



## Effect of sodium alkyl sulfates on electrodeposition of manganese metal from sulfate solutions in the presence of sodium metabisulphite



Subrat Kumar Padhy<sup>a,b</sup>, Bankim Ch. Tripathy<sup>a,b,\*</sup>, Akram Alfantazi<sup>c</sup>

<sup>a</sup> CSIR - Institute of Minerals and Materials Technology, Council of Scientific and Industrial Research, Bhubaneswar 751013, India

<sup>b</sup> Academy of Scientific and Innovative Research (AcSIR), Institute of Minerals and Materials Technology, Bhubaneswar 751013, India

<sup>c</sup> Department of Chemical Engineering, Khalifa University of Science and Technology (The Petroleum Institute), Abu Dhabi, United Arab Emirates

### ARTICLE INFO

#### Keywords:

Manganese  
Sodium alkyl sulfates  
Current efficiency  
Deposit morphology  
Polarization

### ABSTRACT

Electrodeposition of manganese in the presence of selenium compounds results in high current yield. However, selenium compounds are environmentally toxic and hence their use in manganese electrodeposition should be controlled. The main objective of the present study was to avoid the use of selenium compounds during electrodeposition of manganese without compromising with quality and current yield. Thus in the present study electrolytic manganese metal (EMM) has been produced from aqueous manganese(II) sulfate solutions in the presence of sodium alkyl sulfates (SAS) as organic additives. The alkyl sulfates used in the present study are sodium octyl sulfate (SOS), sodium lauryl sulfate (SLS) and sodium tetradecyl sulfate (STS). It was found that addition of SOS at a concentration of  $20 \text{ mg}\cdot\text{L}^{-1}$  was most effective in increasing the cathodic current efficiency from 59% to 67% and in presence of  $10 \text{ mg}\cdot\text{L}^{-1}$  SLS 63.5% cathodic efficiency was obtained. Further in presence of these additives bright and smooth manganese deposits were resulted. It was also observed that increase in alkyl chain length in the additives used in this work affected the deposit morphology and current yield adversely, however in all the cases  $\alpha$ -manganese with (330, 411) as the most preferred plane of orientations were produced. Polarization of cathode takes place in presence of all the organic anionic additives used in the current study and the degree of polarization increases with increase in concentration and chain length of additives.

### 1. Introduction

Manganese metal finds its major application as an alloying element out of which a major portion (~90%) is used for steel preparation. Manganese in steel acts as sulfur fixing agent and increase the strength of steel, improve workability and resistance to wear (Corathers, 2010). Hence the world demand of manganese is directly related to steel industry (Olsen et al., 2007). The electrodeposition of metallic manganese is very difficult due to high reduction potential of manganese(II) ion in aqueous solution ( $E/E^0 = 1.18 \text{ V}$ ). The electrolyte must be highly pure in addition to other operating conditions to have manganese metal through electrolytic path way. Among the two major possible routes (chloride and sulfate media) available for manganese electrodeposition, sulfate medium is the best as compared to chloride medium due to negative impact provided by it (Jacobs and Churchward, 1948; Ilea et al., 1997; Oaks and Bradt, 1936; Bradt and Oaks, 1937; Díaz-Arista et al., 2006). However, recently Cao et al. (2017) studied the recovery of manganese metal by purification and electrorefining method from chloride medium. They reported that increasing deposition time, higher current density and cathode usage frequency resulted in deterioration

of surface quality with reduced current efficiency and increased energy consumption values. Ammonium salt (chloride/sulfate) is added to the manganese solution as an electrolyte mixture prior to electrodeposition. The beneficial effect of ammonium salts in the solution include prevents precipitation of manganese as manganese hydroxide, acts as a buffer, improves manganese ion discharge ability (Gong and Zangari, 2002), and conductivity of the solution (Oaks and Bradt, 1936; Bradt and Oaks, 1937). The available technology for manganese electrodeposition is use of sulfur, selenium or its compounds to increase cathodic current efficiency (Murti et al., 1986; Radhakrishnamurthy and Reddy, 1977; Ilea et al., 1997; Xu et al., 2015). However, introduction of compounds of selenium to the electrolyte reduces the purity of the deposited metal (Selenium free, 2014) by mean of co-deposition and forms manganese selenide at cathode (Fan et al., 2012). Similar thing is also reported by Cao et al. (2017) that the manganese deposits get more impure with increasing concentration of impurities in the catholyte. Increase in selenium concentration of bath is associated with increase in selenium level in the deposit (Lewis et al., 1976). The selenium compounds impart toxic effect on the workers, damage the work place and environment which is an issue at the present days and hence effluents have to

\* Corresponding author at: CSIR - Institute of Minerals and Materials Technology, Council of Scientific and Industrial Research, Bhubaneswar 751013, India.  
E-mail address: [bankimtripathy@gmail.com](mailto:bankimtripathy@gmail.com) (B.C. Tripathy).

be treated in a controlled manner (Vinceti et al., 2001; Aboutalebi et al., 2004; Lemly, 2004; Hagelstein, 2009; Duan et al., 2011). China is the largest producer, consumer and exporter of electrolytic manganese metal (EMM) in the world since 2000. The rapid increase in EMM output in China has caused severe environmental pollution due to the use of selenium compounds to produce EMM (Duan et al., 2011). According to them modifications in the conventional production processes should be changed for cleaner production of manganese metal. Processes waste water of manganese industry contains  $Mn^{2+}$ ,  $Cr(VI)$ ,  $Cr^{3+}$ , and  $NH_4^+$  That can be transferred to leaching section after removal of  $Cr(VI)$  to recover useful chemicals like  $Mn^{2+}$ ,  $NH_4^+$  and to save environment as well as operating cost can be lowered (Xu et al., 2014).

Researchers are trying to find out an alternative to selenium in this regard. Use of Thiourea as an additive results 60–68% current efficiency over a period of 24 h in manganese metal deposition from sulfate bath containing ammonium sulfate as an electrolyte mixture (Hammerquist and Tenn, 1951). On the other hand, attempt made with  $Te(VI)$  didn't impart any positive effect and a maximum current efficiency of 34.1–37.7% was obtained in manganese electro-reduction process at room temperature (Galvanaukaite et al., 2011). Griškonis et al. (2014) studied the effect of  $Te(VI)$  at higher temperature. With increasing bath temperature the incorporation of  $Te$  into the deposited manganese metal increases from 0.9 to 1.6% from an electrolytic bath containing 2.20 mM  $Te(VI)$ . When the temperature of bath increased from 20 to 80 °C, the current efficiency also increased from 37 to 71%. They also reported that with increasing temperature, the manganese metal phase changes from mix  $\alpha$ -Mn &  $\beta$ -Mn to brittle  $\alpha$ -Mn and then to very hard  $\beta$ -Mn form. Electrodeposition of metallic manganese onto H-terminated Si(100) by linear sweep voltammetry at a positive potential, provide a cost-effective method to prepare metallic Mn films on a Si substrate from a solution of 10 mM  $MnCl_2$  and 2 M  $NH_4Cl$ . However the deposit consists of other subsidiary compounds of manganese–silicon and manganese–oxygen that will not meet the requirements made by pure brittle  $\alpha$ -Mn (Zhao et al., 2007).

Additives/surfactants are surface active agents or wetting agents that reduce surface tension in water. These are used in electrodeposition process with an aim to increase cathodic efficiency, brightening of the deposit, reduction in grain size as well as tree formation, promoting leveling of the deposit, reducing stress, power consumption and pitting, modification of crystallographic orientations by adsorption to the electrode surface (Oniciu and Muresan, 1991). The sodium alkyl sulfates containing eight or more than eight number of carbon atoms are used as anionic surfactants (Schwartz and Perry, 1963; Tripathy et al., 1997). In this concern SOS is the first member of the series and its effect on manganese electrodeposition has been studied (Padhy et al. (2016a)). SLS is one of the anionic surfactant of this series widely used as an additive during electrodeposition of different metals. These even at a very low concentration are able to modify the crystal growth, increase the brightness of deposit, current efficiency and produces smooth deposits. These also have a tendency to reduce acid mist during the electrolysis process as they form froth on the surface of the electrolyte (Mohanty et al., 2009; Tripathy et al., 1997).

In our previous work we studied about the effect of presence of sodium octyl sulfate (SOS) in electrolyte during the reduction of manganese(II) ion from sulfate electrolyte. It was found that the presence of SOS resulted in increasing in current efficiency without selenium in the bath. Sodium lauryl sulfate (SLS) used as an additive in the electrodeposition process of metals like Ni (Mohanty et al., 2009, LU Jing et al., 2010), Zn (Tripathy et al., 2003) and produced better result, but not used in metallic manganese electrodeposition. In the present study the effect of sodium lauryl sulfate (SLS) and sodium tetra decyl sulfate (STS) on current efficiency (CE), energy consumption (EC), surface morphology, crystallographic orientation and polarization behavior of cathode were studied and compared to those obtained in presence of sodium octyl sulfate (SOS).

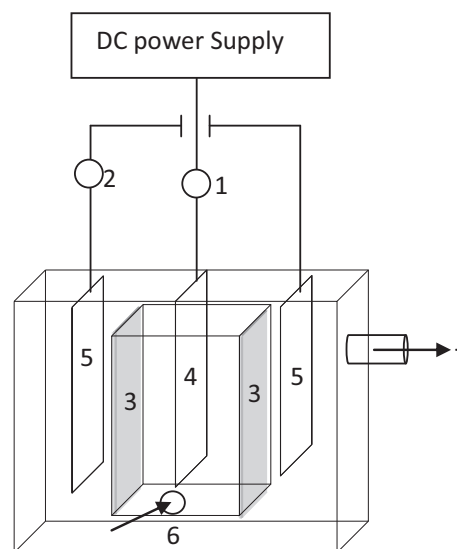


Fig. 1. Schematic diagram of the manganese electrodeposition cell. 1. Ammeter 2. Voltmeter 3. Polypropylene diaphragm 4. Cathode 5. Anode 6. Catholyte inlet 7. Spent electrolyte outlet.

Padhy et al., 2016b.

### 1.1. Experimental details

The manganese electrodeposition cell was made up of perspex sheet with distinct cathodic and anodic chambers separated by means of a polypropylene diaphragm. The inlet and outlet ports are associated with cathodic and anodic chambers respectively for the flow of feed and spent electrolyte using a peristaltic pump. Temperature of the electrolyte is controlled by using a thermostatic water bath [Julabo, Germany]. A single cathode (Stainless steel 316 grade) placed in between two anodes (Pb–Ag (1%)) for the electrolysis and was kept at a distance of 2.5 cm apart from each other. Direct current was supplied from a rectifier [Aplab, India] to carry out the electrolysis. A schematic diagram of the manganese electrodeposition cell is provided in Fig. 1 (Padhy et al. (2016b)).

The manganese electrolytes solution was prepared by using analytical reagent grade Manganese sulfate, ( $MnSO_4 \cdot H_2O$ ) Ammonium sulfate ( $(NH_4)_2SO_4$ ) and sodium meta-bisulfite ( $Na_2S_2O_5$ ) in doubly distilled water. Aqueous solution of ammonia and sulfuric acid were used to correct the pH of the electrolyte. The additives (SLS and STS) were added to the electrolyte when manganese electrodeposition was carried out. All the chemicals used were from Merck chem. Ltd. India.

The surface of cathode was activated prior to the electrolysis while no specific treatment was carried out for the anodes. The cathode was first polished with 400 and 1200 grade silicon carbide paper to mirror finish followed by washing with de-ionized water and then dipped in dilute  $HNO_3$  10% (v/v) for 30 min followed by washing with water. Then these cathodes were treated with sodium silicate and allowed to air dry. The weight of cathode was taken prior to electrodeposition.

The concentration of manganese(II) ion in the feed solution and catholyte used for electrodeposition is  $30 \text{ g} \cdot \text{L}^{-1}$  and  $12 \text{ g} \cdot \text{L}^{-1}$  respectively with  $120 \text{ g} \cdot \text{L}^{-1}$   $(NH_4)_2SO_4$  and  $0.475 \text{ g} \cdot \text{L}^{-1}$   $Na_2S_2O_5$ . The concentration of manganese(II) ion in the solution was analyzed volumetrically and impurities present in very trace amount were analyzed by AAS (Perkin Elmer, Model No. AA200). Required amount of SAS additive was added to the catholyte and feed solution prior to their electrolysis. Electrodeposition of manganese metal was carried out at a current density of  $500 \text{ A} \cdot \text{m}^{-2}$  and temperature of the catholyte was maintained at  $40 \pm 1$  °C. The pH of catholyte and feed solution was maintained at 7 and 3 respectively. Cell voltage during electrolysis was recorded at an interval of 30 min and mean cell voltage was taken to calculate the energy consumption. The plating rate is kept at

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