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Review

Manganese electrodeposition — A literature review

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ABSTRACT

Electrolytic manganese metal has been used in a wide range of applications such as production of steel and aluminum alloys. However, manganese electrowinning is technically and commercially challenging due to a low current efficiency and high cell voltage. Rigorous purification and the use of additives are required for commercial manganese electrowinning. Some effective additives, such as selenium compounds, contaminate the metal and have negative environmental impacts. This literature review summarizes the background information on hydrogen evolution on manganese, manganese electrodeposition and its polarization behavior, effects of impurities, and the effects of additives such as selenium compounds, and their mechanisms in order to provide guidelines for development of cleaner and more efficient manganese electrodeposition conditions.

Electrolytic manganese is conventionally produced from ammonium sulfate media in a diaphragm cell. Hydrogen evolution on manganese in Mn-free electrolyte is very slow compared to manganese deposition. However, it is catalyzed by manganese deposition. With increasing polarization, the manganese deposit structure changes from γ-Mn to α-Mn. Heavy metal impurities (e.g. Ni and Co) are co-deposited with manganese and catalyze the dissolution of manganese and then hydrogen evolution through the formation of galvanic micro-cells, resulting in a low manganese current efficiency. With increasing deposition time, the manganese deposit gradually becomes rougher and more dendritic, resulting in an increase in the rate of manganese dissolution. Smooth and compact deposition reduces the harmful effect of impurities and increases manganese current efficiency. Various additives (typically sulfite and selenite) have been used to counteract the harmful effects of impurities and improve manganese deposit quality. The addition of selenite (or selenate) and sulfite inhibits hydrogen evolution, increases the overpotential of manganese deposition in the low polarization region and decreases the overpotential of manganese deposition in the high polarization region, facilitates the crystallization of stable α-manganese, improves the leveling effects of the electrolyte, and finally increases the manganese current efficiency. The formation of insoluble selenides and sulfides with impurities eliminates or suppresses the generation of galvanic micro-cells and then contributes to an increase in the current efficiency of manganese deposition. Alternative additives should inhibit hydrogen evolution significantly, but manganese deposition to an appropriate degree, promote the formation of α-Mn, function as a leveling agent, have a minimum contamination of the manganese deposit and reducing capacity to stabilize the electrolyte.

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1. Introduction

Manganese is an important industrial metal used as an additive for production of various steels, non-ferrous alloys, electronic components and special chemicals. The manganese ore use is as follows: 38% for silicomanganese, 38% for carbon ferromanganese, 13% for slag, 8% for other alloys, 9% of electrolytic manganese and 2% for electrolytic manganese dioxide (Virga et al., 2013). Electrolytic manganese is mainly used for production of stainless steel, nonferrous alloys, electronics and specialty chemicals. The annual electrolytic manganese production increased from 180,000 to 1,700,000 t between 2000 and 2012 mainly due to the rapid growth in the Chinese electrolytic manganese capacity tied to their robust demand. It is forecasted that the annual demand for electrolytic manganese may grow by 83% from 2012 to 2021 (Virga et al., 2013). The development of technology for electrolytic manganese production has consistently sought more cost effective performance.

The standard reduction potential for Mn^{2+}/Mn is −1.18 V vs. SHE. Manganese is the least noble metal that can be electrodeposited from aqueous solutions on a technical scale. Manganese electrodeposition from ammonium sulfate and chloride media has been most well studied. Electrolytic manganese is conventionally produced from ammonium sulfate media due to some limitations of chloride media such as the removal of chlorine from the anolyte and consumption of ammonia. Chloride systems have several advantages such as a lower energy consumption resulting from a lower cell voltage and a higher current efficiency, the ability to operate at a higher current density and the higher solubility of metals in the process solutions.

The current efficiency, deposit morphology and the crystal structure of the electro-deposited manganese are influenced by the impurities in the electrolyte, the current density and temperature. In carefully prepared and purified solution, coarse grained γ-manganese was deposited with a current efficiency of over 90% (Gamali and Stender, 1962a; Znamenskii et al., 1961). However the presence of heavy metal impurities significantly decreases the manganese deposition current efficiency. Manganese, together with many impurities, is usually leached into aqueous solution from manganese ore. These impurities must be removed before electrowinning. Aluminum and iron can be removed by hydroxide precipitation through neutralization to pH ~ 6.5. Molybdenum, arsenic and silica are removed by co-precipitation. Copper, zinc, nickel and cobalt are removed by addition of ammonium sulfide. However, the current efficiency of manganese deposition from such purified leaching solution is very low and the quality of manganese deposit is poor. This indicates that trace amounts of impurities affect the manganese deposition process. Further purification of manganese electrolyte is very expensive. Appropriate additives have to be used in the industrial production of electrolytic manganese to counteract harmful effects of impurities.

Even without any impurity in solution, additives such as sulfite are required to improve the quality of manganese deposits. As manganese is electrodeposited, manganese deposits gradually become rougher, and nodules grow up and outward, forming cauliflower-like dendritic structures or even “trees”, resulting in trapping of electrolyte in electrolytic manganese, difficulty stripping of manganese deposits from cathodes, and even difficulty in removing cathodes from cells. In addition, nodules tend to be broken off and lost during handling, thus decreasing metal recovery. As manganese deposits become more dendritic, the local real current density deviates more from the ideal current density that corresponds to the maximum manganese current efficiency. In extreme cases, manganese re-dissolves in some local areas due to the loss of cathodic protection. Therefore the manganese current efficiency decreases with increasing deposition time. To limit these effects a shorter plating cycle of manganese is used in comparison to copper, cobalt, zinc and nickel. This requires frequently harvesting of cathodes and a large circulating inventory of cathodes in the stripping and preparation processes. In addition, the catholyte pH is generally maintained at 7 and above by operating with a diaphragm cell. Mn(II) is gradually oxidized by oxygen from air to form MnOOH, affecting manganese deposition and even plugging the porous diaphragm. Some additives have to be used to level manganese deposits and stabilize the catholyte. The use of additives is the key to produce dense high-quality manganese metal at a high current efficiency.

Allmand and Campbell (1924a, 1924b) produced electrolytic manganese from ammonium media in a divided cell in the early 1920s. However, the commercial production of electrolytic manganese from ammonium sulfate systems in a diaphragm cell began in the late 1930s after some additives were used (Dean, 1952).

The addition of a certain amount of S, Se and Te compounds into the electrolyte can significantly improve manganese electrodeposition (Jacobs and Churchward, 1948; Polukarov and Shulgina, 1969; Shulgina and Polukarov, 1966a). SeO_3^{2-} is the most effective among these additives. The manganese deposition current efficiency can reach as high as 96% in the presence of SeO_3^{2-} (Polukarov and Shulgina, 1969; Shulgina and Polukarov, 1966a). However the addition of these additives (especially SeO_3^{2-}) results in the contamination of manganese and may lead to environmental issues at the plant and the product use sites. An alternative additive is needed to improve manganese deposition without contamination of manganese product.

The objective of this review was to collect and analyze the information regarding manganese electrodeposition, the effects of additives and how these improve the manganese current efficiency in order to provide background information for the development of new additives. The review focuses on the fundamental aspects of hydrogen evolution, manganese electrodeposition and the effects of additives in manganese electrowinning.

2. Manganese electrowinning from sulfate media

2.1. Operation conditions

Manganese electrowinning has to be conducted in a diaphragm cell so that manganese can be electrodeposited from the catholyte. The operation conditions vary for different manganese electrowinning processes. For example, with the use of SeO_3^{2-}, the cell operates in the pH range of 7.0–7.5 and high manganese concentrations can be used (Rao et al., 1966) while with the use of SO_2, the pH is generally above 8.0 and with lower manganese concentrations. The effects of the operation conditions (the catholyte composition, current density, temperature and pH) on the manganese electrodeposition from sulfate media with SO_2 have been discussed by Jacob et al. (1946), Louis and Martin (1976) and Araujo et al. (2006). The manganese concentration significantly affects manganese electrodeposition and its optimum value is determined by the other operation conditions. The typical optimum catholyte manganese concentration is around 12 g/L (Araujo et al., 2006; Harris et al., 1977; Jacobs et al., 1946). A lower manganese concentration results in a lower current efficiency. A higher manganese