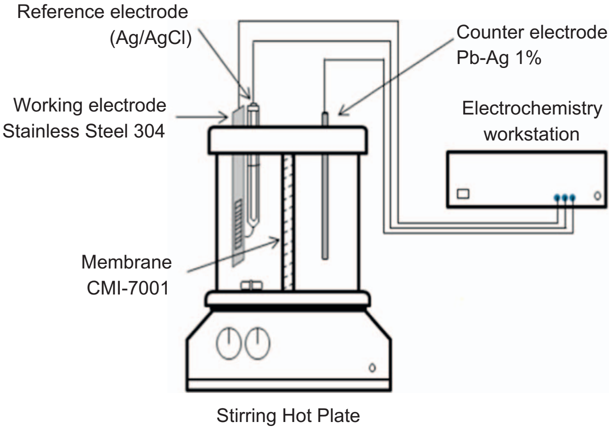

Fig. 2. Schematic diagram of the electrochemical cell used.

The catholyte solution contains 0.27 M of Mn^{2+}, 0.9 M of $(NH_4)_2SO_4$, and 0.27 mM of SeO_2, while the anolyte contains 0.5 M of H_2SO_4. To maintain the selenium concentration constant the experiments were conducted in open-loop system (i.e. the electrolyte was not recycled). It is noteworthy that both electrodes were polished (Sandpaper grade 80, 120, 220 and 800) and washed before each test for 30 min with a solution of sodium silicate (4%).

2.2. Electrochemical tests

The electrochemical study was conducted in a conventional three-electrode electrochemical cell with 30 ml of catholyte solution capacity, which was divided in two compartments with the same anionic membrane used in the electrolysis assays, as illustrated in Fig. 2. A stainless steel plate (3 × 3.5 cm) was used as working electrode and a Pb-Ag (1%) plate was used as the counterelectrode, while the reference electrode was Ag/AgCl and was immersed in a Luggin capillary solution saturated with potassium chloride. It is worth to note that all the results reported in this paper were referenced to the hydrogen standard electrode. The cathodes were polished before each test. The power was supplied by a potentiostat (VersaSTAT 4, Princeton Applied Research).

2.3. Materials

The chemical reagents used to adjust the catholyte composition were hydrated manganese sulfate ($MnSO_4{\cdot}H_2O$), ammonium sulfate ($(NH_4)_2SO_4$), and selenium dioxide (SeO_2). The anolyte was prepared with a sulfuric acid solution and all the chemical regents were of 98% purity and were supplied by Sigma-Aldrich.

3. Results and discussion

To determine whether the action of selenium occurs only at the beginning of the electrodeposition process, a set of tests were performed with two different electrolytes. The first test was conducted keeping the manganese concentration constant (0.27 M) throughout the test, while fixing the selenium concentration (0.27 mM) at the beginning of the test. The second test was conducted by keeping the manganese and selenium constant during the experiment ($Mn^{+2} = 0.27$ M and $SeO_2 = 0.27$ mM).