Study on the Growth Law of Manganese in Electrolysis Process of MnSO$_4$ Solution Containing Magnesium

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Abstract. At present, there was no good industrial removal method for soluble impurity Mg$^{2+}$ in electrolytic manganese industrial production, so MgSO$_4$-MnSO$_4$-(NH$_4$)$_2$SO$_4$ compound salt crystal with minimal solubility was formed by cyclic enrichment in solution. On the one hand, it caused the loss of manganese, ammonium and other main components, on the other hand, a large amount of storage caused environmental pollution. In order to find out the harmful effect of magnesium on the production of manganese in an all-round way, this paper studied the growth and deposition of manganese when the concentration of Mg$^{2+}$ was 25g/L. The results showed that with the increase of electrolysis time, the grain size increases from 42.11μm for 2h to 185.71 μm for 10h, and the current efficiency gradually decreased from 73.3% for 2h to 67.26% for 10h. After 8 hours of electrolysis, the growth rate of grain size and the decrease rate of current efficiency were improved, and there were a certain relationship between them.

Keywords: Mg$^{2+}$, Electrolytic manganese, Electrolytic time, Grain growth, Current efficiency

1. Introduction

As an important basic industrial raw material with large demand, manganese was not only used in the smelting and processing of iron and steel [1], but also widely used in electronic materials, medicine, agriculture and animal husbandry departments [2-5]. China was the most important producer, consumer and exporter of manganese in the world [6-7]. At present, electrolysis had become the main choice in manganese production industry [8,9]. Due to the sulfuric acid leaching process of manganese ore [10], in addition to Mn$^{2+}$, many soluble impurity ions also enter the leaching solution [11]. Mg$^{2+}$ was very active, and there was no effective method to remove it. Therefore, a large amount of Mg$^{2+}$ remained in the leaching solution and electrolyte, and it accumulated continuously. It was as high as 25-30g/L in manganese production system, even reaching saturation [12]. Most of them would form MgSO$_4$-MnSO$_4$-(NH$_4$)$_2$SO$_4$ compound salt crystals with minimal solubility, which on the one hand caused the loss of main components such as manganese and ammonium [13], on the other hand, it caused the blockage of production pipeline, and brought many negative effects on the production process [14]. The output of these compound salt crystals was relatively large. An electrolytic manganese enterprise had an annual output of about 350000 tons. A large number of excavators were needed for regular cleaning in production. The composition of each electrolytic manganese enterprise was not consistent, and the comprehensive utilization rate was low. At present, it could only be stacked,
which not only occupied a lot of land, but also caused great pollution to the environment, which had seriously restricted the development of electrolytic manganese industry in China. The author’s team had studied the equilibrium distribution of Mg\(^{2+}\) in the electrolytic manganese production process [14], and its influence on the physical and chemical properties of electrolyte [15]. On the basis of the above research, this paper would study the growth law of metal manganese electrolysis process when Mg\(^{2+}\) was 25g/L, so as to provide theoretical guidance for its green production.

2. Experiment

2.1. Preparation of Experimental Reagent and Solution

The electrolyte used in this experiment was made by dissolving the manganese sheet in sulfuric acid, adding a certain amount of ammonium sulfate, magnesium sulfate, ammonia water and selenium dioxide after removing impurities. Finally, the qualified electrolyte with Mn\(^{2+}\) concentration of 20g/L, Mg\(^{2+}\) concentration of 25g/L, (NH\(_4\))\(_2\)SO\(_4\) of 100g/L, SeO\(_2\) concentration of 0.04g/l and pH value of 7.2 were obtained.

2.2. Process and Principle of Manganese Electrolysis

The experiment was carried out by diaphragm electrolysis [16]. The electrolysis system was composed of a self-made plexiglass double chamber electrolyzer, a fiber membrane bag separating the positive and negative poles, a 304 stainless steel cathode plate and a Pb-Ag alloy anode plate. The electrolysis temperature was kept constant at 40 (±1)\(^\circ\)C by water bath heating. The constant current in manganese deposition was controlled by DC power supply, and the current density was 450A/m\(^2\). The siphon was used to supply electrolyte continuously to the electrolysis system, and the Mg\(^{2+}\) concentration was controlled to 25g/L. The effects of electrolysis time of 2h, 4h, 6h, 8h and 10h on the growth and deposition of manganese were studied. At the end of the electrolysis experiment, the cathode plate was taken out and put into 3% potassium dichromate for passivation treatment for 2 minutes, then was washed with distilled water and dried. The weight of cathode plate before and after electrodeposition was weighed to calculate the mass of manganese. The electrolytic reaction formula was as follows.

Cathodic reaction:

\[
\text{Mn}^{2+} + 2e^- = \text{Mn}, \quad \varphi^0(\text{Mn}^{2+} / \text{Mn}) = -1.18\text{V} \quad (1)
\]

\[
2\text{H}_2\text{O} + 2e^- = \text{H}_2\uparrow + 2\text{OH}^-, \quad \varphi^0(\text{H}^+ / \text{H}_2) = 0\text{V} \quad (2)
\]

Anodic reaction:

\[
2\text{H}_2\text{O} - 4e^- = \text{O}_2\uparrow + 4\text{H}^+, \quad \varphi^0 = 1.229\text{V} \quad (3)
\]

\[
\text{Mn}^{2+} + 2\text{H}_2\text{O} - 2e^- = \text{MnO}_2 + 4\text{H}^+, \quad \varphi^0 = 1.228\text{V} \quad (4)
\]

2.3. Calculation and Characterization

The cell voltage was collected in real time during electrolysis. The weight of cathode plate before and after electrodeposition was weighed to calculate the mass of manganese, and the current efficiency calculation formula was as follows [17],

\[
\eta = \frac{\text{The actual quality of the product on the electrode}}{\text{Theoretical quality calculated by Faraday 's Law} \times 100\%} = \frac{\Delta m}{Clt} \times 100\% \quad (5)
\]

Where, \(\eta\): current efficiency, %

\(\Delta m\): Cathode manganese electrodeposition quality, g

\(C\): The electrochemical equivalent of manganese, 1.025(g·A\(^{-1}\)·h\(^{-1}\))

\(I\): Current intensity, A

\(t\): electrolysis time, h

The manganese plate on the cathode plate was stripped and analyzed by SEM, and the
microstructure was analyzed by scanning electron microscope su8020 of Hitachi Company. The grain size was obtained by averaging 10-15 grain sizes on the electron microscope photos.

3. Results and Discussion

3.1. Current Efficiency and Cell Voltage
When the electrodeposition time was 2h, 4h, 6h, 8h, 10h, the current efficiency and cell voltage of manganese electrodeposition were shown in figure 1.

![Figure 1](image)

**Figure 1.** Variation curve of current efficiency and cell voltage.

It could be seen from figure 1 that the electrodeposition time had a great influence on the current efficiency and had a negative correlation, which was consistent with the literature report [17]. During the electrolysis process, the cell voltage fluctuated to a certain extent, but it was relatively stable, with the range of 4.03-4.09 v. In the early stage of electrodeposition, the current efficiency decreased from 73.3% to 72.42% when the electrolysis time increased from 2h to 4h. The current efficiency decreased to 71.19% at 6h in the middle stage of electrodeposition. The current efficiency decreased to 69.51% when the electrodeposition time was extended to 8h. The current efficiency decreased to 67.26% after 10 h electrolysis. It could be seen that the current efficiency decreased faster and faster with the prolongation of electrodeposition time. This was due to the high concentration of Mg$^{2+}$ in the electrolyte, which made the overall ion concentration in the solution higher. With the prolongation of electrodeposition time, Mg$^{2+}$ continuously formed MgSO$_4$-MnSO$_4$-(NH$_4$)$_2$SO$_4$ compound salt crystal with minimal solubility. They precipitated from the solution, not only caused the loss of manganese, ammonium and other effective components, but also blocked the transmission pipeline, which made the electrolyte diffusion and circulation not smooth, and reduced the current efficiency of manganese electrolysis and increases the production cost.

3.2. Growth and Deposition of Electrolytic Manganese
The effects of electrolysis time of 2 h, 4 h, 6 h, 8 h and 10 h on the micro morphology and grain growth of manganese electrodeposition were investigated. The change rules were shown in figure 2 and figure 3.
Figure 2. SEM picture of cathode manganese after different electrolysis time.

Figure 3. Relationship between current efficiency and grain size.

It could be seen from figure 2 and figure 3 that the current efficiency of manganese electrolysis decreased with the prolongation of electrodeposition time, and there was a certain relationship between the current efficiency and the growth size of cathode manganese grains. According to the scanning electron microscope observation of cathode manganese at different electrolysis time, the growth of metal manganese conformed to the mechanism of screw dislocation [18]. During electrolysis, manganese ions nucleated and grew on the cathode plate and covered the whole cathode plate. With the increase of electrolysis time, manganese ions grew further on the basis of the previous stage. From the micro morphology, the structure of the cathode manganese sheet was relatively dense, and the grains existed in the form of polygonal particles with similar size, and the average grain size was 42.11 μm. When the electrolysis time was prolonged to 4 h, the hierarchical and regular ladder stripes were observed on the surface of the particles. The average grain size increased by 35.68 μm to
77.79 μm, and the current efficiency was reduced by 0.88%. When the electrolysis time was prolonged to 6 h, a pyramid top was observed on the surface of the particles [19]. The average grain size increased by 29.41 μm to 107.2 μm, and the current efficiency decreased by 1.23%. When the electrolysis time was prolonged to 8 h, the ladder like stripes on the surface of the particles increased and became more obvious, but they were gradually irregular compared with the previous stripes and pyramid top. The average grain size of the grains increased by 28.05 μm to 135.25 μm, and the current efficiency decreased by 1.68%. When the electrolysis time reached 10 h, the manganese grains continued to grow on the basis of the previous stage, and were still growing layer by layer in general [20]. The average grain size increased by 50.46 μm to 185.71 μm, and the current efficiency decreased by 2.25%. In conclusion, in the early and middle stage of electrolysis, the grain growth rate decreased slightly and the current efficiency decreased rate increased. In the later stage of electrolysis, the current efficiency decrease rate increased with the rapid increase of grain growth rate. This was because in the early and middle stage of electrolysis, the growth rate of manganese was limited, the cathode surface changed little, and the current density fluctuated little with experimental design, which made the current efficiency decrease slowly. With the prolongation of electrolysis time, manganese grains continued to grow on the basis of the previous stage, which made the density of manganese deposition decreased, the flatness of cathode surface was worse, and the cathode area increased, which indirectly reduced the cathode current density. Too low cathode current density would reduce the current efficiency [21], so the rapid growth of grains led to the rapid decrease of current efficiency.

4. Conclusion
The growth law of manganese in the electrolysis process of manganese sulfate solution containing magnesium was studied. With the increase of electrolysis time, the current efficiency decreased gradually, which was 73.3% at 2h and 67.26% at 10h. The fluctuation of cell voltage was small, and the range was 4.03v-4.09 v. With the prolongation of electrolysis time, the grain size of cathode manganese increased from 42.11 μm of 2h to 185.71 μm of 10h. There was a certain relationship between the efficiency of manganese electrodeposition and the grain size of cathode manganese. In the early and middle stage of electrolysis, the cathode manganese deposition was relatively dense, and the grains existed in the form of polygonal particles with similar size. The current efficiency decreased slowly with the slow growth of grain size. With the prolongation of electrolysis time to the later stage, the growth rule of cathode manganese was still lamellar layer by layer, and the current efficiency decreased rapidly with the rapid growth of grain size. Therefore, the existence of Mg²⁺ had a negative impact on the manganese electrolysis process. The research on adjusting the power supply system by optimizing the electrolysis conditions and reducing the environmental pollution caused by removing magnesium ions would be the focus of future research.

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