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# Influence of sodium silicate on manganese electrodeposition in sulfate solution

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**Abstract:** The influences of sodium silicate on manganese electrodeposition in sulfate solution were investigated. Manganese electrodeposition experiments indicate that a certain amount of sodium silicate can improve cathode current efficiency and initial pH 7.0–8.0 is the optimized pH for high cathode current efficiency. The analyses of scanning electron microscopy (SEM) and X-ray diffraction (XRD) indicate the compact morphology and nanocrystalline structure of electrodeposits. X-ray photoelectron spectrometry (XPS) analysis shows that the elements of Mn, Si and O exist in the deposit. The solution chemistry calculations of sulfate electrolyte and sodium silicate solution indicate that species of  $Mn^{2+}$ ,  $MnSO_4$ ,  $Mn(SO_4)_2^{--}$ ,  $Mn^{2+}$ ,  $MnSiO_3$ ,  $Mn(NH_3)^{2+}$ ,  $SiO_3^{2-}$  and  $HSiO_3^{-}$  are the main active species during the process of manganese electrodeposition. The reaction trend between  $Mn^{2+}$  and Si-containing ions is confirmed by the thermodynamic analysis. In addition, polarization curve tests confirm that sodium silicate can increase the overpotential of hydrogen evolution reaction, and then indirectly improve the cathode current efficiency. **Key words:** electrodeposition; manganese; sodium silicate; electrodeposit structure; hydrogen evolution reaction

## **1** Introduction

Manganese metal has been widely used in stainless steels and alloying with Ni, Zn and Sn [1–3]. Manganese is also the most electro-negative metal [4]. Metallic manganese is primarily electrodeposited from aqueous sulfate solutions. The electrolyte is composed of manganese sulfate and ammonium sulfate with trace Se-containing additive. Manganese sulfate is commonly obtained from leaching solution of manganese ores.

The rapid development of manganese industry has led to the decrease of manganese ore grade markedly. The conventional techniques used for ore beneficiation contain gravity separation, magnetic separation, froth flotation, pyrometallurgy and hydrometallurgy. The froth flotation, used as a selective processing method, is promising for ore beneficiation, as it has various advantages in terms of applicability, adaptability, operation, efficiency and economics. Sodium silicate, as depressant or dispersant, is widely used as regulating reagent in the flotation of minerals [5,6]. In iron ore flotation, sodium silicate is used to disperse the kaolinite in a wide range of pH value [7]. Regarding the flotation mechanism of sodium silicate, there are few publications available. The depression mechanism of sodium silicate is primarily the adsorption action of the hydrolysis products of sodium silicate, which produces a number of monomeric, polymeric and colloidal species. GONG et al [8] advocated that polymeric silicate species in concentrated solutions provided a depressing effect on iron oxide due to the strong adsorption of the polymeric silicate species onto the iron oxide surface, thus hindering it from collector adsorption. Sodium silicate was also widely used in the froth flotation of manganese minerals. PARRENT [9] found that the degree of selectivity of pyrolusite was fixed as sodium silicate was added in flotation of manganese oxide ores, regardless of dosages and particle sizes of sodium oleate and sodium silicate. In the study of ANDRADE et al [10], it was found that the inhibition effect of sodium silicate at pH 9.0 was more efficient in depressing quartz than rhodonite, especially for lower concentrations of sodium silica, whereas the flotation response of rhodochrosite was only slightly influenced at both pH 9.0 and pH 11.0.

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However, the adsorption of sodium silicate on manganese ore surface results in a certain amount of silicate species remaining in the floated manganese ores. These residual species at a certain level can exert some effects on the subsequent process of manganese electrodeposition.

However, manganese electrodeposition process is particularly sensitive to impurities, which significantly influence the current efficiency, morphology and crystal structure of electrodeposited manganese. This is attributed to that standard reduction potential for  $Mn^{2+}/Mn$  is -1.18 V (vs SHE). Metallic impurities can decrease the overpotential of hydrogen evolution and hence lead to the decrease of cathode current efficiency [11,12]. And the deleterious influences of metallic impurities on the morphology of zinc electrodeposit have been analyzed [13]. Thus, the impurities in the electrolyte are strictly removed to gain high purity manganese during industrial production process of metallic manganese [14]. Furthermore, appropriate additives, such as SeO<sub>2</sub> and SO<sub>2</sub>, should be added into electrolyte to improve cathode current efficiency and quality of electrodeposited manganese. However, few literatures are available regarding effects of organic impurities on manganese electrodeposition process. DING et al [15] confirmed the beneficial effects of N-based auxiliary additives on manganese electrodeposition. PADHY et al [12] found that quaternary amine additives improved the morphology and crystal structure of manganese electrodeposits. As for the influence of sodium silicate on electrodeposited metal, previous study [16] indicated that the addition of silicates into the electrolyte of zinc led to the formation of a physical barrier to hinder aggressive ions from penetrating. In addition, it was reported that metal coatings can be electrodeposited from Si-containing electrolyte to improve the morphology and anti-corrosion behavior [17,18]. However, information regarding the effect of silicate species on manganese electrodeposition is not available.

In this work, the influences of sodium silicate on manganese electrodeposition were investigated systematically, based on the analyses of manganese electrodeposition experiments, characterization of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) pattern, X-ray photoelectron spectrometry (XPS) analysis, solution chemistry calculations, thermodynamics and cathode polarization.

### 2 Experimental

#### 2.1 Reagents and solutions

The catholyte contained analytical grade manganese

sulfate, ammonium sulfate, selenium dioxide and sodium silicate. Ammonia and sulfuric acid were used to adjust the pH of the catholyte. Reagents of analytical grade are dissolved in deionized water. Unless otherwise specified, catholyte components were as follows: 0.55 mol/L  $Mn^{2+}$ , 0.91 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 3.6×10<sup>-4</sup> mol/L SeO<sub>2</sub>, 8.2×10<sup>-4</sup> mol/L Na<sub>2</sub>SiO<sub>3</sub> and pH 7.0. The anolyte contained 0.91 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

#### 2.2 Electrodeposition experiment

The experiments of electrodepositing manganese were carried out in a divided plexiglass cell, which consisted of anode and cathode compartments (each effective volume of 100 mL) separated by a diaphragm, a cathode and an anode. The cathode was used with AISI 301 stainless steel sheet and polished with metallographic sandpaper, with a geometrical surface area of 27 mm×70 mm (single-side effective surface area of 1080 mm<sup>2</sup>), and a thin layer of epoxy resin was coated on the other surface. The cathode was rinsed with acetone and deionized water. Prior to electrodeposition experiment, the cathode was immersed in a 4% Na<sub>2</sub>SiO<sub>3</sub> solution for 5 min. PbSn<sub>0.4</sub>Ag<sub>0.014</sub>Sb<sub>0.014</sub> alloy was used as anode with a geometrical surface area of 20 mm× 70 mm (single-side effective surface area of 740  $\text{mm}^2$ ), and a thin layer of epoxy resin was also applied on the other surface. The anode and cathode were placed at a constant distance of 12.0 mm from the diaphragm. The electrolyte temperature was controlled within (30±1) °C by a thermostatic control. The catholyte was mixed by magnetic stirring. The experiments of electrodepositing manganese were carried out subsequently. After electrolysis, the cathode was withdrawn, washed with deionized water thoroughly after the experiments of electrodepositing manganese. Subsequently, the passivation treatment with a 3% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution for 1.0 min was carried out, washed thoroughly with deionized water, and dried in an oven. The electrodeposits were weighed and scraped carefully from the cathode surface. Based on mass gained by the cathode, cathode current efficiency  $(\eta)$  was calculated by [19]

$$\eta = \frac{p}{E_{\rm Mn} J_{\rm c} A_{\rm c}} \left(\frac{\Delta m_{\rm c}}{\Delta t}\right) \times 100\% \tag{1}$$

where  $\Delta m_c/\Delta t$  is the mass gain of the cathode over the time interval  $\Delta t$  (g/s);  $A_c$  is the effective cathode area (m<sup>2</sup>);  $J_c$  is the applied current density (A/m<sup>2</sup>); p is the purity of the electrodeposited manganese;  $E_{\rm Mn}$  is the electrochemical equivalent of metallic manganese (1.025 g/(A·h)).

#### 2.3 Characterization procedure

The manganese electrodeposits were analyzed by

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