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Preparation of high-purity indium by electrorefining①

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Abstract: The application of indium requires high purity indium as material, and the high purity indium has been prepared by electrorefining. The selection and preparation of electrolyte in electrorefining indium were investigated, and the effect of component of electrolytic solution on electrolytic refining was also studied. Compared with electrolyte of $InCl_3$-HCl, electrolyte of $In_2(SO_4)_3$-H_2SO_4 has higher stability and lower corrosivity, electrolytic solution can be heated at low temperature, and bath is open and simple, which makes operation more convenient. The results show that the voltage can be kept at 0.3-0.5 V, and the content of indium can exceed 99.999% when the content of indium(Ⅲ) ion and sodium chloride are 80-120 g/L. The bench-scale test of electrolysis was carried out, and the product of indium reaches the national standard of 99.999% high purity indium.

Key words: high-purity indium; electrorefining; component of electrolyte
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1 INTRODUCTION

The demands for indium have increased in recent years because it is used in the ITO thin-film, Ⅲ-Ⅴ semiconductor, fluorescent materials and metallorganic compound etc[1]. These applications need high purity indium as raw materials. The methods of purifying indium include ionic exchange, vacuum distillation, region smelting, low halide and electrorefining[2-11]. Electrorefining, with short process flow, simple and convenient operation and little investment, is a usual purification method. Both the selection of electrolyte and control of component of electrolyte are very important for removing impurities, which have been reported little in China[12-14]. The selection and preparation of electrolyte and effect of component of electrolyte on electrorefining were investigated in this paper.

2 EXPERIMENTAL

2.1 Principle of experiment

In electrorefining, the rude indium is used as anode, the high purity indium as cathode, and $In_2(SO_4)_3$-H_2SO_4 solution as electrolyte. According to the electrochemical theory, indium dissolves on the anode:

$$In - 3e \rightarrow In^{3+} \qquad \varphi^0 = -0.33\ V$$

The standard potentials of metals such as Fe, Al, Zn and Ga are lower than that of indium, therefore, these metals will dissolve in advance, and stay in electrolyte. Metals like Ag, Cu, whose standard potentials are higher than that of indium, will not dissolve and drop into the bottom of the bath, settle in the mud of the anode.

Indium deposits on cathode:

$$In^{3+} + 3e \rightarrow In \qquad \varphi^0 = -0.33\ V$$

Metals such as Fe, Al and Zn will not deposit on the cathode and stay in electrolytic solution because of their lower standard potentials and concentration.

2.2 Procedure of experiment

Some pre-purified indium(99.9%) was dissolved in low concentration solution of H_2SO_4, then some sulfocarbamide and gelatin solution were added into, and pH value was adjusted to 2-3. The solution was dropped into electrolytic bath with agitation. Electrolysis was done in different conditions and the electrolyzed products were dried by vacuum dry box made by Shanghai Laboratory Apparatus Chief Works, 2K-82B type. The acidity of solution was measured by pH meter and the content of impurity of metals was measured by ICP-AES.

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3 RESULTS AND DISCUSSION

3.1 Selection and preparation of electrolytic solution

In electrorefining of indium, the electrolyte is $InCl_3$-HCl or $In_2(SO_4)_3$-H_2SO_4. $InCl_3$-HCl solution has some disadvantages: the reaction of indium dissolving in HCl solution is very slow and the solution must be heated; because of the volatilization of HCl, the loss rate of HCl is large during the course of preparing electrolyte; other new impurities will be brought in electrolyte because of the fugitiveness and corrosiveness of HCl; the bath must be sealed because poisonous chlorine will be given off on anode.

Compared with electrolyte of $InCl_3$-HCl, the $In_2(SO_4)_3$-H_2SO_4 solution has higher stability and lower corrosiveness, the electrolytic solution can be heated at low temperature, and the bath is open and simple, which make operation more convenient.

The concentration of H_2SO_4 solution must be low because the solubility of $In_2(SO_4)_3$ is low in high concentration solution of H_2SO_4 (Table 1). In addition, the concentrated sulfuric acid has strong oxidisability, and sulfur will form during preparing electrolytic solution. Therefore, the concentration of H_2SO_4 should be controlled at 20%-40%. When pH value of electrolyte is excessively lower, NaOH should be portionwise added into electrolyte and the solution shuld be agitated so that $In(OH)_3$ can be dissolved in time, otherwise, a great deal of white deposition of $In(OH)_3$ will bring trouble for adjusting pH of electrolytic solution.

Table 1 Relation between solubility of indium sulfate and concentration of sulfuric acid (%)

Concentration of sulfuric acid	3.6	10.3	20.2	25.3	28.2	41.3	53.4	90.2
Solubility of indium sulfate	51.2	40.8	30.4	24.8	21.6	6.5	0.75	0.07

3.2 Effect of concentration of In^{3+} on electrolysis

The influence of the content of In^{3+} on the effect of electrolysis was investigated by changing the content of In^{3+} in the conditions of 25 ℃, bath voltage 0.3-0.5 V, current density 100 A/m^2. The result is shown in Fig. 1.

It is shown that the suitable concentration of indium is 80-120 g/L, and the best is 100 g/L; the quality of indium will be worse when its concentration is too high or low. When the content of indium is too low, the cathode potential will increase. Therefore, the impurity will deposit in indium and the product of indium will not be dense. When the content of indium is too high, the density and viscosity of electrolyte will increase. Therefore, the anode mud and other impurity grain in electrolyte will settle down slowly, which leads to the content of impurity in the cathode high, and the product can not meet the standard of 99.999% high-purity indium. The level of impurities in product of indium in different contents of indium at 25 ℃ is shown in Table 2.

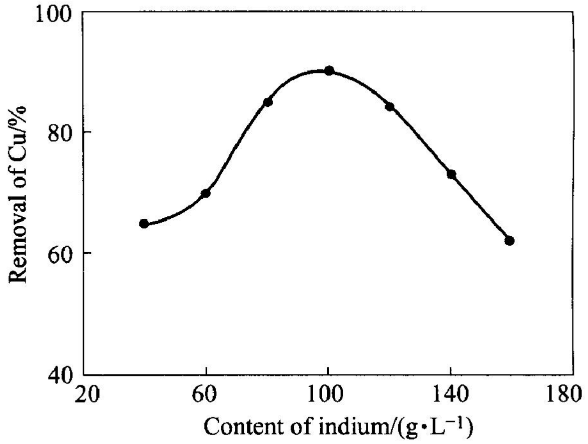

Fig. 1 Relation between content of In^{3+} and removal rate of Cu

Table 2 Level of impurity in indium in different content of In^{3+} at 25 ℃ (mass fraction, 10^{-6})

Impurity	Content of In^{3+} /(g·L^{-1})						
	40	60	80	100	120	140	160
Cu	3.1	1.6	0.80	0.75	0.74	1.5	2.8
Fe	3.0	1.4	0.70	0.74	0.79	1.6	2.7
Pb	5.1	4.4	1.7	1.5	1.4	4.2	5.0
Ag	1.1	0.9	0.65	0.41	0.52	0.8	1.0
Sn	4.1	2.7	1.9	1.6	1.8	2.5	3.9
Cd	0.68	0.49	0.41	0.32	0.33	0.50	0.70
Tl	2.4	1.7	0.85	0.71	0.75	1.6	2.7
Zn	2.5	1.8	1.0	0.72	1.3	1.7	2.4

3.3 Effect of pH on quality of product

Under the conditions of 25 ℃, bath voltage 0.3-0.5 V, current density 80 A/m^2, indium was electrolyzed at pH 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 4.5 respectively, and the content of tin in product indium was measured. The results are shown in Fig. 2.

When pH is between 2 and 3, the content of tin is lower; when pH is lower than 2.5, the content of tin decreases with pH value increasing; when pH value is lower than 1.0, the discharging phenomenon of H^+ on the cathode is very serious and the product in-

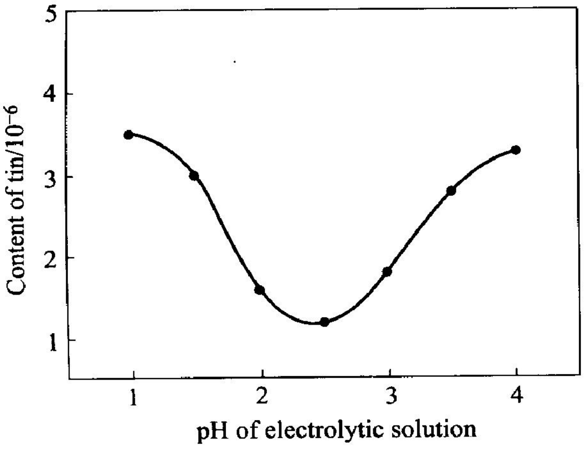

Fig. 2 Relation between pH and content of tin

dium looks like loose sponge, whose absorbability is so strong that it can absorb insoluble materials such as anode mud in the electrolytic solution; when pH is higher than 2.5, the content of tin increases with pH increasing. Because indium is easy to hydrolyze at higher pH and is transformed into white deposition of In(OH)$_3$, so some impurities such as Sn, Pb will deposit altogether with indium.

3.4 Effect of concentration of NaCl on electrolysis

NaCl is added as auxiliary electrolyte in order to enhance the conductivity of electrolytic solution[15]. The concentration of NaCl can affect the migration velocity of ion. The influence of content of NaCl on bath voltage was investigated by changing the content of NaCl under the conditions of 25 ℃, current density 100 A/m^2. The results are shown in Fig. 3.

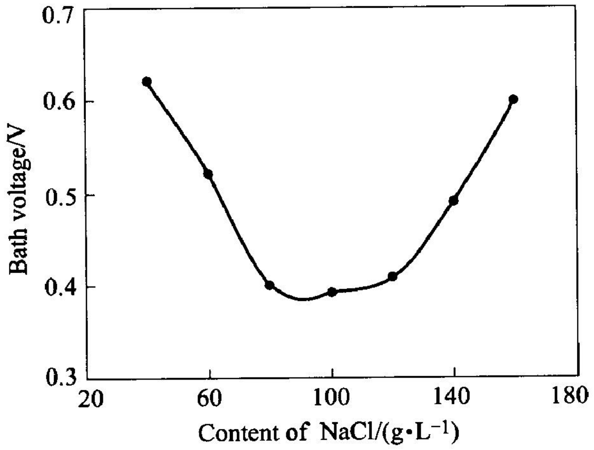

Fig. 3 Relation between cell voltage and content of sodium chloride

When the content of NaCl is higher than 120 g/L, the migration of ion is hindered, so the resistance of solution increases, therefore, the bath voltage increases. When the content of NaCl is lower than 80 g/L, the transfer number of ions is smaller, the conductivity decreases, and the bath voltage increases. Therefore, the suitable concentration of NaCl is 80 – 120 g/L, and the bath voltage will be 0.3 – 0.5 V.

3.5 Effect of electrolysis

Impurities in indium can be removed through twice electrolytic refining by controlling the component of electrolyte and selecting suitable electrolytic conditions. The XRD pattern (Fig. 4) of the product is similar with 5-0641 minor correction. After twice electrolytic refining, the product of indium was analyzed by ICP-AES. The results (see Table 3) show that the impurity contents satisfy the national standard of 99.999% high purity indium[16].

3.6 Bench-scale tests of electrolysis

The bench-scale tests of electrolysis was carried out, and the conditions are shown in Table 4.

5 000 g indium was refined, the product of initial electrorefining was 1 985 g, the product of secondary electrorefining was 3 103 g, and the loss rate of indium was 0.21%. The technical data of bench-scale tests of electrolysis are shown in Table 5, and the contents of impurities in product are shown in Table 6.

Table 6 shows that the level of initial electro-refining product exceeds 99.99%, and the second-

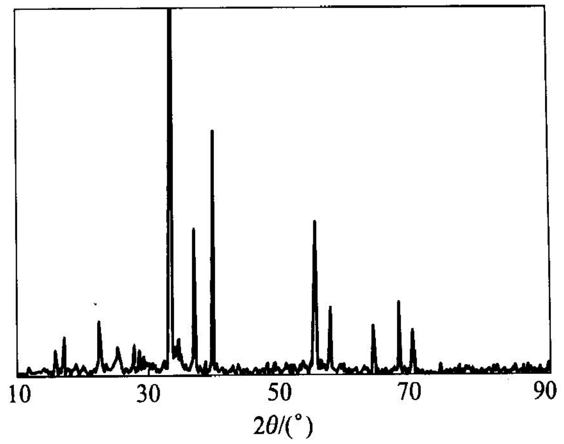

Fig. 4 XRD pattern of sample

Table 3 Level of impurity in indium in electrolytic refining (mass fraction, 10^{-6})

Impurity	Ag	Pb	Cu	Cd	Al	Fe	Zn	Sn	Tl	Mg	Si	S	Ni	As
Initial refining	0.3	1.5	0.7	0.3	0.5	0.7	0.6	1.4	1.5	0.5	1.5	1.2	0.5	0.5
Secondary refining	0.1	1.0	0.1	0.1	0.3	0.4	0.4	1.0	1.0	0.1	1.0	1.0	0.4	0.5
In-05 Standard	0.5	1.0	0.4	0.5	0.5	0.5	0.5	1.5	1.0	0.5	1.0	1.0	0.5	0.5

Table 4 Technical conditions of bench-scale tests of electrolysis

Process	Current density/ (A·m^{-2})	Bath voltage/ V	Temperature/ ℃	pH	Interelectrode distance/ mm
Initial electrorefining	80-100	0.3-0.4	28-35	2.0-3.0	80
Secondary electrorefining	50-80	0.2-0.3	20-30	2.0-2.5	70

Table 5 Technical data of bench-scale tests of electrolysis

Process	Test No.	Recovery rate of indium/ %	Current efficiency/ %	Bath voltage/ V	Rate of anode mud/ %	Rate of residual electrode/ %	Time of electrolysis/ h
Initial electrorefining	1-1	99.58	99.21	0.34	0.15	31.5	150
	1-2	99.67	99.35	0.36	0.20	34.2	140
	1-3	99.36	99.40	0.32	0.23	36.1	120
Secondary electrorefining	2-1	99.90	100	0.27	—	37.4	155
	2-2	99.84	100	0.24	—	32.3	150
	2-3	99.68	100	0.21	0.03	35.8	144

Table 6 Content of impurity in product of indium (mass fraction, %)

Product	Test No.	Pb	Cd	Sn	Zn	Fe	Al	Tl	Cu	In
Initial electrorefining	1-1	0.000 24	0.000 09	0.000 31	0.000 34	0.000 40	0.000 30	0.000 54	0.000 05	99.998
	1-2	0.000 37	0.000 07	0.000 28	0.000 24	0.000 35	0.000 28	0.000 47	0.000 06	99.998
	1-3	0.000 30	0.000 08	0.000 34	0.000 28	0.000 29	0.000 34	0.000 44	0.000 04	99.996
	1-4	0.000 40	0.000 07	0.000 32	0.000 25	0.000 34	0.000 37	0.000 40	0.000 07	99.997
Secondary electrorefining	2-1	0.000 15	0.000 03	0.000 14	0.000 08	0.000 07	0.000 04	0.000 14	0.000 03	99.999 3
	2-2	0.000 12	0.000 05	0.000 12	0.000 06	0.000 06	0.000 03	0.000 10	0.000 02	99.999 4
	2-3	0.000 10	0.000 04	0.000 10	0.000 07	0.000 05	0.000 04	0.000 10	0.000 03	99.999 4
	2-4	0.000 14	0.000 04	0.000 12	0.000 06	0.000 07	0.000 04	0.000 11	0.000 02	99.999 3

ary electrorefining product exceeds 99.999%, which reaches the national standard of 5N high purity indium.

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