



## Selenium reaction mechanism in manganese electrodeposition process



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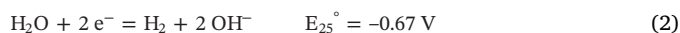
### ABSTRACT

A difficulty for the electrochemical deposition is the high negative electrolytic potential of the  $Mn^{+2}/Mn^{\circ}$  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 to 1,700,000 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  $Mn^{+2}/Mn^{\circ}$  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:



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:

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