



Gallium recovery by cyclone electrowinning from alkaline electrolyte with titanium cathode

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Abstract: A process for gallium recovery by cyclone electrowinning was proposed to inhibit concentration polarization and improve current efficiency (CE). The diffusion coefficient of GaO_2^- in 120 g/L NaOH solution was determined to be $1.65 \times 10^{-7} \text{ cm}^2/\text{s}$ by electrochemical study. The effect of various parameters on gallium electrowinning was investigated, and the optimum conditions were determined as: titanium cathode, current density of 750 A/m^2 , gallium concentration of 39.9 g/L, NaOH concentration of 120 g/L, and circulation flow of 200 L/h. Under these conditions, the CE and gallium recovery of electrowinning were 47.9% and 90.2%, respectively. The precipitated gallium can be easily separated from the cathode, and the final purity of gallium after washing was 99.993%. The energy consumption (EC) of gallium cyclone electrowinning was about $9048 \text{ kW}\cdot\text{h/t}$. Overall, it is suggested that cyclone electrowinning is a promising process for gallium production with high CE and low EC.

Key words: gallium; cyclone electrowinning; GaAs waste; current efficiency

1 Introduction

Gallium is a scattered metal that occupies an important position in many emerging fields, such as semiconductors, light emitting diode (LED), catalysis, and medical [1–6]. It also performs outstanding potential in the future of cleaner energy [7–9]. Recently, the total demand for gallium has continuously increased. However, as a scattered metal, the abundance of gallium in the Earth's crust is extremely low and has no independent deposits worth mining [10,11]. Therefore, gallium is mainly recovered as a byproduct of the metallurgical process. Recovery from the Bayer process and zinc hydrometallurgical process are the main sources of gallium recovery [12–15]. However, as the high-grade gallium resource diminishes, gallium is gradually in short supply [16]. The production of

gallium in the electronic industry generates a large amount of gallium-containing electronic waste, and the grade of which is much higher than that of primary mineral resources [17,18]. If it can be used effectively, the contradiction between the supply and demand of gallium can be alleviated to a certain extent [19,20].

Gallium arsenide is one of the major uses of gallium [21]. During the production and processing of GaAs, a large amount of high-grade cutting waste is generated, which needs to be effectively recovered [22,23]. At present, the recovery process of GaAs wastes mainly includes the acid leaching process, alkali leaching process, bioleaching process and pyrolysis process [24–32]. Electrowinning is a necessary process for all processes [33]. However, gallium electrowinning suffers from severe hydrogen evolution reaction (HER), which results in a low current efficiency (CE) [34,35].

The typical current efficiency (CE) of recent commercial production can only reach ~10%. WANG et al [36] applied sulfuric acid to activating the anode surface so that the induced time was shortened from 4.75 h to 20 min, and the CE was 4%. LIU et al [34] used nickel anode for Ga electrowinning in the presence of S^{2-} ions, and the CE decreased to 4.02% for 9 h electrowinning. LI et al [37] used SUS304 as anode for gallium electrowinning in 4 mol/L NaOH solution, and the CE of 6.30% was obtained. Therefore, it is urgent to develop an efficient electrowinning process for gallium production.

Cyclone electrowinning is an enhanced electrowinning technology that can effectively enhance mass transfer and eliminate concentration polarization through the high-speed circulating flow of electrolytes [38–41]. Therefore, the recovery of gallium by cyclone electrowinning can effectively improve the CE and quality of the gallium cathode.

In this work, gallium electrochemical behavior and cyclone electrowinning in alkaline electrolyte were studied using the arsenic removal solution after gallium arsenide alkaline leaching as raw material. Cyclic voltammetry (CV) studies were carried out to investigate the electrochemical behavior of gallium. Subsequently, cyclone electrowinning in alkaline electrolyte was carried out corresponding to the electrochemical study. Combining theoretical research with expanded experiments, the optimal conditions for gallium electrowinning were obtained, and the mechanisms were explained.

2 Experimental

2.1 Materials and apparatus

In the electrochemical study, ultra-pure water (resistivity $>18 \text{ M}\Omega \cdot \text{cm}$) was prepared by an

ultra-pure water machine (ZOOMAC-L, Zhongwo Water Environmental Protection Technology Co., Ltd., China). Sodium hydroxide (semiconductor grade), potassium hydroxide (analytical research grade), and gallium oxide (analytical research grade) were supplied by Aladdin Reagent Co., Ltd. (Shanghai). In the cyclone electrowinning study, the electrolyte was the arsenic removal solution in dealing with gallium arsenide waste. The detailed chemical components are listed in Table 1. The main impurity of the electrolyte used is arsenic, and also contains a small amount of aluminum and silicon. In the acidic system, it is easy to generate highly toxic arsine, while the alkaline system avoids the formation of this by-product.

Table 1 Chemical components of cyclone electrowinning electrolyte (g/L)

Ga	As	Al	Si	NaOH
39.9	4.12	0.29	0.10	80

The electrochemical study was carried out by an electrochemical workstation (PGSTAT302N, Autolab, Switzerland). The work electrode (WE) was a $10 \text{ mm} \times 10 \text{ mm}$ titanium sheet covered with epoxy resin on one side in the CV study. The counter electrode was a $20 \text{ mm} \times 20 \text{ mm}$ platinum sheet. The reference electrode was a Hg/HgO electrode due to the alkaline electrolyte.

The cyclone electrowinning study was carried out by a cyclone electrolyzer that mainly consists of a DC power supply, electrolyzer, flowmeter, transfer pump, circulation tank, and heating mantle. The schematic diagram is presented in Fig. 1. The Ti/($\text{IrO}_2\text{-Ta}_2\text{O}_5$) rod was selected as the anode to better deal with alkali corrosion and reduce the energy consumption (EC) [42].

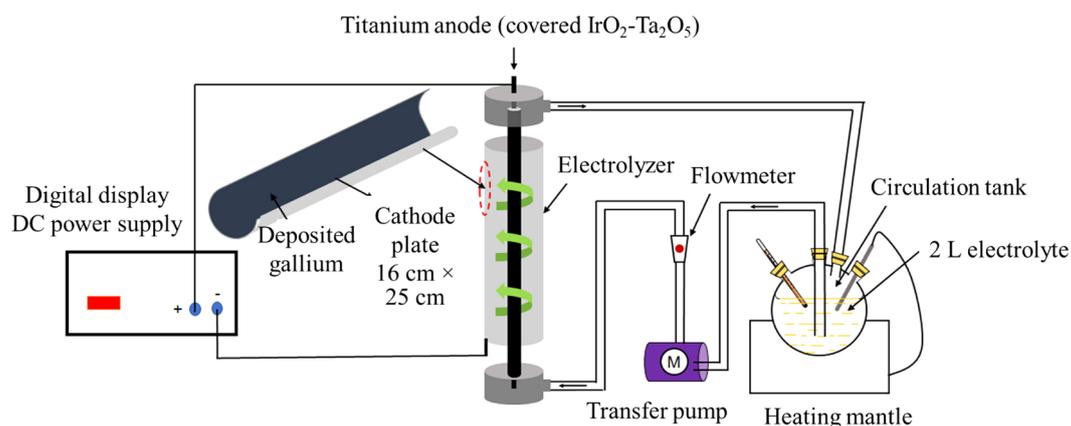


Fig. 1 Schematic diagram of gallium electrowinning process

2.2 Procedures

In the electrochemical study, the electrolyte was prepared by mixing ultrapure water, sodium hydroxide, and gallium oxide in a stoichiometric ratio and heating at 95 °C for 6 h. Before the experiment, the WE was polished by sandpaper from low to high mesh (3.8–65 μm). Then, the sections were rinsed with ultra-pure water in an ultrasonic bath sonicator for 5 min. Nitrogen was passed into the electrolyte to remove dissolved oxygen. Subsequently, the electrodes and the salt bridge were connected, and experiments were carried out by the electrochemical workstation. To ensure the reliability of the results, each group of CV curves was measured at least three times until the results are stable.

In the cyclone electrowinning study, 2 L electrolyte was added to the circulation tank. The heating mantle and transfer pulp were switched on until the temperature reached 30 °C. Then, the DC power supply was switched on, and galvanostatic electrowinning started. Every time, a 5 mL electrolyte sample in the circulation tank was siphoned to determine the concentration of gallium. After electrowinning, the gallium attached to the cathode surface and flushed to the bottom of the cell was collected. The crude gallium obtained was washed with oxalic acid and dried under vacuum, and then the mass and purity of the dried gallium were determined.

The gallium recovery, CE and EC were calculated by Eqs. (1)–(3):

$$R_{\text{Ga}} = 1 - \frac{c_1 V_1}{c_0 V_0} \times 100\% \quad (1)$$

$$\eta = \frac{c_0 V_0 - c_1 V_1}{Itk} \times 100\% \quad (2)$$

$$W = \frac{1000 E}{\eta k} \quad (3)$$

where R_{Ga} is the recovery of gallium, c_0 is the initial concentration of electrolyte, c_1 is the final concentration of electrolyte after electrowinning, V_0 is the initial volume of electrolyte, V_1 is the final volume of electrolyte, η is the CE of cyclone electrowinning, I is the current during electrowinning, t is the total time of electrowinning, k is the electrochemical equivalent of gallium (0.86724 g/(A·h)), W is the EC, and E is the cell voltage.

2.3 Analytical techniques

In the electrochemical study, all electro-

chemical signals, including voltage, current, and charge, were recorded by the electrochemical workstation. In the cyclone electrowinning study, the gallium concentration of the electrolyte and the purity of the deposited gallium were determined by ICP–OES and ICP–MS, respectively.

3 Results and discussion

3.1 Electrochemical analysis

The CV curves of 120 g/L NaOH, and 20 g/L Ga electrolyte measured under different scan rates (ν) are presented in Fig. 2(a). As shown, the redox peaks of gallium occur in the gallium electrolyte. Compared with the blank electrolyte, depolarization is more likely to occur in the gallium electrolyte. The reduction current of gallium appears at -1.6 V and reaches a peak at -1.75 V [43]. As the potential shifts negatively, the HER gradually dominates. The oxidation peak of gallium appears when the potential moves to -1.14 V.

Based on the Randles–Sevcik equation (Eq. (4), at 25 °C), the square of the scan rate is proportional to the peak current in the CV curves. Therefore, the diffusion coefficient of gallium ions can be determined by the slope of the fitted curve:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} c \nu^{1/2} \quad (4)$$

where I_p is the cathodic peak current, n is the number of electrons transferred in the redox reaction, A is the electrode area, D is the diffusion coefficient, c is the gallium bulk concentration of the electrolyte, and ν is the scan rate.

The CV curves and fitted curves are shown in Fig. 2. As shown in Fig. 2(b), the potential at the peak current shifts negatively with increasing scan rate, which indicates that the reduction of gallium is an irreversible reaction. The peak current of gallium reduction increases with increasing scan rate, which is caused by concentration polarization. The peak current and peak voltage at different scan rates are summarized in Table 2. As shown in Fig. 2(c), the square of the scan rate and the cathodic peak current present a good linear relationship fitting by the Randles–Sevcik equation. The diffusion coefficient of GaO_2^- in 120 g/L NaOH solution can be determined by the slope of the fitted curve, i.e., $D = 1.65 \times 10^{-7} \text{ cm}^2/\text{s}$. Due to the low diffusion coefficient of gallium ions, concentration polarization is likely to occur when gallium ion

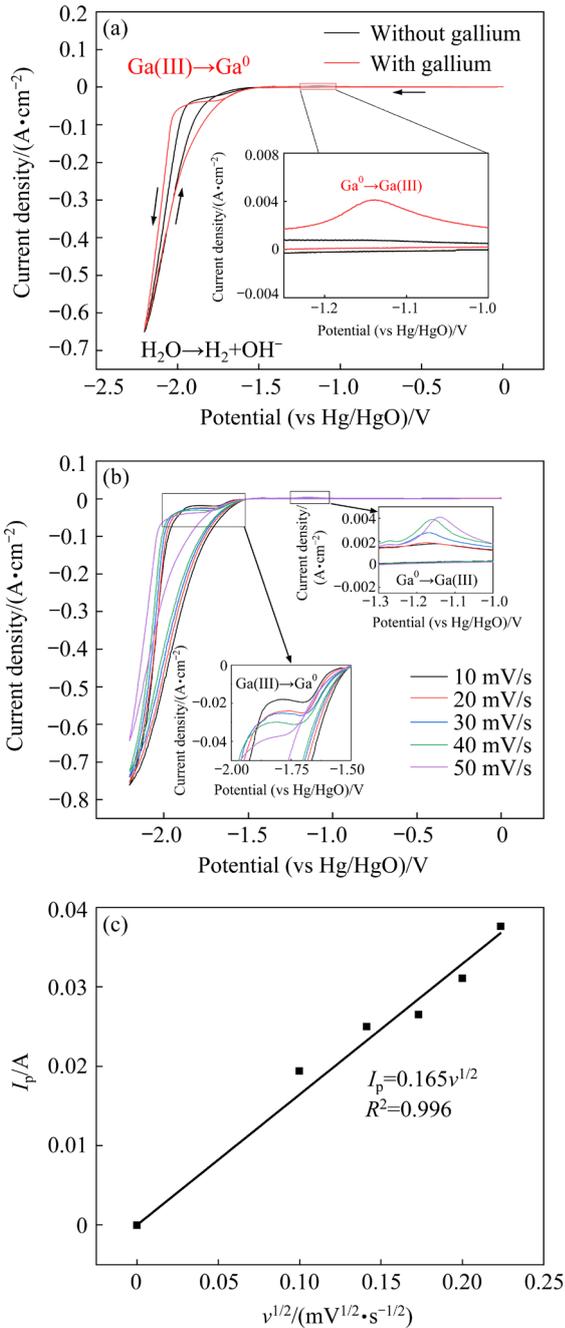


Fig. 2 Cyclic voltammetry curves of blank and gallium electrolytes (a); Cyclic voltammetry curves of gallium electrolyte under different scan rates (b); Randles-Sevcik equation fitted curve (c)

Table 2 Peak current and peak voltage at different scan rates

Scan rate/ (mV·s ⁻¹)	Peak current/A	Peak potential (vs Hg/HgO)/V
10	0.0194	-1.697
20	0.025	-1.703
30	0.0265	-1.711
40	0.0311	-1.737
50	0.0376	-1.816

transfer is only by diffusion. Therefore, forced convection is necessary to enhance the mass transfer process and improve the CE.

3.2 Cyclone electrowinning analysis

Based on the above electrochemical studies, large-scale cyclone electrowinning experiments were carried out. The effect of cathode materials, current density, gallium concentration, NaOH concentration, and circulating flow on CE and gallium recovery was investigated to confirm the theoretical studies and explore the optimal parameters for gallium cyclone electrowinning.

3.2.1 Effect of cathode materials

The effect of cathode materials on CE and gallium recovery was investigated. As shown in Fig. 3(a), the CE was generally lower than 30% due to severe HER. The CE and recovery were the lowest with the copper cathode, followed by SUS304. While using 316, Ti, Zn, Sn, and Pb cathodes, the CE and recovery rate were much higher, which was mainly due to their higher HER

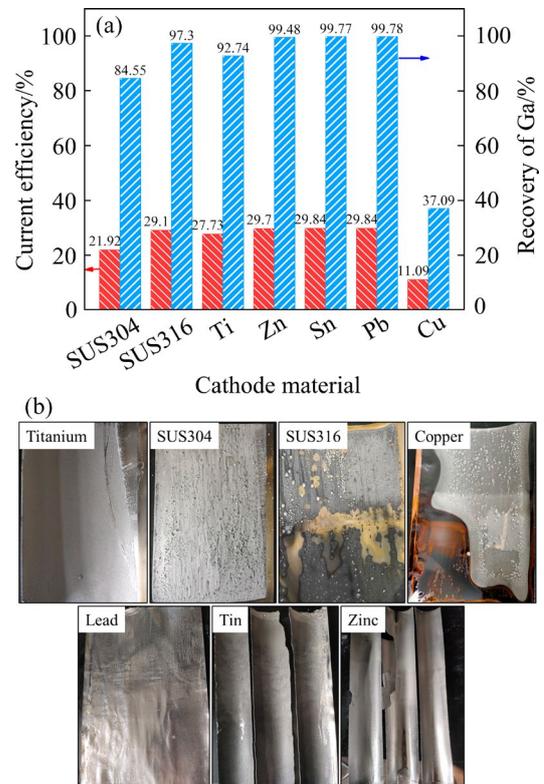


Fig. 3 Effect of cathode materials on CE and gallium recovery (Current density of 500 A/m², gallium concentration of 39.88 g/L, NaOH concentration of 80 g/L, circulation flow of 200 L/h, and time of 14 h) (a); Photographs of different cathodes after gallium deposition (b)

overpotentials. However, as shown in Fig. 3(b), both the Pb and Zn cathodes with the highest CE and gallium recovery were fractured because the deposited gallium formed a fragile alloy with them. Moreover, although the CE and gallium recovery with SUS316 and Pb cathodes are higher than those with Ti cathode, the gallium deposited on the surface is difficult to mechanically separate from them. However, the gallium on the titanium surface can be easily separated and partially concentrated at the bottom of the electrolyzer with the flushing of the electrolyte. Therefore, it can be considered that the use of titanium electrodes is the most suitable for gallium recovery by cyclone electrowinning and

was used in subsequent experiments.

3.2.2 Effect of current density

The effect of current density on CE and gallium recovery was investigated. As shown in Fig. 4(a), the CE increases first from 28.7% to 36.3% with the increase of current density from 250 to 750 A/m². Further increasing the current density to 1250 A/m² decreased the CE to 30.4%. The current density is positively correlated with the cell potential during electrowinning. When the current density is low, the gallium reduction reaction is limited by the electron transfer step. Because the standard potential of HER is more positive, gallium reduction is in an inferior status. However, when the

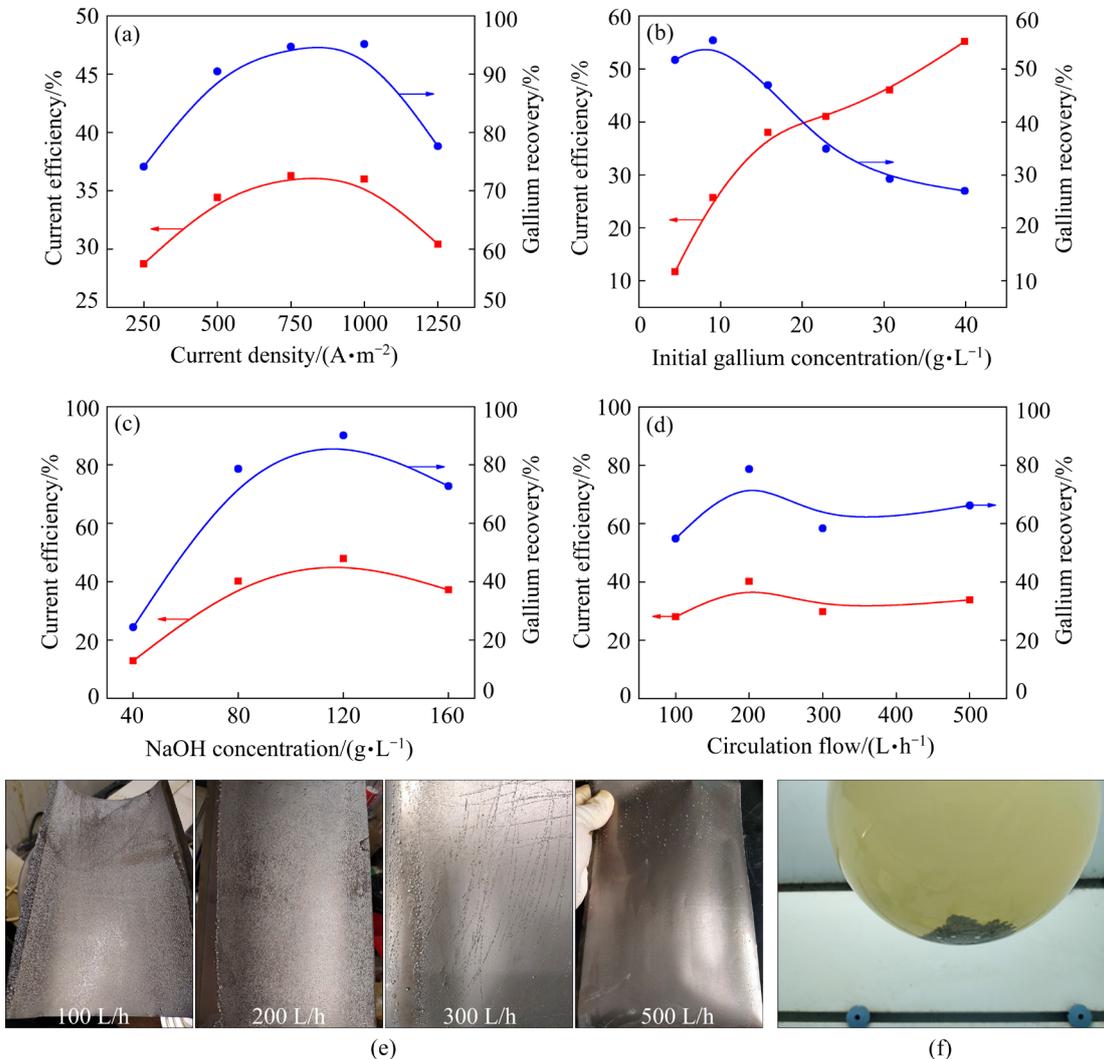


Fig. 4 Effect of different parameters on CE and gallium recovery: (a) Effect of current density (gallium concentration of 39.88 g/L, NaOH concentration of 80 g/L, circulation flow of 200 L/h, and constant charge); (b) Effect of initial gallium concentration (current density of 750 A/m², NaOH concentration of 80 g/L, circulation flow of 200 L/h, and time of 1.5 h); (c) Effect of NaOH concentration (current density of 750 A/m², gallium concentration of 39.88 g/L, circulation flow of 200 L/h, and time of 6 h); (d) Effect of circulation flow (current density of 750 A/m², gallium concentration of 39.88 g/L, NaOH concentration of 80 g/L, and time of 6 h); (e) Photographs of cathodes after electrowinning at different circulating flows; (f) Flushed gallium in circulation tank at circulating flow of 500 L/h

current density is too high, the kinetics limiting step is gradually turned into a mass transfer step. Since the diffusion coefficient of hydrogen ions is much larger than that of gallium ions, the CE decreases again. Furthermore, AsH_3 , a highly toxic gas, is more likely generated at high overpotential. Therefore, although increasing the current density can shorten the production cycle, maintaining an appropriate current density or overpotential during gallium electrowinning is necessary in consideration of EC. The current density of 750 A/m^2 was adopted in subsequent experiments.

3.2.3 Effect of gallium concentration

The effect of the initial gallium concentration on CE and gallium recovery is presented in Fig. 4(b). The average CE increases from 11.7% to 55.1% with the increase of initial gallium concentration from 4.43 to 39.9 g/L. Although the gallium recovery efficiency decreases from 51.7% to 27.0% with the increase of initial gallium concentration, the difference of concentration (i.e., the mass of deposited gallium) at the same time still increases. The reason for the significant improvement in CE is that the actual evolution potential is more positive at a high gallium concentration based on the Nernst equation. Moreover, concentration polarization and HER are more likely to occur when the gallium concentration is low. Therefore, it is necessary to maintain a high gallium concentration during the electrowinning process to save EC. The initial gallium concentration of 39.9 g/L was adopted in subsequent experiments.

3.2.4 Effect of NaOH concentration

The effect of NaOH concentration on CE and gallium recovery is shown in Fig. 4(c). The average CE increases from 12.9% to 47.9% as the NaOH concentration increases from 40 to 120 g/L. Further increasing the NaOH concentration to 160 g/L decreases the CE to 37.2%. The trend of gallium recovery with NaOH concentration is similar to that of the CE. The increase of NaOH concentration has two sides for gallium electrowinning. On the one hand, it increases the conductivity of the electrolyte, which benefits the migration of ions. On the other hand, it increases the viscosity of the electrolyte, which is detrimental to the mass transfer process. Combining these two factors, the maximum CE and recovery are obtained at a NaOH concentration of 120 g/L, which was adapted in subsequent experiments.

3.2.5 Effect of circulation flow

The effect of circulation flow on CE and gallium recovery was investigated. As shown in Fig. 4(d), the average CE increases first from 28.0% to 40.2% with the increase of circulation flow from 100 to 200 L/h, while it decreases to 29.8% when the circulation flow increases to 300 L/h. Further increasing the circulation flow to 500 L/h increases the CE again to 33.8%. The trend of gallium recovery with NaOH concentration is similar to that of the CE. Increasing circulation flow is beneficial to inhibiting the concentration polarization and improving CE. However, as shown in Figs. 4(e) and (f), when the circulating flow is too high, the gallium precipitated on the cathode surface is easily washed away by the high-speed flowing electrolyte. Since the nucleation of gallium on the surface of the titanium cathode requires a larger activation energy than the continuous growth of precipitated gallium, the CE and recovery decrease with increasing circulating flow. Moreover, the EC also increases with the increase of circulating flow in commercial production. Therefore, the circulating flow of 200 L/h with the maximum CE was adopted in subsequent experiments. The density of gallium is much higher than that of water, and the interfacial tension of gallium water is very large. Therefore, the flashed gallium did not disperse in the electrolyte in practice, but settled spontaneously to the bottom of the electrolyzer or the circulation tank, which can be easily collected after electrowinning.

3.3 Optimized experiment analysis

Based on the above single-factor experiments, the parameters of the optimized experiment were determined to be as follows: titanium cathode, current density of 750 A/m^2 , gallium concentration of 39.9 g/L, NaOH concentration of 120 g/L, and circulation flow of 200 L/h. Under these conditions, the CE and gallium recovery of electrowinning for 6 h were 47.9% and 90.2%, respectively. The final gallium concentration of the electrolyte after electrowinning was reduced to 4.53 g/L, while the arsenic concentration remained almost the same. The average cell voltage and EC were 3.76 V and 9048 kW·h/t, respectively.

The gallium generated by electrowinning is shown in Figs. 5(a) and (b). A part of the gallium adhered to the surface of the titanium cathode, and

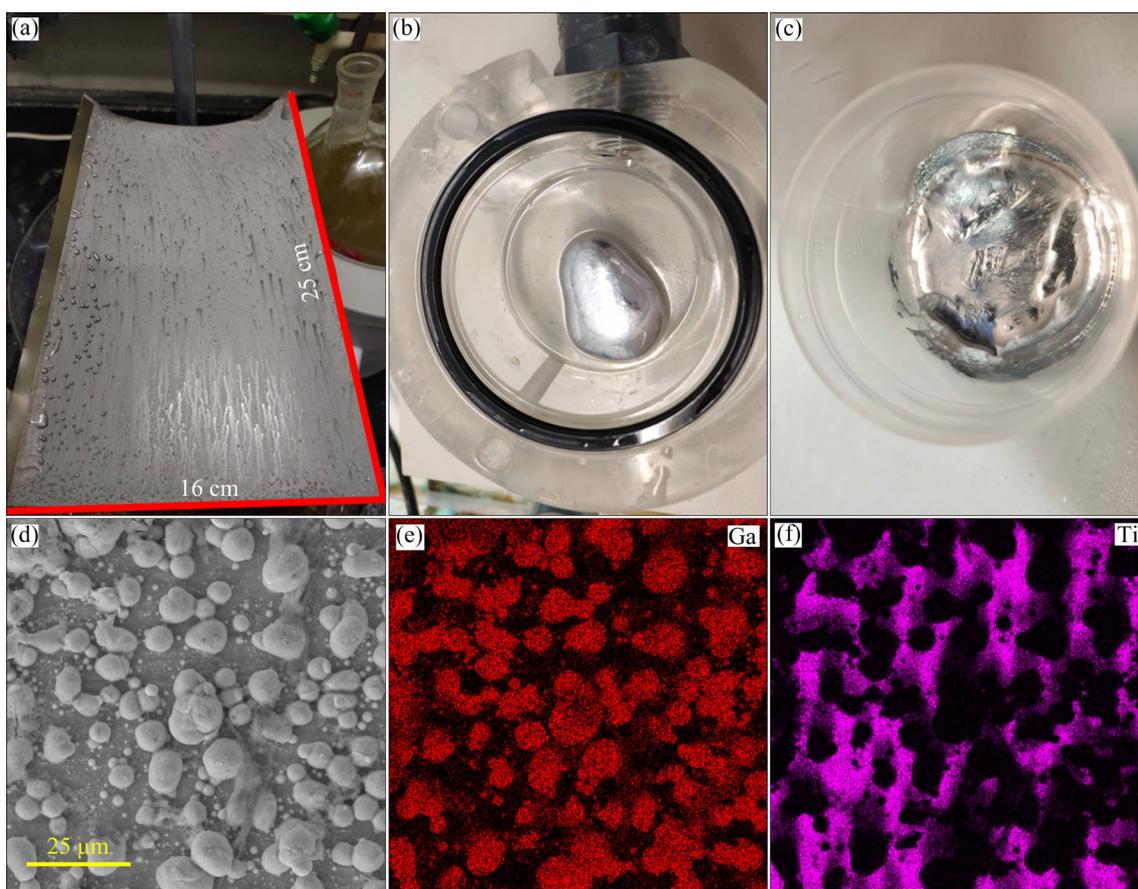


Fig. 5 Titanium cathode with adhered gallium after electrowinning (a); Gallium deposited on bottom of electrolyzer (b); Crude gallium washed with dilute hydrochloric acid and ultrapure water (c); SEM image (d) and surface scanings (e, f) of titanium cathode after electrowinning

the other part was deposited on the bottom of the electrolyzer. The adhesion of the precipitated gallium to the surface of the titanium cathode is not strong and easy to separate. The collected gallium was washed several times with dilute hydrochloric acid and ultrapure water. The impurity composition of the crude gallium is shown in Table 3 by ICP–MS. It can be seen that the content of other impurities such as arsenic, aluminum and silicon is extremely low, which has little impact on the product quality of crude gallium. Therefore, it can be considered that the impurities at these concentrations have little effect on the cyclone electrowinning. The final purity of gallium (Fig. 5(c)) was determined to be 99.993% by subtracting the total impurities, which can be directly used for the subsequent purification processes [44]. The SEM and surface scanings of titanium cathode after electrowinning are shown in Fig. 5(d). It can be seen that gallium appears as dispersed small particles on the surface of the

cathode, which indicates that the interfacial tension between gallium and titanium is large and easy to separate.

Table 3 Impurities composition of washed crude gallium (10^{-6})

As	Al	Si	Zr	Cr	Cu	
1.61	1.79	<10	0.31	2.54	10.1	
Fe	Mg	Mn	Ni	Pb	Zn	Sn
16.1	6.33	12.1	3.55	0.18	1.20	1.00

4 Conclusions

(1) The electrochemical behavior of gallium reduction in alkaline electrolytes was investigated. The diffusion coefficient of GaO_2^- in 120 g/L NaOH solution was determined to be $1.65 \times 10^{-7} \text{ cm}^2/\text{s}$ by the Randles–Sevcik equation.

(2) The effect of various parameters on gallium electrowinning was explored. The optimum

conditions for electrowinning were determined as follows: titanium cathode, current density of 750 A/m², gallium concentration of 39.9 g/L, NaOH concentration of 120 g/L, and circulation flow of 200 L/h. Under these conditions, the CE and gallium recovery of electrowinning are 47.9% and 90.2%, respectively.

(3) The precipitated gallium can be easily separated from the cathode. The final purity of gallium after washing is 99.993%, which can be directly used for subsequent purification processes.

(4) The EC of gallium cyclone electrowinning is 9048 kW·h/t. The application of cyclone electrowinning can effectively improve the CE for gallium electrowinning.

CRedit authorship contribution statement

Zhi-peng XU: Conceptualization, Experimental investigation, Writing – Original draft; **Zuo-wei LIU:** Conceptualization, Experimental investigation, Writing – Original draft; **Xue-yi GUO:** Funding acquisition, Writing – Review & editing; **Dong LI:** Funding acquisition, Writing – Review & editing; **Ming-jin ZOU:** Experimental investigation, Writing – Original draft; **Qing-hua TIAN:** Funding acquisition, Writing – Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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采用钛阴极从碱液中旋流电积回收镓

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摘 要: 为了抑制浓差极化并提高电流效率, 提出一种旋流电解法回收镓的工艺。通过电化学研究确定 GaO_2^- 在 120 g/L NaOH 溶液中的扩散系数为 $1.65 \times 10^{-7} \text{ cm}^2/\text{s}$ 。考察各种参数对镓电积的影响, 确定电积的最佳条件为: 钛阴极、电流密度 750 A/m^2 、镓浓度 39.9 g/L 、NaOH 浓度 120 g/L 、循环流量 200 L/h 。在这些条件下, 电积的电流效率和镓回收率分别为 47.9% 和 90.2%。析出的镓较易从阴极上分离, 经过洗涤后的镓最终纯度为 99.993%。镓旋流电积能耗约为 $9048 \text{ kW}\cdot\text{h/t}$ 。该研究表明旋流电积是一种具有高电流效率和低能耗的有前途的镓生产工艺。
关键词: 镓; 旋流电积; 砷化镓废料; 电流效率

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