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Influence of sodium oleate on manganese electrodeposition in sulfate solution

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ABSTRACT

The influence of sodium oleate (NaOL) on manganese electrodeposition from sulfate solution was systematically investigated in terms of cathode current efficiency, solution chemistry calculation and thermodynamic analysis, polarization curves and Fourier transform infrared spectroscopy (FT-IR) analysis. The experimental results show that NaOL concentration and pH present a multiple effect on cathode current efficiency. According to the solution chemistry calculations of sulfate electrolyte and NaOL, it is found that $MnSO_4$, $Mn(SO_4)_2^{2-}$, Mn^{2+}, $Mn(NH_3)^{2+}$, and OL^- and $(OL)_2^{2-}$ are the main active species, respectively. The reaction trend between OL^- and Mn^{2+} ions was evaluated by thermodynamic analysis. Finally, the influence of NaOL on hydrogen evolution reaction and manganese electrodeposition was investigated. And the coordination reaction of OL^- and Mn^{2+} was analyzed by FT-IR.

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1. Introduction

Rhodochrosite ($MnCO_3$) and pyrolusite (MnO_2) are the most common manganese ores. The original manganese-rich ores are being overexploited at an astonishing rate due to flourishing demand for metallic manganese. The grade of rhodochrosite has decreased from 18%–20% to 13%–15% in several manganese-concentrated areas (Liu et al., 2014). It is necessary to use mineral processing technology for beneficiation of manganese ores. The conventional techniques used for manganese ore beneficiation include gravity separation, magnetic separation, froth flotation, pyrometallurgy and hydrometallurgy. Among these, froth flotation is generally used as an effective and favorable mineral processing method. It has various advantages over the other techniques in terms of applicability, adaptability, operation, efficiency and economics (Altun et al., 2006; Akbar et al., 2015). The froth flotation, used as a selective processing method, has been used to obtain specific separations from complex ores, such as oxidized minerals and non-metallic ores (Zech et al., 2012; Shi et al., 2012; Aparajith et al., 2010). Manganese ore has been also processed by froth flotation separation (Song and Lu, 1994; Parrent, 2012).

NaOL, due to the active carboxyl functional groups, is commonly used as a collector in the flotation of numerous minerals, such as hematite, ilmenite and calcite (Shibata and Fuerstenau, 2003; Liu et al., 2015; HernáinzBermúdez de Castro and Gálvez Borrego, 1996). NaOL is also commonly used for manganese mineral flotation. Electrokinetic analyses were used to interpret the flotation and interfacial behavior of manganese dioxide with oleate as a collector (Fuerstenau and Shibata, 1999). The results indicate that there are two flotation and adsorption peaks in this system, and oleate ions are the active species at both peaks. The performance of oleic acid is inferior to that of linoleate hydroxamic acid in froth flotation of manganese minerals (Zhou et al., 2015). Based on zeta potential determinations, the mechanism of NaOL collector was investigated in micro-flotation tests of manganese minerals and quartz (Andrade et al., 2012). However, a large dosage of NaOL is required when it is used in the flotation of manganese minerals because carboxylate of NaOL is the least selective of all collectors used in mineral flotation, which might lead to a certain amount of NaOL remaining in the floated manganese minerals. This may have some potential effects on subsequent processes.

Manganese deposition is affected by any amount of impurity. The effects of metal impurities on manganese electrodeposition and hydrogen evolution have been studied (Lu et al., 2014; Araujo et al., 2006). In the industrial production of electrolytic manganese, impurities in the electrolyte are strictly removed to obtain high purity manganese (Wei et al., 2007; Xu et al., 2015). 99.9% purity of manganese products was obtained by electrolysis from purified electrolyte (Sancho et al., 2009). There is little information regarding the effects of organic and inorganic additives on manganese electrodeposition in the literature. Ding et al. (Ding et al., 2014) confirmed the beneficial effects of N-based ammonium thiocyanate, thiourea and polyacrylamide on the manganese electrodeposition process. Padhy et al. (Padhy et al., 2015) studied the effect of quaternary amine additives on manganese electrodeposition and appraised their effects on the morphology and crystal structure of electrodeposited manganese. The purity of electrodeposited manganese is 99.90% to 99.98% using

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25 mg/L to 90 mg/L sodium benzene sulfonate (Gong and Zangari, 2002). Regarding the influence of NaOL on metal electrodeposition, there are few reports involving the use of NaOL in the production of nano-particles (Hahn et al., 2015; Wen et al., 2008). No publications are available regarding the effect of NaOL on manganese electrodeposition.

In this study, the influence of NaOL on manganese electrodeposition was investigated, based on the calculations of solution chemistry and thermodynamics, electrochemical tests and Fourier transform infrared spectroscopy (FT-IR).

2. Materials and methods

2.1. Reagents and solutions

The catholyte was prepared by dissolving analytical grade manganese sulfate, ammonium sulfate, selenium dioxide and NaOL in deionized water. Analytical grade ammonia and sulfuric acid were used to adjust the pH of the catholyte solution. Unless otherwise specified, the catholyte composition is as follow: 0.55 mol/L Mn^{2+}, 0.91 mol/L $(NH_4)_2SO_4$, 3.6×10^{-4} mol/L SeO_2, 3.5×10^{-5} mol/L NaOL and pH 7.0; the anolyte is 0.91 mol/L $(NH_4)_2SO_4$.

2.2. Electrodeposition experiment

The electrodeposition experiments of manganese were carried out in a divided cell, and the electrolytic membrane reactor was made of acryl glass in our laboratory. An AISI 301 stainless steel sheet was used as the cathode with a geometrical surface area of 2.7 cm × 7.0 cm (single-side effective surface area of 10.8 cm^2), and a thin layer of epoxy resin was applied on one side of the cathode. The anode was made of $PbSn_{0.4}Ag_{0.014}Sb_{0.014}$alloy (Hengyang Yuanming Industry Co., Ltd., China) with a geometrical surface area of 2.0 cm × 7.0 cm (single-side effective surface area of 7.4 cm^2), and a thin layer of epoxy resin was also applied on one side of the anode. The anode and cathode were placed at a constant distance of 1.2 cm from the anion-exchange membrane. The cathode was immersed in 4% Na_2SiO_3 solution for 5.0 min. Electrolyte temperature was controlled at 30 ± 1 °C by a thermostatic controller. The initial pH 7.0 was maintained by adjustment with analytical grade ammonia and sulfuric acid, and the electrolyte pH was measured continuously using a pH meter. After electrolysis, the cathode was withdrawn, and washed with deionized water thoroughly. Subsequently, the cathode was passivated by a 3% potassium dichromate solution for 1.0 min, washed thoroughly with deionized water, and dried in an oven. The deposited plate was weighed and scraped carefully from the cathode surface. Based on mass weight gained by the cathode, cathode current efficiency was calculated using Eq. (1) (Ren et al., 2012).

$$\eta = \frac{p}{E_{Mn} I_c A_c} \left(\frac{\Delta M_c}{\Delta t} \right) \times 100\% \tag{1}$$

In Eq. (1), $\Delta M_c/\Delta t$ is the mass weight gain of the cathode over the time interval Δt (g/s); A_c is the effective cathode area (m^2); I_c is the applied current density (A/m^2); p is the purity of the electrodeposited manganese; E_{Mn} is the electrochemical equivalent of metallic manganese (1.025 g/(A·h)). Software of FactSage 5.5 was used for solution chemistry calculation in this study.

2.3. Cathode polarization test

The cathode polarization tests were carried out by using a CHI760E electrochemical workstation in a conventional three-electrode glass cell with 100 mL electrolyte at 25 ± 1 °C. An AISI 301 stainless steel sheet coated with epoxy resin was used as the working electrode, leaving an exposure area of 0.25 cm^2 for the cathode polarization test. The surface was finely polished with 400, 800 and 1200 mesh metallographic sandpaper successively. The electrode was then cleaned in acetone and deionized water by using an ultrasound cleaner. A platinum sheet (2.8 cm^2) was used as a counter electrode, and the reference electrode was a saturated calomel electrode. All potentials are reported with reference to the saturated calomel electrode through a Luggin capillary. The cathode potential was scanned in the potential range from −0.4 V to −2.0 V at a rate of 10 mV/s.

2.4. FT-IR spectral acquisition

FT-IR tests were performed to investigate the effect of molecular structure of NaOL on manganese electrodeposition. NaOL and its residual product usually float on the suspension surface, due to their insolubility in hot water and lower density. After Mn deposition, the catholyte was heated and filtered, then distilled and concentrated to remove water. The liquid samples obtained after manganese electrodeposition were characterized by FT-IR. FT-IR spectra of samples were acquired in the infra-red region (400–4000 cm^{-1}) using an ABB MB3000 FT-IR spectrophotometer (Clairet Scientific, Northampton, UK). The spectrophotometer is equipped with a deuterated triglycine sulfate detector and KBr as the beam splitter. The absorbance values of all FT-IR spectra were recorded at each data point in triplicate.

3. Results and discussion

3.1. Manganese electrodeposition analysis

3.1.1. Effect of NaOL concentration on cathode current efficiency

To investigate the effect of NaOL on cathode current efficiency, NaOL concentration was varied from 0 mol/L and 6.9×10^{-5} mol/L under the optimized conditions: 0.55 mol/L Mn^{2+}, 0.91 mol/L $(NH_4)_2SO_4$, 3.6×10^{-4} mol/L SeO_2, pH 7.0, cathode current density of 4×10^{-2} A/cm^2, electrodeposition temperature and time of 30 °C and 60 min. The results are plotted in Fig. 1. As illustrated in Fig. 1, current efficiency increases significantly from 76.3% to 85.6% when NaOL in the catholyte increases from 0 mol/L to 3.0×10^{-5} mol/L, and current efficiency remains nearly unchanged when NaOL increases from 3.0×10^{-5} mol/L to 4.0×10^{-5} mol/L. The current efficiency decreases slightly when NaOL exceeds 4.0×10^{-5} mol/L. The current efficiency is influenced by two competitive reactions, H^+ reduction and manganese deposition, taking place on the cathode surface. NaOL, an anionic surfactant, has a polar group that can adsorb onto the electrode surface and a non-polar group that can be oriented toward the electrode surface, thus forming a hydrophobic surface that has a tendency to hinder cations from transferring and obtaining electrons from the electrode interface. The increase of current efficiency may be attributed to the inhibition of the hydrogen evolution reaction on the electrode surface. Moreover, the adsorption of oleate anions on the cathode surface can improve the cathode polarization, which facilitates the formation of manganese

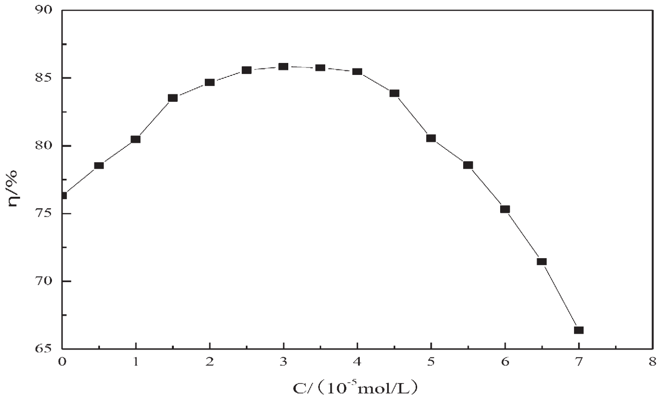

Fig. 1. Effect of NaOL concentration on cathode current efficiency (0.55 mol/L Mn^{2+}, 0.91 mol/L $(NH_4)_2SO_4$, 3.6×10^{-4} mol/L SeO_2, pH 7.0, 4×10^{-2} A/cm^2, 30 °C and 60 min).

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