The effects of Mg$^{2+}$ concentration, (NH$_4$)$_2$SO$_4$ concentration and current density on electrolytic manganese process

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Abstract

In this paper, the effects of Mg$^{2+}$ concentration, (NH$_4$)$_2$SO$_4$ concentration and current density on the current efficiency, cell voltage and morphology of electrolytic manganese metal were studied. The current efficiency of electrolytic manganese decreased with the increase of Mg$^{2+}$ concentration in the electrolyte; Increasing the concentration of (NH$_4$)$_2$SO$_4$, the current efficiency of electrolytic manganese showed a gradually increasing trend. By changing the current density, the current efficiency of electrolytic manganese increased first and then decreased. When the current density was 400 A·m$^{-2}$, the current efficiency was the highest, it was about 66.63%. The cell voltage in the process of manganese electrolysis was independent of Mg$^{2+}$ concentration and (NH$_4$)$_2$SO$_4$ concentration, but only positively related to current density. Through the macroscopic analysis of the cathode plate, the greater the current efficiency was, the brighter the color of the metal manganese sheet was, it shew a silver white, and the dendritic growth of metal manganese was less. From the microscopic morphology of the manganese metal sheet, the electrolytic manganese metal was formed by stacking metal manganese sheets, each metal manganese sheet exhibited a regular hexagonal structure, the shape was similar to a ‘pyramid’, it had a better compactness, in which the better the current efficiency was, the better the compactness of the electrolytic manganese metal was. Under different experimental conditions, crystal plane (330,411) was strongest and best orientation for the growth of electrolytic manganese. Cyclic voltammetry experiments showed that Mg$^{2+}$ did not beneficial to electrodeposition of manganese, the increase of (NH$_4$)$_2$SO$_4$ was beneficial to improve the current efficiency, and it was consistent with the conclusion of electrolysis experiment.

1. Introduction

Manganese was of great significance in industrial production. It not only played an important role in improving performance as an important alloy material in non-ferrous metallurgy, but also it was a popular raw material in battery industry [1, 2]. In China, manganese sulfate solution was obtained by leaching manganese ore by sulfuric acid, and then electrolysis process was used to obtain manganese metal [3, 4]. However, during the leaching process of minerals, it was inevitable that many impurity ions will be introduced, iron ions and other heavy metal ions could be removed by hydrolysis precipitation and sulfidation [5, 6]. The the standard electrode potential of Mg was $-2.36$ V, it was smaller than $-1.158$ V of Mn$^{2+}$ [7, 8]. Mg$^{2+}$ did not participate in the electrode reaction, and its existence would not pose a threat to the purity of manganese metal. Therefore, research on magnesium ion in manganese sulfate solution was rarely reported.

In fact, with the extension of production time, magnesium would continue to enrich in solution and would caused a series of effects on the entire electrolytic system [9, 10]. Because the ion concentration was positively correlated with the viscosity of the leaching solution, it would reduce the H$^+$ mass transfer rate, the ore sample...
could not perform sufficient chemical reactions and reduce the leaching rate of manganese. During the leaching process, calcium and magnesium crystals may be generated to block the leaching tank [11–13]. The increase in density and viscosity led to decreasing in the mass transfer rate of ions in the electrolyte, which affected the current efficiency of manganese. As ammonium sulfate was an indispensable additive in electrolytic manganese, a large amount of ammonium magnesium double salt crystals were formed in the electrolyte to block the pipeline. According to the survey of Tianyuan manganese group in Ningxia, the amount of crystals generated in the electrolyte was about 50% of the amount of manganese metal, which must be cleaned daily with an excavator, and because of the difficulty of comprehensive utilization, a large number of crystals could only be stored in storage, occupying space and causing serious environmental pollution. A small amount of compound salt crystals would adhere to the surface of the generated metal manganese, affecting the quality of electrolytic manganese.

To the above-mentioned hazards of magnesium ions, some researchers had taken many ways to conduct magnesium removal research [14–16], other researchers found that magnesium ions affect the leaching process, density, conductivity, viscosity and surface tension of manganese sulfate solution, the author of this paper had studied the equilibrium distribution of magnesium ions in the electrolytic manganese system [10, 17], but there was very few studies on the effect of magnesium on electrolytic manganese. Otherwise, It was believed that current density and ammonium sulfate concentration were the main influencing factors in the industrial production process of manganese electrolysis [18]. Industrial production practice generally believed that increasing the cathode current density and ammonium sulfate concentration was beneficial to increase the current density. However, a series of theoretical researches are rarely carried out.

Based on the above problems, this article would study the electrolysis process of manganese in MgSO₄•(NH₄)₂SO₄•MnSO₄ system. The effects of Mg²⁺ concentration, (NH₄)₂SO₄ concentration and current density on the current efficiency, energy consumption, macrostructure and crystal growth direction of cathode manganese sheets were studied. This study would provide important theoretical guidance for the development of the electrolytic manganese industry.

2. Experimental details

2.1. Experimental instrument

The two-chamber electrolytic cell was used in the electrolytic manganese experiment, and it was made of plexiglass, its size was 150 mm × 100 mm × 110 mm, in which the cathode chamber and the anode chamber were separated by a diaphragm. The cathode and anode for electrolysis were respectively made of 316 stainless steel and lead–silver alloy (silver content of 1%), the effective size of cathode was 50 mm × 70 mm, and that of the anode was 30 mm × 70 mm because there were many holes in the anode plate, and the distance between the two electrode plates was 2.5 cm. The water bath pot (Changzhou, China) was used to keep the electrolytic temperature constant and DC power supply was used to control the current of electrolytic manganese process. The experimental device of electrolytic manganese was shown in figure 1.

2.2. Experimental raw materials

The manganese metal sheets used in the experiment were taken from Zunyi TianCi Electrolytic Manganese Plant in Guizhou Province of China. The experimental raw materials were manganese sheets, ammonium sulfate, magnesium sulfate and distilled water, in which distilled water was made by laboratory. The MnSO₄ electrolyte was prepared by solving the manganese sheets in sulphide acid, than it was purified by SDD (sodium dimethyl dithiocarbamate) to remove heavy metal impurities on the surface of manganese sheets. Finally, the pH of the electrolyte was adjusted to 7.2 by ammonia water.

Figure 1. The diagram of experimental device for electrolytic manganese Anode solution; 2-Anode plate; 3-Diaphragm; 4-Cathode plate; 5-Electrolyte; 6-DC power supply.
2.4. Experimental process

A certain amount of electrolytic manganese sheet was weighed and the heavy metal impurities on their surface were washed with dilute nitric acid. After being washed with distilled water, they were dissolved in sulfuric acid (1:1) to prepare MnSO$_4$ solution, it would be as the electrolyte and its volume was 40 l. The requirement of electrolyte for manganese metal electrolysis was very high, even the solution prepared by analytic reagent must be purified, otherwise the metal manganese could not be found in the cathode. Therefore, the removal of heavy metals was indispensable. From Table 1, the Fe and Cu could meet the electrolysis requirements in the MnSO$_4$ solution before purification, and it was necessary to remove the Co and Ni. The Co and Ni were removed from the electrolyte by SDD (65 °C, 1 h, the addition was three thousandths). SDD was one kind of vulcanizing agent, it was used to remove heavy metals, SDD was used as a high–molecular flocculant to neutralize surface charge and avoid dendritic crystals of electrolytic manganese products [19].

From Table 1, the heavy metal impurities Ni and Co in the solution could be removed well by using SDD, and the iron could be removed by the way and the removal rate was 45%, because the solubility of FeS was very low. The concentration of Mn$^{2+}$ in MnSO$_4$ solution was determined to be 37.2 g l$^{-1}$ by chemical titration of (NH$_4$)$_2$Fe(SO$_4$)$_2·6$H$_2$O. Each experiment required 2 l solution.

2.5. Analysis and calculating

During the electrolysis, the cell voltage was collected. After electrolysis for 12 h, the cathode plate was removed from the electrolytic cell and passivated by potassium dichromate solution.

2.3. Solution preparation and purification

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### Table 1. Impurity concentration in electrolyte.

| Element | Before purification ($\mu$g/ml) | After purification ($\mu$g/ml) | Standard content ($\mu$g/ml) |
|---------|--------------------------------|-----------------------------|----------------------------|
| Co      | 11.81                          | 0.11                        | 0.5                        |
| Ni      | 32.35                          | 0.67                        | 1                          |
| Cu      | 3.36                           | 2.98                        | 5                          |
| Fe      | 1.63                           | 0.89                        | 15–20                      |

2.4. Experimental process

1. A certain amount of MgSO$_4$ and (NH$_4$)$_2$SO$_4$ were added to the prepared MnSO$_4$ solution and diluted to 4 l, in order to improve the current efficiency of manganese, a small amount of SeO$_2$ (0.04 g l$^{-1}$) was added, SeO$_2$ was a key additive in industrial EM processes, although many types of new additives had been reported [20, 21], and the pH of the electrolyte was adjusted to 7.2 with ammonia water.

2. During the electrolysis process, the temperature of the electrolytic cell was controlled at 45 °C and the current density was 400 A m$^{-2}$. In the industrial production process of electrolytic manganese, the concentration of Mg$^{2+}$ in the electrolytic cell was about 20 ~ 25 g l$^{-1}$. The effects of Mg$^{2+}$ concentration (15 g l$^{-1}$, 20 g l$^{-1}$, 25 g l$^{-1}$, 30 g l$^{-1}$, 35 g l$^{-1}$) and (NH$_4$)$_2$SO$_4$ concentration (80 g l$^{-1}$, 90 g l$^{-1}$, 100 g l$^{-1}$, 110 g l$^{-1}$, 120 g l$^{-1}$) on the electrolytic manganese process were studied.

3. When the effect of Mg$^{2+}$ concentration and (NH$_4$)$_2$SO$_4$ concentration had been completed, the effect of current density on the electrolytic manganese process would be studied, and the current density of 300 A m$^{-2}$, 350 A m$^{-2}$, 400 A m$^{-2}$, 450 A m$^{-2}$, 500 A m$^{-2}$ would be considered.

4. During the electrolysis, the cell voltage was collected. After electrolysis for 12 h, the cathode plate was removed from the electrolytic cell and passivated by potassium dichromate solution (3%). After washing, drying and weighing, the current efficiency and energy consumption of manganese electrolysis was calculated, the manganese sheet on the cathode plate was removed and analyzed by SEM, and the micro-morphology under different electrolysis conditions was obtained.

2.5. Analysis and calculating

X-ray diffraction (XRD) of electrolytic manganese was carried out by an x-ray powder diffract-meter (D8 ADVANCE; Bruker, Germany), and the microstructure of the electrolytic manganese was analyzed by a field emission scanning electron microscope (Hitachi, Japan). The current efficiency was calculated according the follows.

$$\eta = \frac{P_{\text{Actual}}}{P_{\text{Theoretical}}} \times 100\% \quad (1)$$

$$P_{\text{Theoretical}} = C \times I \times \varepsilon \quad (2)$$

Among the above formula,

*P*$_{\text{Actual}}$–Actual manganese production, g;
Theoretical manganese production, g;
\( \eta \) - Current efficiency, %;
C - Electrochemical equivalent of manganese metal, 
\[ C = 1.025 \text{ (g \cdot A}^{-1} \cdot \text{h}^{-1}) \];
I - Electrified current, A;
\( \varepsilon \) - Electrolytic time, h;

And the energy consumption was calculated according the follows.

\[ EC = E / (\eta \times C) \]  

\( EC \) - Energy consumption, kWh/kg;
\( \eta \) - Current efficiency, %;

Electrochemical equivalent of manganese metal, 
\[ C = 1.025 \text{ (g \cdot A}^{-1} \cdot \text{h}^{-1}) \]

The cyclic voltammetry curve was carried out by Shanghai Chenhua electrochemical workstation, and three electrodes system was adopted. The working electrode was made of 316 stainless steel with an area of 10 mm \( \times \) 10 mm. The counter electrode was platinum electrode with an area of 10 mm \( \times \) 10 mm. The reference electrode was mercury-mercurous sulfate electrode. In the cyclic voltammetry experiment (CV), the scanning potential range was set at \(-0.5 \sim -2.25 \text{ V}\), and the scanning speed was set at 2 mV s\(^{-1}\). The preparation of the solution and experimental conditions were the same as those in the electrolysis experiment, and the experimental temperature was 45 \(^{\circ}\)C.

3. Results and discussion

3.1. Effect of Mg\(^{2+}\) on electrolytic manganese process

When the \((\text{NH}_4)_2\text{SO}_4\) concentration was 110 g l\(^{-1}\), current density was 400 mA \( \cdot \) m\(^{-2}\), the effect of Mg\(^{2+}\) was studied. When the electrolysis lasted 12 h, the cathode plate was taken out from electrolytic cell, and put into the solution with potassium dichromate for passivation immediately, then they were washed, dried and weighted. The effect of Mg\(^{2+}\) concentration on current efficiency and cell voltage was shown in figure 2.

The results showed that the current efficiency was greatly affected by the Mg\(^{2+}\) concentration. With the increasing of Mg\(^{2+}\) concentration in the electrolyte, the current efficiency showed a gradual downward trend, and the cell voltage was relatively stabled at 4.612–4.776 V, energy consumption increased from 6.547 kW\( \cdot \)h kg\(^{-1}\) to 7.441 kW\( \cdot \)h kg\(^{-1}\). When the concentration of Mg\(^{2+}\) increased from 15 g l\(^{-1}\) to 25 g l\(^{-1}\), the current efficiency decreased sharply from 68.73% to 65.21%. Continue to increase the Mg\(^{2+}\) concentration in electrolyte to 35 g l\(^{-1}\), the current efficiency decreased slowly to 62.54%. This was because that with the increasing of the Mg\(^{2+}\) concentration in the electrolyte, Mg\(^{2+}\) formed complex salt crystals with NH\(_4\)\(^{+}\) and Mn\(^{2+}\) ions in the electrolytic cell easily, which caused the beneficial components of the electrolyte to be decreased. At the same time, the crystallization would also cause blockage of electrolyte transportation pipeline, and they were not conductive in the electrolyte. In addition, Mg\(^{2+}\) could also increased the viscosity of the electrolyte, increased the electrical resistance of electrolytic, which would cause the decreasing of the current efficiency.

From the formula (3), EC was proportional to cell voltage and inversely proportional to current efficiency, as
could be seen from figure 2, with the increase of Mg$^{2+}$ concentration, EC increased gradually. Therefore, the lower the concentration of magnesium ion was, the better the electrolysis would be.

The macroscopic photographs of the electrolytic manganese metal sheet produced under different Mg$^{2+}$ concentration conditions were recorded by a camera, and the results were shown in figure 3. It could be seen that when the Mg$^{2+}$ concentration in the electrolyte was low, the manganese metal sheet exhibited silvery white color and the compactness was better. With the increasing of Mg$^{2+}$ concentration in the electrolyte, the color of that darkened gradually, the metal particles on the edge of the cathode plate became thick and even grew into many burrs, which would affect the quality of electrolytic metallic manganese products, current efficiency would reduced due to tip discharge, this was consistent with the change of current efficiency mentioned above.

The effect of Mg$^{2+}$ concentration on the electrolytic manganese process was analyzed by SEM, the results were shown in figure 4. It could be seen that the electrolytic manganese was formed by layers of regular sheet, and each metal sheet exhibited a regular hexagon, this phenomenon was similar to that in literatures [22–24]. Due to the growth angle of manganese metal sheet was large, it presented a 'pyramid' shape and exhibited a silvery white color. With the increases of Mg$^{2+}$ concentration, it could be seen that the surface of electrolytic manganese particles became smoother and the rhombus of the hexagon was becoming blurred. This was because the growth angle of metal sheet was smaller, growing in the direction near parallel to the plate. In contrast, the cathode area decreases and the cathode current density increased, the compactness of metal particles was reduced. Therefore, with the increase of magnesium ion concentration, current efficiency decreased and energy consumption increased, which would lead to more dendritic electrolytic manganese on the cathode plate, and the surface was rough, and the color darkened gradually.

The figure 5 showed the cyclic voltammetry curve of manganese electrolyte when the Mg$^{2+}$ concentration was 15 g l$^{-1}$, 20 g l$^{-1}$, 25 g l$^{-1}$, 30 g l$^{-1}$ and 35 g l$^{-1}$ respectively. The cathode current was attributed to the current generated by the reduction reaction of Mn$^{2+}$ and H$^+$ on the electrode surface, and the anodic current was attributed to the oxidation current produced by dissolution of electrodeposited manganese.
It could be seen from the figure that the basic characteristics of cyclic voltammetry curves of electrolytic manganese solutions with different Mg²⁺ concentrations were similar. In the process of scanning to the negative potential direction, when the voltage was from $-0.5 \, \text{v}$ to $-1.45 \, \text{v}$, there was basically no cathodic current flowing through the circuit, indicating that no reduction reaction occurred at this stage. When the voltage was less than $-1.45 \, \text{v}$, the cathode current began to increase. It was found that a large number of bubbles were generated near the electrode plate in this process, and the hydrogen evolution reaction occurred. When the voltage was around $-1.95 \, \text{v}$, an obvious reduction peak appeared. This was because a large amount of NH₄⁺ in the solution discharged on the stainless steel surface, and part of NH₄⁺ adsorbed on the stainless steel surface was replaced by H₂O, so that this part of H₂O had not participated in a large number of discharge reactions [25]. With the further negative scanning of cathode potential, the cathode current increased rapidly, and the main reaction in this stage was manganese electrodeposition [26]. It could be observed that with the increase of Mg²⁺ concentration, the
When the scanning direction was positive, the rate of manganese electrodeposition began to decrease, accompanied by a trend of dissolution. When the scanning voltage was $-1.95\,\text{v} \sim -1.85\,\text{v}$, the current kept 0 A unchanged, because the rate of manganese electrodeposition and dissolution was low, and the dynamic balance was maintained, which showed that the quality of manganese electrodeposition on the plate did not change [28].

When the positive scanning was continued, the anode current began to increase rapidly and an obvious oxidation peak appeared, which was because the manganese deposited on the electrode surface dissolved to form $\text{Mn}^{2+}$. The slope of current curve decreased with the increase of $\text{Mg}^{2+}$ concentration, which indicated that the amount of manganese deposited on the cathode plate surface decreased gradually [29]. $\text{Mg}^{2+}$ was not beneficial to electrodeposition of manganese, and the current efficiency decreased with the increase of $\text{Mg}^{2+}$ concentration.

### 3.2. Effect of $(\text{NH}_4)_2\text{SO}_4$ on electrolytic manganese process

When $\text{Mg}^{2+}$ concentration was 25 g l$^{-1}$, current density was 400 mA cm$^{-2}$, the effect of the $(\text{NH}_4)_2\text{SO}_4$ was studied. The effect of $(\text{NH}_4)_2\text{SO}_4$ concentration on current efficiency was shown in figure 6. The results showed that with the increase of $(\text{NH}_4)_2\text{SO}_4$ concentration in electrolyte, the current efficiency of manganese electrolysis increased gradually, and the cell voltage remained stable. When the concentration of $(\text{NH}_4)_2\text{SO}_4$ was increased from 80 g l$^{-1}$ to 100 g l$^{-1}$, the current efficiency was increased from 64.75% to 66.62%. When the concentration of $(\text{NH}_4)_2\text{SO}_4$ in electrolyte was continuously increased to 120 g l$^{-1}$, the current efficiency of electrolytic
manganese only increased from 66.62% to 66.97%, it could be seen that (NH₄)₂SO₄ had little effect on the improvement of current efficiency in this range. And the energy consumption decreased from 6.859 kW·h·kg⁻¹ to 6.741 kW·h·kg⁻¹, it negatively correlated with current efficiency. This was because the addition of ammonium sulfate to the electrolyte could increase the concentration of ions in the electrolyte, and the conductivity of the electrolyte increased gradually, the cell voltage decreased. And increased the pH of the electrolyte, it was equivalent to reducing the concentration of hydrogen ions, and the production of hydrogen near the cathode was inhibited, as a result, the precipitation rate of manganese metal in cathode was promoted, therefore, the current efficiency was improved. When the concentration of (NH₄)₂SO₄ continued to be increased, the ion concentration in the electrolyte became saturated, and the crystallization was formed easily, the crystallization would have a lot of negative effects on electrolytic production. For example, it would result in the loss of beneficial components in the electrolyte, blockage of pipes, delay the electrolysis process, and make the current efficiency increase gently. Considering synthetically, the suitable concentration of (NH₄)₂SO₄ in the process of electrolytic manganese was 110 g l⁻¹.

After passivation by potassium dichromate, the macroscopic photographs of electrolytic manganese metal sheets produced under different ammonium sulfate concentration were recorded by camera, and was shown in figure 7. The effect of (NH₄)₂SO₄ on macroscopic photographs was obvious. It could be seen that with the increase of (NH₄)₂SO₄ concentration in electrolyte, the color of electrolytic manganese sheets became silver white, and the dendritic manganese metal disappeared gradually, the compactness of the grown manganese particles increased gradually.

The electrolytic manganese sheets obtained from the electrolysis experiment were analyzed by SEM with different ammonium sulfate concentration, the results were shown in figure 8. It could be seen that with the increase of the (NH₄)₂SO₄ concentration in electrolyte, the growth angle of the manganese metal in the cathode plate became larger, the compactness of metal particles increased gradually, the dendritic crystals decreased from the above macroscopic charts, and the hexagonal structure of the metal manganese became more obvious. The growth mode of the sheet was developed from a spherical shape to a ‘pyramid’, which would improve the

![Figure 7. Macroscopic chart of electrolytic manganese tablets at different (NH₄)₂SO₄ concentrations. Duration of electrolysis 12 h, Mg²⁺ 25 g l⁻¹, Current density 400 A·m⁻²: (a): (NH₄)₂SO₄ 80 g l⁻¹, (b): (NH₄)₂SO₄ 90 g l⁻¹, (c): (NH₄)₂SO₄ 100 g l⁻¹, (d): (NH₄)₂SO₄ 110 g l⁻¹, (e): (NH₄)₂SO₄ 120 g l⁻¹.](image)
quality of the manganese metal product, at the same time the current efficiency was increased and the energy consumption was decreased gradually.

The figure 9 showed the cyclic voltammetry curve of manganese electrolyte when the concentration of (NH$_4$)$_2$SO$_4$ was 80 g l$^{-1}$, 90 g l$^{-1}$, 100 g l$^{-1}$, 110 g l$^{-1}$ and 120 g l$^{-1}$ respectively.

It could be seen from the figure that when the concentration of NH$_4^+$ was different, the basic characteristics of cyclic voltammetry curve were basically the same, which was similar to the basic characteristics when the Mg$^{2+}$ concentration was different. When the voltage reached $-1.45$ V, the cathode current began to increase. It was also found in the experiment that a large number of bubbles were generated near the electrode plate, which was caused by hydrogen evolution reaction. When the negative scanning voltage reached $-1.95$ V, an obvious reduction peak appeared, which was due to the discharge of NH$_4^+$ on the stainless steel surface. The corresponding peak potential showed a positive trend with the increase of NH$_4^+$ concentration. The reason was that the increase of (NH$_4$)$_2$SO$_4$ would break the ionization equilibrium between H$^+$ and OH$^-$ in the solution,

![Figure 8. The SEM of electrolytic manganese sheets at different (NH$_4$)$_2$SO$_4$ concentrations. Duration of electrolysis 12 h, Mg$^{2+}$ 25 g l$^{-1}$, Current density 400 A m$^{-2}$. (a): (NH$_4$)$_2$SO$_4$ 80 g l$^{-1}$, (b): (NH$_4$)$_2$SO$_4$ 90 g l$^{-1}$, (c): (NH$_4$)$_2$SO$_4$ 100 g l$^{-1}$, (d): (NH$_4$)$_2$SO$_4$ 110 g l$^{-1}$, (e): (NH$_4$)$_2$SO$_4$ 120 g l$^{-1}$.](image)
and reduce the concentration of free H\(^+\) in the solution [25]. Which had a certain inhibitory effect on the production of hydrogen and further promoted the electrodeposition of manganese. With the cathode potential moving to negative, the slope of polarization curve changed abruptly, which corresponded to the initial precipitation potential of manganese in quasi steady state polarization. With the increase of NH\(_4\)^+ concentration, the corresponding initial precipitation potential showed a positive trend. It showed that increasing (NH\(_4\))\(_2\)SO\(_4\) reduced the overpotential of manganese precipitation on the electrode plate, and made the competitive reaction between H\(^+\) and Mn\(^{2+}\) tend to manganese deposition. When the negative scanning continued, the cathodic current increased rapidly, and the main reaction in this stage was manganese electrodeposition. At the same scanning potential, with the increase of (NH\(_4\))\(_2\)SO\(_4\) concentration, the cathode current increased gradually and the current efficiency also increased, which also proved that the increase of (NH\(_4\))\(_2\)SO\(_4\) concentration could promote manganese electrolysis.

In the process of positive scanning, when the scanning voltage was \(-1.95\) v \(-\) \(-1.85\) v, the current was 0 A, and the dynamic balance between manganese electrodeposition and dissolution is maintained. With the increase of voltage, the anode current increased rapidly and an obvious oxidation peak appeared, which was due to the dissolution of manganese deposited on the electrode surface to form Mn\(^{2+}\). When the current was 0, it meant that manganese had been completely dissolved, and the oxidation peak area was the amount of electrodeposited manganese. With the increase of ammonium sulfate concentration, the peak area increased, which indirectly proved that the amount of electrodeposition increased with the increase of ammonium sulfate concentration. Therefore, increasing the concentration of ammonium sulfate could inhibit the hydrogen evolution reaction.
and promote the manganese evolution reaction to a certain extent. This was consistent with the conclusion of electrolysis experiment.

3.3. Effect of current density on electrolytic manganese process

When Mg\(^{2+}\) concentration was 25 g l\(^{-1}\), (NH\(_4\))\(_2\)SO\(_4\) concentration was 110 g l\(^{-1}\), the effect of the current density was studied. The effect of current density on current efficiency was shown in figure 10. It could be seen from figure 8 that when the concentration of (NH\(_4\))\(_2\)SO\(_4\) and Mg\(^{2+}\) in the electrolyte were constant, with the increase of the current density, the current efficiency increased first and then decreased, and the cell voltage increased gradually. When the current density increased from 300 A m\(^{-2}\) to 400 A m\(^{-2}\), the current efficiency increased from 65.32% to 66.23%, and the cell voltage increased from 4.125 V to 4.629 V. When the current density continued to be increased to 500 A m\(^{-2}\), the current efficiency decreased from 66.23% to 64.92%, and the cell voltage increased from 4.629 V to 4.938 V. Energy consumption was negatively correlated with current density, with the increase of current density, energy consumption increases from 6.325 kW h kg\(^{-1}\) to 7.424 kW h kg\(^{-1}\). This was because during the process of electrolysis, increasing the current density could increase the cell voltage. In theory, it could also increase the hydrogen evolution overvoltage, hinder the hydrogen evolution and promote the manganese precipitation. But high current density must be matched with good solution circulation and high purity electrolyte, if the solution cycle was not up to date or the solution purity was not high, it would lead to the depletion of manganese ions in the cathode region or the discharge of impurities. As a result, the current efficiency decreased when the current density was too high. Moreover, if the current density was too high, it would produce dendritic products, which would affect the quality of electrolytic manganese products. Considering comprehensively, the current density in the electrolytic manganese was 400 A m\(^{-2}\).

After passivation by potassium dichromate, the macroscopic photographs of electrolytic manganese metal sheets produced under different current densities were recorded by camera, as shown in figure 11. It could be

![Figure 11. Macroscopic chart of electrolytic manganese sheet generated at different current densities. Duration of electrolysis 12 h, Mg\(^{2+}\): 25 g l\(^{-1}\), (NH\(_4\))\(_2\)SO\(_4\): 110 g l\(^{-1}\). (a): 300 A m\(^{-2}\), (b): 350 A m\(^{-2}\), (c): 400 A m\(^{-2}\), (d): 450 A m\(^{-2}\), (e): 500 A m\(^{-2}\).](image)
seen that when the current density increased from 300 A·m$^{-2}$ to 350 A·m$^{-2}$, the compactness of electrolytic manganese metal improved gradually, and the current efficiency increased. The color of manganese metal sheet became silver white. When the current density continued to be increased, the compactness of the manganese metal sheet became worse, and the large-grained metal manganese began to be appeared, the quality of dendritic metal manganese increased, and its color changed from silvery white to gray.

The electrolytic manganese sheets obtained from electrolytic experiments were analyzed by SEM under different current densities, the analysis results were shown in figure 12. When the current density increased from 300 A·m$^{-2}$ to 400 A·m$^{-2}$, the compactness of electrolytic manganese was improved gradually, and the lamellar structure of layers was more obvious. When the current density was 400 A·m$^{-2}$, the appearance of manganese metal had begun to show a spherical shape. However, due to the larger growth angle of metallic manganese, the electrolytic metal manganese was still regularly distributed on the cathode plate. As the current density continued to be increased, the growth angle and crystal area of manganese metal decreased gradually, resulting in an irregular spherical and dendritic growth, and the compactness became poor. Therefore, with the increase

**Figure 12.** The SEM of electrolytic manganese sheets produced at different current densities. Duration of Electrolysis 12 h, Mg$^{2+}$ 25 g l$^{-1}$, (NH$_4$)$_2$SO$_4$ 110 g l$^{-1}$. (a): 300 A·m$^{-2}$, (b): 350 A·m$^{-2}$, (c): 400 A·m$^{-2}$, (d): 450 A·m$^{-2}$, (e): 500 A·m$^{-2}$. 
of current density, the growth angle of manganese metal sheet would decreased, which would affect the surfacial quality of products and the current efficiency of manganese.

3.4. The distribution of magnesium
Magnesium accumulation had many effects on the electrolytic manganese system, and the authors had also carried out relevant studies in the previous stage [17]. In this part, the distribution of magnesium in electrolysis process would be studied. The microscopic morphology of electrolytic manganese was analyzed. During the experimental process, the white crystals existed on the surface of the electrolytic manganese by naked eyes. At the same time, the presence of Mg could be seen in the EDS spectrum of SEM (figure 13, table 2). it could be inferred that in the process of electrolytic manganese, a small amount of complex salt crystals would form and adhere to the surface of metal manganese, and the weight of Mg was only 0.18%, this amount was very small and belonged to entrainment generation. which would affect the quality of electrolytic manganese. The equilibrium distribution of Mg in the electrolytic manganese system was studied, the Mg in the catholyte and the anode solution was determined by EDTA titration, and the manganese and the anode mud were dissolved in the acid, so that the Mg was analyzed by the atomic absorption spectrophotometer. The results show that in the whole electrolytic manganese system, the Mg$^{2+}$ concentration of the electrolyte solution and anode solution was very close, they were 14.64 g l$^{-1}$ and 14.98 g l$^{-1}$ respectively. The Mg in the electrolyte solution was 12.68%, that in anode solution was 86.88%, that in manganese sheet was 0.085% and that in anode slag was 0.346% (table 3). Therefore, the Mg of very small amount entrained into the metal manganese sheets and the anode mud, and most of them were recycled and enriched in the system with the anode solution.

![Figure 13. The SEM and EDS spectrum of electrolytic manganese. Duration of electrolysis 12 h, Mg$^{2+}$ 15 g l$^{-1}$, (NH$_4$)$_2$SO$_4$ 110 g l$^{-1}$, Current density 400 A m$^{-2}$.](image)

### Table 2. Elemental weight fraction and atomic fraction of electrolytic manganese.

Duration of electrolysis 12 h, Mg$^{2+}$ 15 g l$^{-1}$, (NH$_4$)$_2$SO$_4$ 110 g l$^{-1}$, Current density 400 A m$^{-2}$.

| Element | Weight(%) | Atom(%) |
|---------|-----------|---------|
| Mn      | 92.77     | 82.95   |
| O       | 7.05      | 16.72   |
| Mg      | 0.18      | 0.33    |
| Total   | 100       | 100     |

### Table 3. The equilibrium distribution of Mg in manganese sulfate electrolysis. Duration of electrolysis 12 h, Mg$^{2+}$ 15 g l$^{-1}$, (NH$_4$)$_2$SO$_4$ 110 g l$^{-1}$, Current density 400 A m$^{-2}$.

| Project                  | Quality(g) | Weight(%) | Concentration(g/l) |
|--------------------------|------------|-----------|--------------------|
| Electrolyte solution(0.52 l) | 7.61       | 12.68     | 14.64              |
| Anode solution (3.48 l)   | 52.13      | 86.88     | 14.98              |
| Manganese sheet           | 0.051      | 0.085     | —                  |
| Anode slag                | 0.207      | 0.346     | —                  |
| Total                     | 60         | 100       | —                  |
3.5. Crystal orientation

When the current density was 400 A m\(^{-2}\), the \((\text{NH}_4)_2\text{SO}_4\) concentration was 110 g l\(^{-1}\), adding a certain amount of \(\text{Mg}^{2+}\), the XRD diffraction diagram of electrolytic manganese in different conditions were shown in figures 12–14. The relative peak strength of XRD diffraction diagram were shown in table 4. It could be observed from figures 14–16 that the crystal plane \((330,411)\) was the strongest and best orientation for the growth of electrolytic manganese crystal when the 2\(\theta\) was 43°, regardless of the change of \(\text{Mg}^{2+}\) concentration, \((\text{NH}_4)_2\text{SO}_4\) concentration and current density. It could be inferred from the optimal crystal plane index that the crystal morphology of electrolytic manganese was \(\alpha\)-manganese. The higher the concentration of \(\text{Mg}^{2+}\) in the electrolyte was, the lower the strength of most crystal planes were, which indicated that the crystallinity of electrolytic manganese decreased and the compactness decreased gradually (table 4, figure 14). When the concentration of \(\text{Mg}^{2+}\) was 15 g l\(^{-1}\), the crystallinity of manganese was the strongest. Under this condition, the crystal orientation of electrolytic manganese was \((330,411) > (332) > (422) > (431,510) > (444) > (550) > (444)\).

When the \(\text{Mg}^{2+}\) concentration was 25 g l\(^{-1}\), the current density was 400 A m\(^{-2}\), adding a certain amount of \((\text{NH}_4)_2\text{SO}_4\), the crystal plane strength of the electrolytic manganese increased gradually, and the crystallinity became stronger gradually (table 4, figure 15). It indicated that \((\text{NH}_4)_2\text{SO}_4\) could increase the conductive ion
concentration of the electrolyte during the electrolysis process, which was beneficial to production of electrolytic manganese. When the concentration of \((\text{NH}_4)_2\text{SO}_4\) was 110 g l\(^{-1}\), the strongest peak was except for, the peak strengths of \((422), (431,510)\) were relatively high, which indicated that under these conditions, more manganese atoms would accumulated on these crystal planes.

When the \(\text{Mg}^{2+}\) concentration was 25 g l\(^{-1}\), the \((\text{NH}_4)_2\text{SO}_4\) concentration was 110 g l\(^{-1}\), with the increase of the current density, it could be seen that the peak strength of most crystal planes fi rst increased and then decreased (table 4, figure 16). and the peak intensity of the crystal plane was the largest when the current density was 400 A \(\cdot\) m\(^{-2}\). It was indicated that the production of electrolytic manganese under this condition had the best crystallinity, and the crystal orientation also changed as follows: \((330,411) > (332) > (721) > (431,510) > (444) > (422)> (550)\). Combined with the current efficiency and microscopic morphology of electrolytic manganese, it could be inferred that the greater the crystal plane strength was, the better the crystallinity of electrolytic manganese was, and the higher the current efficiency was. From the point of view of crystal orientation, the following rules existed in the electrolysis process. The lower the concentration of magnesium ion was, the better the electrolysis process was. Increasing the concentration of ammonium sulfate was beneficial to electrolysis, but when the concentration was greater than 110 g l\(^{-1}\), it may

**Table 4.** The effects of XRD pattern of manganese metal.

| Experimental condition | Additive | Crystal orientations (relative intensities) |
|------------------------|----------|-------------------------------------------|
| \(\text{Mg}^{2+}/(\text{g/l})\) |          |                                           |
| 15                     | 100      | 21.33                                     |
| 20                     | 100      | 18.80                                     |
| 25                     | 100      | 20.01                                     |
| 30                     | 100      | 16.92                                     |
| 35                     | 100      | 16.61                                     |
| \(\text{(NH}_4)_2\text{SO}_4/(\text{g/l})\) |          |                                           |
| 80                     | 100      | 17.54                                     |
| 90                     | 100      | 17.11                                     |
| 100                    | 100      | 18.12                                     |
| 110                    | 100      | 20.85                                     |
| 120                    | 100      | 21.2                                      |
| \(\text{Current Density}/\text{A}\cdot\text{m}^{-2}\) |          |                                           |
| 300                    | 100      | 12.40                                     |
| 350                    | 100      | 10.74                                     |
| 400                    | 100      | 16.95                                     |
| 450                    | 100      | 15.68                                     |
| 500                    | 100      | 14.24                                     |

**Figure 16.** XRD pattern of electrolytic manganese at different current densities. Duration of electrolysis 12 h, \(\text{Mg}^{2+} 25 \text{ g l}^{-1}, (\text{NH}_4)_2\text{SO}_4 110 \text{ g l}^{-1}\), a: (330,411); b: (332); c: (422); d: (431,510); e: (444); f: (550); g: (721).
lead to negative effects. When the current density was 400 A·m⁻², it was more suitable, too large or too small were unfavorable to the electrolysis process.

4. Conclusions

In this paper, the laboratory experiment of electrolytic manganese was carried out. The effects of Mg²⁺ concentration, current density and (NH₄)₂SO₄ concentration on the process of electrolytic manganese were investigated, and the reasonable electrolytic conditions were determined. The growth mode of metal manganese under different electrolytic conditions was obtained by macro and micro analysis of metal manganese. The following conclusions were drawn:

(1) The concentration of Mg²⁺ in electrolyte had a great influence on the current efficiency of manganese electrolysis. With the increase of Mg²⁺ concentration in electrolyte, the current efficiency of manganese decreased gradually. The cell voltage was constant at 4.612–4.752 V. When the concentration of Mg²⁺ increased from 15 g l⁻¹ to 35 g l⁻¹, the current efficiency of manganese decreased from 68.73% to 62.54%, energy consumption increased from 6.547 kW·h·kg⁻¹ to 7.441 kW·h·kg⁻¹. Cyclic voltammetry experiments also showed that Mg²⁺ was not beneficial to electrodeposition of manganese, and the current efficiency decreased with the increase of Mg²⁺ concentration.

(2) With the increase of (NH₄)₂SO₄ concentration in electrolyte, the current efficiency of manganese increased gradually, and the cell voltage remains constant. When the concentration of (NH₄)₂SO₄ increased from 80 g l⁻¹ to 120 g l⁻¹, the current efficiency of manganese electrolysis increased from 64.75% to 66.97%. Cyclic voltammetry experiments also showed that increasing the (NH₄)₂SO₄ concentration could inhibit the hydrogen evolution reaction and promote the manganese evolution reaction to a certain extent. In other words, the increase of ammonium sulfate was beneficial to improve the current efficiency.

(3) When the concentration of (NH₄)₂SO₄ and Mg²⁺ in electrolyte was constant, the current efficiency of manganese increased first and then decreased with the increase of current density, and the cell voltage increased gradually. The current efficiency of manganese electrolysis increased from 65.32% to 66.23% when the current density increased from 300 A·m⁻² to 400 A·m⁻², and decreased from 66.23% to 64.92% when the current density increased from 400 A·m⁻² to 500 A·m⁻², while the cell voltage increased from 4.125 V to 4.938 V, energy consumption increased from 6.325 kW·h·kg⁻¹ to 7.424 kW·h·kg⁻¹. Therefore, in the process of manganese electrolysis, the more reasonable electrolytic conditions were as follows: lower Mg²⁺ concentration, current density was 400 A·m⁻², (NH₄)₂SO₄ concentration was 110 g l⁻¹.

(4) By means of SEM analysis of electrolytic manganese, the micro-structure of electrolytic manganese was formed by layers of manganese sheets. The different electrolyte composition and electrolytic conditions made the growth angle of manganese sheets different, and the distribution of manganese sheets on the cathode plate also was different, which led different compactness of cathode manganese particles. The dendritic growth of manganese was more obvious with the increase of Mg²⁺ concentration, the smaller the current efficiency was, the worse the compactness of cathode manganese was. In contrast, the higher (NH₄)₂SO₄ concentration was, the denser the cathode manganese grew. The higher the current efficiency was, the smaller the growth angle of manganese was, and the clearer the edges and corners of hexagon became. The strongest and best crystal growth orientation for electrolytic manganese was (330,441).

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Data availability statement

No new data were created or analysed in this study.

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