ABSTRACT

Of dissertation for the doctor of philosophy degree (PhD)

specialty 6D72000 - "Chemical technology of inorganic substances"

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Modernization of electrochemical refining of indium with application of computational methods.

The dissertation is devoted to the development and improvement of the technology of high-purity indium from rough indium grade In-2 by electrochemical refining. In the course of the work, a comprehensive study of the kinetics of the discharge of ionic indium was carried out, simulation modeling was used to optimize the design of the electrolyzer, the possibilities of reducing energy consumption were demonstrated, and a method for obtaining metallic indium with a purity of 99.99989% by reaction electrolysis was also proposed. The influence of factors influencing the rate of stages of electrode efficiency in the electrochemical use of modern electrochemical methods and advanced theoretical models has been studied and analyzed.

All research within the framework of the dissertation were conducted for the first time, the results are presented in the form of articles, including in a peer-reviewed journal, and abstracts of reports of international conferences.

Relevance of the research topic.

The sharp increase in demand for indium in the world market is directly related to the production of indium tin oxide (ITO). ITO has many unique properties: transparency, high electrical conductivity, good adhesion to glass, and others. The emergence of a material with the above properties made it possible to quickly develop the production of touch screens, solar panels and create a demand for high-purity indium. Previously, indium antimonides, phosphides and nitrides were used in the manufacture of transistors and microchips. In addition, due to the low frictional force, indium was used to coat bearings in Formula 1 cars. The low melting point of indium and its alloys made it possible to use them to extinguish fires in warehouses and other specialized places. The main applications for indium are: touch screens, LEDs, batteries, medical technology, photovoltaic technology, and construction equipment.

The amount of indium consumed largely depends on the global display production. For example, in 2012, the world produced 935 tons of refined indium, and the amount of refined indium from the processing of industrial waste was 550 tons. In recent years, the demand for indium has skyrocketed due to the growth in LCD monitor production. Currently, about 50% of the indium produced is used in the production of LCD screens. South Korea, the world's largest producer of indium, produced 1,450 tonnes in 2015 alone, and China, Japan and Taiwan are also major indium producers. According to the United Nations Environment Program, the degree of recycling of indium in the world according to 2015 data

was only 1%. Demand for indium from secondary sources rose sharply after a number of mining companies in China stopped processing and recovering indium from zinc tailings. JSC "Kazzinc", which previously produced about 1 ton of black indium grade In-2 per year from zinc dust in our country, stopped the production of indium in 2019. The Ural Mining and Processing Plant (UMMC-Holding) is the only enterprise in the post-Soviet space that is currently engaged in the production of indium in the amount of 6-10 tons per year, which includes two plants belonging to the Chelyabinsk Zinc Plant and Electrozinc. These numbers are negligible compared to global manufacturing capacity. Considering that more than 40% of the raw materials required for the production of zinc UMMC-Holding receives from the territory of the Kostanay and Akmola regions of the Republic of Kazakhstan, then for our country this is a good challenge for the development of its own technologies for the production of rare metals. Russia exports 5-8 tons of indium produced in the country and uses only 1 ton in the domestic market for the production of electronics. If the price of indium in 2014 was 700-780 US dollars, on the contrary, in November 2015, due to the increase in supply, the price in the world market fell to 240-285 US dollars. Recently, the price of indium has fluctuated between $ 530 and $ 700.

The economic value of indium metal production is growing from year to year, and the global production capacity of indium shows an annual growth from 5% to 10%. Considering that the global production capacity of indium reaches 900-2000 tons per year, 10% annual growth is a great indicator and stimulates the development of environmentally friendly and economically efficient technologies that make it possible to extract indium from secondary raw materials and man-made waste. Therefore, one of the most pressing problems is the development and development of technologies for the production of high-purity indium.

The purpose of the thesis is development of a cheap and environmentally friendly method for obtaining high-purity indium by improving the technology of electrochemical refining of rough indium, grade In-2, produced in the Republic of Kazakhstan using calculation methods.

To achieve the goal, the following tasks were set:

1. Comprehensive study of the kinetics of electrochemical deposition of indium from aqueous electrolytes.
2. Determination of the optimal composition of the levelling additive, which makes it possible to improve the quality of the cathode deposit, based on an in-depth study of the kinetics of the stage of electrochemical nucleation.
3. Optimization of electrolysis conditions by studying the influence of the electrolyte composition, solution pH, temperature and depressant additive on the rate of indium anodic dissolution.
4. Development of a simulation model of the electrochemical refining of indium in COMSOL Multiphysics using the results of studying the kinetics of the discharge-ionization of indium.
5. Carrying out electrochemical refining of indium under optimal conditions determined on the basis of kinetic studies and modeling; determination of the purity of the resulting cathode deposit.

Objects of study: rough indium grade In-2, indium anodes modified with bismuth, simulation model of indium refining.

Subject of research: Kinetics and mechanism of electrode reactions occurring during the electrochemical refining of indium, kinetics of electrochemical crystallization of indium, modelling of electrode reactions.

Research Methods. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), chronoamperometry (CA), electrolysis, rotating disc electrode (RDE), scanning electron microscopy (SEM), optical emission spectroscopy with inductively coupled plasma (ICP-OES), inductively coupled plasma mass spectroscopy (ICP-MS), modelling in COMSOL Multiphysics.

The source base and research materials are 174 sources of literature on electrochemical deposition and electrorefining of indium, as well as on other areas of chemistry and natural science related to the topic of this study.

Scientific novelty:

- Using the method of electrochemical impedance spectroscopy, the rate constants of the stages of charge transfer and mass transfer of the electrochemical reduction of indium from aqueous chloride electrolytes have been found, the limiting stage of the electrode reaction and the mechanism of the electrochemical reduction of indium corresponding to the chemical-electrochemical mechanism have been determined. The kinetics of the electroreduction of indium on various solid electrodes was studied, and it was found that the rate of the electrodeposition of indium on a titanium electrode is slightly higher compared to other solid electrodes.

- The stage of electrochemical nucleation has been studied in detail and it has been established that tetrabutylammonium chloride has an inhibitory ability of dendrite formation during the electrodeposition of indium, which makes it possible to obtain dense cathode precipitates at its low concentrations. Also, electrochemical deposition of indium from protonated betaine-bis (trifluoromethylsulfonyl) imide ionic liquid was studied for the first time.

- It was found that the use of bismuth as a depressant additive accelerates the anodic dissolution of indium, reducing the activation energy of the process and anodic overvoltage.

- A simulation model for the electrorefining of indium was developed based on the kinetic data of the discharge-ionization of indium in the COMSOL Multiphysics program.

- A method has been developed for obtaining metallic indium with a purity of 99.99989% by optimizing the conditions of electrolysis.

The theoretical significance of the study. As a result of a comprehensive study of the kinetics of electrochemical reduction of indium, a lot of quantitative data on the kinetics of the reaction and on the influence of various factors: surfactants, the nature of the electrode material, and the composition of the electrolyte on the kinetics of the electrode reaction were obtained. These data were used to simulate the electrode reaction in the context of this dissertation work and

may in the future contribute to the development of the electrochemistry of rare metals in general and the electrochemistry of indium in particular.

Practical value. The method of electrochemical refining of indium presented in the dissertation allows deep refining of rough indium of the In-2 brand, produced in the Republic of Kazakhstan, and obtaining a product with high added value - indium of the In000 brand. The simulation model presented in this paper can be used to improve the design of electrolyzers for refining other metals.

The main provisions to be defended:

1. Methods for studying the kinetics of electrochemical reduction of indium on solid electrodes.

2. Aqueous electrolyte containing tetrabutylammonium chloride, as well as an electrolyte based on protonated betaine bis-(trifluoromethylsulfonyl) imide ionic liquid, which makes it possible to obtain high-quality indium cathode precipitates; electrolysis conditions.

3. Simulation model of electrochemical refining of indium.

4. A new method for producing metallic indium with a purity of 99.99989%.

The main results of the dissertation research are reflected in 7 scientific papers, including:

- in 4 article published in a periodical indexed by the Web of Science database;
- in 3 articles published in scientific journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in 9 abstracts of reports at national and foreign international conferences and symposia.

The structure and scope of the dissertation.

The dissertation consists of an introduction, three sections, a conclusion, as well as a list of sources used from 174 items. The work is presented on 142 pages, contains 71 figures and 27 tables.

Based on the results of the dissertation research, the following conclusions are made:

1. The kinetic characteristics of the electrochemical reduction of In^{3+} ions from a perchlorate-chloride electrolyte on an indium electrode have been determined. The results of impedance measurements showed that the process is carried out according to a chemical-electrochemical mechanism, as evidenced by the presence of the Gerischer impedance.

2. The limiting stage of the electrochemical reduction of indium was determined by comparing the rate constants of the charge transfer (k) and mass transfer (m) steps, and it was found that the limiting step was diffusion. It was found that the effective mass transfer rate constant is $1.3\ 10^{-4}$ cm/s, and the value of the charge transfer rate constant calculated as a result of impedance measurements was $3.06\ 10^{-3}$ cm/s.

3. The electrochemical reduction of indium in platinum, glassy carbon, titanium electrodes has been studied, and the values of k and m have been found by electrochemical methods. The k and m values of the electrochemical reduction of

indium on the titanium electrode were 11.2×10^{-3} cm/s and 4.5×10^{-4} cm/s, respectively. It has been established that the use of titanium electrodes allows the electrolysis of indium at high current densities, providing a high current efficiency.

4. In order to obtain a dense cathode deposit during electrochemical refining, indium was deposited on a glassy carbon electrode from an electrolyte containing tetrabutylammonium chloride. It has been found that the addition of 10^{-4} M tetrabutylammonium chloride to the electrodeposition electrolyte has a levelling effect. The addition of 10^{-4} M tetrabutylammonium chloride reduces the average radius of indium crystal centers in the cathode deposit from 12.5 microns to 5.7 microns, at a cathodic polarization of 310 mV, and contributes to an increase in the density of the cathode coating, which is confirmed by the results of scanning electron microscopy.

5. A simulation model for the electrochemical refining of indium in COMSOL Multiphysics has been developed using the numerical values of the experimentally determined kinetic characteristics of the discharge – ionization reactions of indium. This model allows you to optimize the design of the electrolyzer, to select the most effective electrolysis conditions.

6. The efficiency of using reaction electrolysis in the electrochemical refining of indium has been determined. As a result, it was found that the use of bismuth as a depressant additive facilitates the anodic dissolution of indium in modified anodes and reduces the activation energy of the process. The purity of cathode indium obtained by electrochemical refining using a modified indium anode - A2 was 99.99989%, which corresponds to the In000 grade. Analysis of the composition of electrorefined indium by ICP-MS and ICP-OES methods showed that the total concentration of impurities (Zn, Pb, Cd, Cu, Fe, Ni, As, Sn, Tl) in purified indium decreases to 1.1 ppm.

Assessment of the completeness of the solutions to the tasks. All the tasks set for solving the purpose of this dissertation are solved in full.

Thus, the objectives of the dissertation research were achieved on the basis of studying the kinetics of the discharge-ionization of indium using modern electrochemical and computational methods, a method was developed for the electrochemical refining of rough indium (In-2) to a purity corresponding to the In000 grade.

Assessment of technical and economic efficiency of the solutions proposed in the thesis. The solutions presented in this dissertation can become the basis for the production of products with high added value - metal indium of the In000 brand.