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Electrolytic Recovery of Indium from Copper Indium Gallium Selenide Photovoltaic Panels: Preliminary Investigation of Process Parameters

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Abstract: The European Green Deal emphasizes the development of renewable energy sources to combat climate change. However, as photovoltaic expansion accelerates, so does the potential for increased waste, necessitating effective material recycling strategies. Indium, a scarce and valuable element crucial to the production of photovoltaic panels, underscores the necessity for efficient recycling practices to reduce reliance on virgin resources. In a recent laboratory analysis, a CIGS photovoltaic panel underwent a series of processes including crushing, grinding, and homogenization. The concentration of indium, vital for recycling, was meticulously analyzed using ICP-MS and validated through microscopic and composition analyses. Subsequent extraction utilizing 3 M HCl and H_2O_2, followed by electrolysis, yielded a remarkable up to 52% indium recovery within a 48-h timeframe. Importantly, the study encompassed both averaged panel samples and samples from the absorbing layer, emphasizing the comprehensive approach required for efficient recycling. This underscores the critical importance of optimizing recycling processes to mitigate the environmental impact associated with the disposal of photovoltaic panels. By maximizing indium recovery, not only are environmental impacts reduced, but the long-term sustainability of renewable energy technologies is also ensured. This highlights the interconnectedness of recycling practices with the broader goals of achieving a circular economy and securing the viability of renewable energy systems in the fight against climate change.

Keywords: indium recovery; photovoltaic panel; CIGS; electrolysis

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1. Introduction

The sustainable economic development of every country is closely tied to resource availability. Ensuring stable resource supplies is crucial for many industrial sectors that produce essential goods to meet diverse societal needs. Population growth, dynamic industrialization, the transition towards ecological transportation and energy systems, constantly increasing demand, and new technological innovations are the main factors driving increased demand for critical resources.

The development of technologies based on renewable energy sources is also associated with a continuous demand for critical resources. Resource recovery is therefore crucial to ensuring supply. Hence, research is necessary to develop resource recovery technologies. As the popularity of renewable energy sources such as solar energy grows, it is important for all associated infrastructure to be sustainable. Recycling CIGS panels aligns with efforts towards sustainable development by addressing potential issues related to electronic waste

accumulation and resource utilization. The production process of photovoltaic panels, especially in terms of resource extraction and processing, generates a certain ecological footprint. Recycling CIGS panels helps minimize this footprint because recovered resources can be reused, reducing the amount of electronic waste going to landfills. It also contributes to efficient energy use since reusing recovered resources eliminates the need for mining and processing new ones, which often involves high energy consumption and provides materials for the production of new photovoltaic panels. This closed-loop approach to material circulation is crucial for the sustainable development of the photovoltaic industry [1–4].

Although crystalline silicon dominates the photovoltaic (PV) market, thin-film technologies such as CIGS (copper indium gallium selenide) panels have gained attention due to their high absorption coefficients, flexibility, and potential for lower production costs. As of recent market data, CIGS panels account for approximately 2–3% of global PV production, with annual production capacities estimated at around 1 GW in the past few years. While relatively small in market share, CIGS panels are expected to generate increasing volumes of waste in the coming decades, particularly as earlier generations of these panels reach their end of life [5,6].

Forecasts suggest that by 2030, thousands of tons of CIGS-based PV waste will enter the recycling stream annually, creating a growing need for recovery strategies targeting their critical raw materials, especially indium and gallium [7].

A typical CIGS photovoltaic module contains approximately [8–10]:

- 65–75% glass (by weight);
- 10–15% polymer layers (e.g., EVA, back contact);
- 5–10% metals such as aluminum, molybdenum, and copper;
- <2% semiconducting layer, which includes copper, indium, gallium, and selenium;
- Indium content typically ranging from 100 to 300 ppm, depending on thickness and manufacturer specifications.

Given the limited global reserves and rising demand for indium in high-tech applications, developing efficient recovery technologies from end-of-life CIGS panels is both environmentally and economically justified.

CIGS panels are a type of second-generation thin-film photovoltaic technology, renowned for their high efficiency, lightweight design, and flexibility. These panels utilize a thin layer of copper indium gallium selenide (CIGS) deposited onto a substrate, enabling the production of versatile and cost-effective solar modules. With their favorable performance in low-light conditions and potential for integration into various surfaces, CIGS panels present a promising alternative to traditional silicon-based solar technologies, particularly in applications where weight and adaptability are crucial factors. However, despite these advantages, a major challenge associated with the widespread deployment of CIGS panels lies in the limited availability of critical raw materials used in their production. Indium, in particular, is a key component of the CIGS semiconductor and is primarily obtained as a by-product of zinc extraction. Both indium and gallium are listed among the European Union's critical raw materials due to their economic importance and supply risks. As a result, the recovery of these elements from end-of-life CIGS panels is essential for promoting resource sustainability, reducing dependence on primary raw materials, and supporting the long-term scalability of CIGS technology in the renewable energy sector [11,12]. Effective waste management and recycling of CIGS solar panels are critical due to the toxic nature of the material, which can pose serious environmental risks and potential health hazards, including lung toxicity. While indium is a critical component in CIGS photovoltaic cells due to its role in enabling high-efficiency energy conversion, its presence in end-of-life modules raises significant environmental and occupational health concerns. Although not as widely recognized as other toxic metals, indium has gained

attention in recent years for its potential harmful effects, particularly in its oxidized forms. Exposure to indium—especially in the form of indium oxide, a common by-product in the processing and recycling of CIGS panels—has been linked to serious respiratory issues. Research indicates that inhalation of indium-containing dust or fumes can lead to chronic pulmonary conditions, including interstitial lung disease and alveolar proteinosis. Unlike many metals that pose greater risks in their ionic or soluble forms, indium oxide presents dangers even in its particulate state, further complicating safe recovery operations. As the use of indium continues to expand across the electronics and renewable energy sectors, addressing its toxicological profile becomes crucial. Future recycling strategies for CIGS modules must incorporate not only efficient metal recovery techniques but also protective measures to minimize human exposure and environmental release, ensuring that the transition to clean energy does not come at the cost of health and safety [13–15].

The focus of this article and the associated research on CIGS photovoltaic panels can be attributed to several key factors that make CIGS technology particularly relevant for current and future solar energy applications. Firstly, CIGS solar cells have gained considerable attention in the photovoltaic industry due to their high efficiency and potential for low-cost production. CIGS modules have demonstrated superior energy conversion efficiency compared to many other thin-film technologies, making them a prominent choice for sustainable energy generation. Additionally, CIGS technology is known for its flexibility and lightweight characteristics, which opens up possibilities for a wider range of applications compared to traditional crystalline silicon-based solar cells. These unique features make CIGS modules increasingly popular in both industrial-scale and emerging energy solutions. Secondly, CIGS modules contain valuable and critical materials such as Ga, In, and Ag, which are in high demand for various high-tech applications [7]. As the global transition to renewable energy accelerates, the need for efficient recycling technologies becomes paramount to ensure the sustainability of this growing industry. CIGS panels, due to their material composition, are of particular interest when it comes to recovering these scarce and high-value elements. This has sparked considerable research into improving recycling methods and minimizing environmental impact. Lastly, CIGS technology is widely considered to be at the forefront of thin-film solar cell development, with significant ongoing research aimed at improving the efficiency and lifespan of these panels. Focusing research on CIGS provides an opportunity to not only advance the recycling methods for a widely used technology but also to address the broader challenges of material recovery and waste management in the solar panel industry [11,16].

CIGS panels are known for their lightweight and flexible design, which provides significant advantages over traditional crystalline silicon solar cells. These advantages include enhanced applicability in various installation scenarios, from residential rooftops to more unconventional surfaces. The structure of a CIGS panel is multi-layered, with each layer serving a specific purpose to maximize the efficiency of light absorption and energy conversion. Below, a schematic diagram is presented, illustrating the layers of a CIGS solar panel (Figure 1).

Below is a short description of the individual layers of a CIGS panel.

The **front contact layer** serves a protective function. The front layer in CIGS panels is typically made of materials that are transparent to sunlight, allowing it to penetrate freely into the absorber layer. The most commonly used materials are thin-film layers of silicon dioxide (SiO_2) or zinc oxide (ZnO). In ITO (indium tin oxide) panels, zinc oxide can be replaced by aluminum or gallium.

The **protective layer** is a crucial element ensuring the longevity of CIGS panels while also needing to be sufficiently transparent to allow light to pass through to the absorber

layer. The composition of this layer may vary depending on the specific panel design and manufacturer preference.

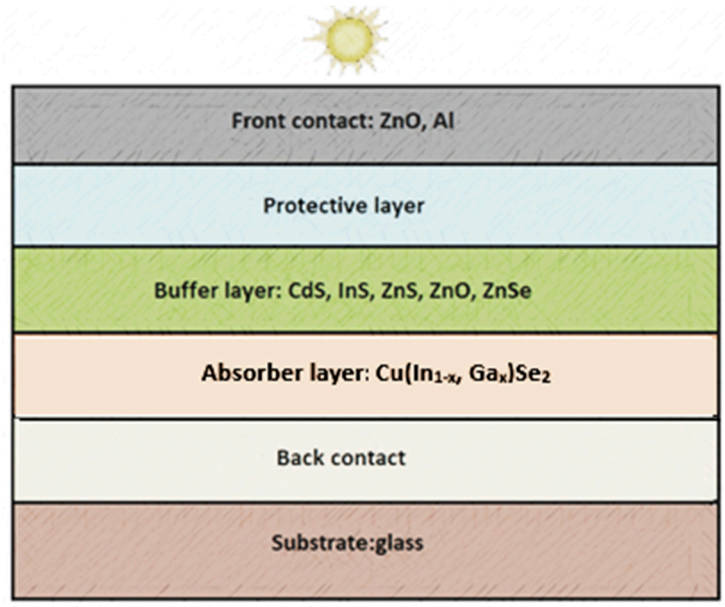


Figure 1. A diagram depicting the layers of a CIGS panel [17–19].

The **buffer layer** plays a role in ensuring the efficiency and stability of panels. In the case of CIGS panels and other thin-film photovoltaic panels, the buffer layer is often used between the absorber layer and the current-collecting layer. The main goals of the buffer layer are:

- Minimizing carrier loss: The buffer layer helps minimize carrier recombination, which can occur at the interface between the absorber layer and the current-collecting layer. Recombination is the process where charge carriers (electrons and holes) combine and lose their energy, which is undesirable as it affects the efficiency of solar energy conversion.
- Improving electrostatic balance: The buffer layer helps maintain electrostatic balance between the absorber layer and the current-collecting layer, which is crucial for effective charge carrier transport.
- Protection of the absorber layer: The buffer layer also serves a protective role, shielding the absorber layer from damage and the effects of atmospheric conditions.
- Improving panel structure coherence: Adding a buffer layer can improve the coherence of panel structures, which is crucial for achieving uniform and efficient solar energy conversion.

In the case of CIGS panels, a semiconductor-based buffer layer, such as CdS, is typically used. However, it is worth noting that the development of photovoltaic technologies is dynamic, and different panels may use different materials in the buffer layer depending on the technology and production process.

The **CIGS absorber layer** plays a crucial role in converting light energy into electrical energy. It is the layer where photons of sunlight are absorbed, leading to the generation of electrical current. The main components of the absorber layer are copper, indium, gallium, and selenium. The absorber layer in CIGS panels is typically very thin, on the order of a few micrometers, which is one of the characteristic features of thin-film photovoltaic panel technology. This structure allows for flexibility, reduced production costs, and application on various types of surfaces.

The **back contact layer** acts as the current-collecting electrode on the reverse side of the panels. It is a crucial layer for efficiently collecting charge carriers generated in the absorber layer as a result of sunlight absorption. Typically, the back contact layer in CIGS panels consists of materials with conducting properties. This layer can be relatively thin, allowing for the free flow of electrical current. Materials such as molybdenum are commonly used in this layer [17–20].

CIGS photovoltaic panels based on copper, indium, gallium, and selenium compounds typically have a long lifespan, often exceeding 25 years. The durability of these panels depends on various factors, such as production quality, operating conditions, the quality of materials used, and applied technologies. Recycling CIGS photovoltaic panels is crucial, especially in the context of growing interest in renewable energy sources. Copper and gallium, which are key components of CIGS panels, are critical resources. Their resources are limited, and recycling allows for the efficient recovery of these valuable materials while also minimizing the need for new, limited resources [21,22]. The significant recovery of indium underscores its crucial role in the production of photovoltaic panels and highlights the necessity for efficient recycling practices to alleviate reliance on virgin resources. Indium, a scarce and valuable element, is a vital component in the production of high-efficiency solar cells, making its recovery essential for the sustainability of renewable energy technologies and the circular economy. Thus, optimizing indium recovery processes not only mitigates environmental impact but also ensures the long-term viability of renewable energy systems. One of the methods used for metal recovery from spent photovoltaic panels is electrolysis. Indium can undergo electrodeposition from a variety of electrolyte solutions, such as cyanide, sulfate, and chloride [21–23].

Gu et al. [24] recovered valuable components from spent CIGS modules by combining electrochemical techniques with dehydration and distillation processes. Initially, the leaching solution of CIGS undergoes a two-step electrodeposition process to recover selenium and copper. Subsequently, the remaining solution is distilled to recycle hydrochloric acid (HCl) and crystallize indium and gallium chlorides. The obtained hydrates are then dehydrated through refluxing with thionyl chloride ($SOCl_2$). Following this step, anhydrous $InCl_3$ is recovered and separated from $GaCl_3$ via a straightforward filtration process. $GaCl_3$ is further separated from $SOCl_2$ through distillation. The recovery rates for indium and gallium are high, at approximately 99.99% and 99.98%, respectively, with corresponding purities of around 99.99%. As part of this study, an attempt was made to simplify this process.

Liu et al. [25] proposed a recycling process for Cu, In, and Ga from CIGS-based thin-film solar panels using a multi-step approach. Initially, the panels are separated layer by layer based on the different thermal strains of materials. Subsequently, annealing is conducted to remove Se, followed by leaching with nitric acid to facilitate individual metal extraction. In the extraction step, In is extracted into the organic phase using di-(2-ethylhexyl) phosphoric acid, leaving Cu and Ga in the aqueous phase. Ga is then extracted using the same agent under different conditions, while nearly pure Cu remains in the residual solution. Metal hydroxide precipitates are formed by adding ammonium hydroxide to the solutions. Under optimized conditions, a recovery rate of over 90% for In, Ga, and Cu can be achieved. Finally, the hydroxides are recycled and converted into metal oxides with a purity exceeding 99% through calcination. This approach offers an effective pathway for recycling and recovering these valuable metals from waste CIGS thin-film solar panels.

One study [26] investigated the potential of benign leaching conditions for recovering primarily silver and indium from production waste of flexible CIGS solar cells while also assessing contamination levels from other industrial elements in the leachate. Selective

leaching of contaminants was also explored to obtain purer streams of valuable metals for reuse in new products. The results showed that increasing acid concentration and surface to liquid ratio led to higher leaching yields of Ag and In but also increased contamination. Complete Ag recovery and 85% In recovery were achieved with 2 M HNO_3 and A:L of 1:3 cm^2/mL after 24 h of leaching at room temperature. Leaching with 0.5 M HNO_3 extracted 85% Ag and 30% In under the same conditions, with reduced contamination levels. Additionally, leaching with 0.1 M HNO_3 showed promise for achieving higher Ag purity through an initial step of Zn-selective leaching for 1 h.

The method proposed by Hu et al. [27] outlines an oxidative roasting-leaching-extraction process for recovering valuable metals from spent copper indium gallium selenide materials. Initially, the spent CIGS materials undergo roasting to convert copper, indium, and gallium from selenides to oxides while volatilizing selenium. Subsequently, hydrochloric acid leaching is employed to dissolve the oxides under optimized conditions: 4 mol/L acid concentration, 80 °C temperature, 3 h leaching time, and a liquid–solid ratio of 10 mL/g, resulting in high leaching rates of 99.98% for copper, 93.40% for indium, and 96.86% for gallium. In a subsequent step, indium and gallium are sequentially extracted from the solution using P204 solvent extraction, achieving extraction rates exceeding 99.92% for indium and 99.34% for gallium, while copper remains minimally extracted. Utilizing hydrochloric acid as the stripping agent leads to stripping rates of 99.90% for indium and 99.93% for gallium. These findings demonstrate the efficacy of this method for the efficient recovery and separation of copper, indium, and gallium from spent CIGS materials.

Various methods have been developed for recovering valuable metals from spent CIGS panels, each with unique environmental implications. One approach involves electrochemical techniques combined with dehydration and distillation to separate selenium, copper, indium, and gallium, achieving high purity levels. Another method focuses on layer-by-layer separation based on thermal strains, followed by annealing, acid leaching, and selective extraction using organic solvents, resulting in efficient metal recovery. Additionally, controlled leaching conditions have been explored to recover silver and indium while minimizing contamination. Oxidative roasting to convert metal selenides into oxides, followed by hydrochloric acid leaching and solvent extraction, has also shown high recovery rates. Recycling of CIGS panels, however, requires careful consideration of the environmental impacts of each method. While mechanical and innovative techniques offer potential advantages, they require further optimization to minimize their ecological footprint. Advanced methods, such as electrodeposition and selective recovery, show considerable promise in reducing the impacts of global warming and toxicity. These methods contribute to more efficient material recovery and minimize environmental risks associated with the disposal and recycling of end-of-life solar panels, ultimately supporting resource sustainability and waste reduction [19,28–30].

2. Materials and Methods

2.1. Preparation of the Photovoltaic Panel for Laboratory Studies

For laboratory studies, a CIGS photovoltaic panel from NICE Solar Energy GmbH was used, measuring 27 cm × 39.5 cm and with a thickness of 6 mm. The total weight of the panel was 1826 g (Figure 2).

The panel was broken into smaller pieces using a hammer and then ground in a planetary mill. The resulting mixture was mixed and homogenized, and laboratory samples were taken for analysis (referred to as P1–P6 in the conducted research) (Figure 3).

Considering that the CIGS photovoltaic panel is constructed from various materials including glass and the part that absorbs solar energy, the panel was also examined for the possibility of fragmentation and separation of elements richer in extracted resources.

Therefore, to confirm the presence of indium in the panel, a powdered average sample of the panel was subjected to microscopic analysis as well as composition analysis using a high-resolution scanning electron microscope. The same analysis was also performed on a sample isolated from the dark (energy-absorbing) part of the panel, whose macroscopic image is presented in Figure 4.



Figure 2. The CIGS photovoltaic panel from NICE Solar Energy GmbH, which was utilized for laboratory studies.



Figure 3. The ground and homogenized CIGS photovoltaic panel prepared for laboratory studies.

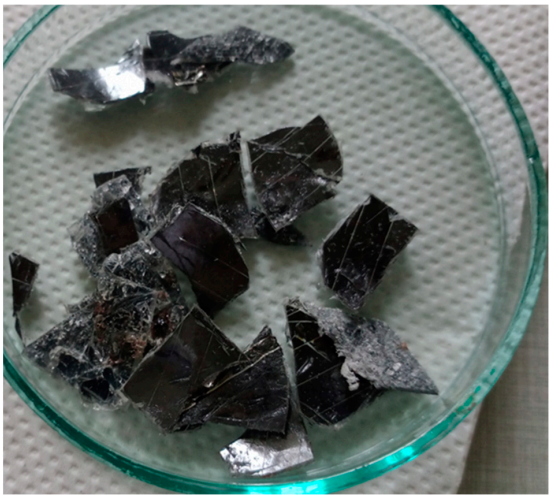


Figure 4. The absorber layer of the CIGS panel.

2.2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

To assess the efficiency of the electrolysis process, samples were collected from the electrolyzed solutions at various predetermined time intervals, with each sample being 100 µL. Subsequently, 1900 µL of 1 M HNO_3 was added to each sample, and they were analyzed using ICP-MS. Additionally, investigations were conducted on the initial sample, comprising ground and homogenized CIGS photovoltaic panels. To achieve this, the sample underwent mineralization using a microwave oven (MARS6, CEM) with 0.5 g of the sample, 6 mL of HNO_3, 2 mL of HCl, and 2 mL of H_2SO_4. The mineralized sample was then diluted and subsequently analyzed using ICP-MS.

Nitric acid (V) 67–69%, hydrochloric acid 36%, and sulfuric acid (VI) 93–98%, used for leaching and mineralization, were produced by ROMIL (high-purity acid dedicated to trace metal analysis). Hydrogen peroxide (35%) used for the experiments was sourced from Merck KGaA. For instrument calibration, the Tuning Solution from LGC Standards containing Ce, Co, Li, Mg, Tl, and Y at a concentration of 1.00 µg/L in 2% HNO_3 was employed.

In the samples, In (m/z 115) was determined using an Agilent 7900 mass spectrometer. Certified reference materials from CPAChem for In at a concentration of 100 mg/L in 2% HNO_3 and a multi-element solution (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn) at a concentration of 1000 mg/L in 6.5% HNO_3 from Supelco were used for the determination of In contents using ICP-MS. The apparatus was calibrated using the Tuning Solution from LGC Standards containing Ce, Co, Li, Mg, Tl, and Y at a concentration of 1.00 µg/L in 2% HNO_3.

2.3. Scanning Electron Microscopy

Microscopic examinations were conducted using a high-resolution scanning electron microscope JEOL JSM-7500F (JEOL Ltd., Tokyo, Japan) equipped with an attachment for chemical composition analysis in micro areas (AZtecLiveLite Xplore 30, Oxford Instruments NanoAnalysis, High Wycombe, UK). The microscope features the following detectors:

- Secondary Electrons (SE) detector used for imaging the surface morphology of materials.
- Backscattered Electrons (BSE) detector utilized for imaging with chemical composition contrast.
- Transmission Electron Detector (TED) employed for observing "thin" samples in transmission mode.

2.4. Electrolysis Operating Conditions

The setup used for electrolysis is depicted in Figure 5.

A beaker containing the electrolyte solution was placed on a magnetic stirrer. Throughout the process, the solution was stirred at 200 rpm using a magnetic stirrer. The electrolysis was conducted using a potentiostat-galvanostat ATLAS 0931. (Atlas-Sollich Zakład Systemów Elektronicznych, Banino, Poland) Three electrodes were immersed in the solution:

- A chlorosilver electrode type RL-100 was used as a reference electrode. It contains a Ag/AgCl half-panel immersed in a non-exchangeable, potassium chloride solution saturated with silver chloride. The reference half-panel is shielded by an outer chamber filled with an intermediate (protective) solution, which is in contact with the sample under investigation via an external electrolytic connector. A 4.0 M potassium chloride solution is used as the intermediate solution.
- A platinum electrode type EPt-01 served as the counter electrode. Its potential depends on the redox equilibrium in the solution. It cannot be used independently but rather in conjunction with a reference electrode with a potential largely independent of the composition of the solution under study. Both electrodes, when connected to a

pH/millivoltmeter, form a redox potential measurement panel. The indicator element of the electrode is a platinum ring permanently attached to the end of the glass body.

- A carbon electrode, specifically the Glassy Carbon Voltammetry Electrode (BASMF2012-1EA, Bioanalytical Systems, Inc. (BASi®), West Lafayette, IN, USA), was used as the working electrode. Its main advantages include temperature resistance, high hardness and durability, a wide potential window, and chemical stability.

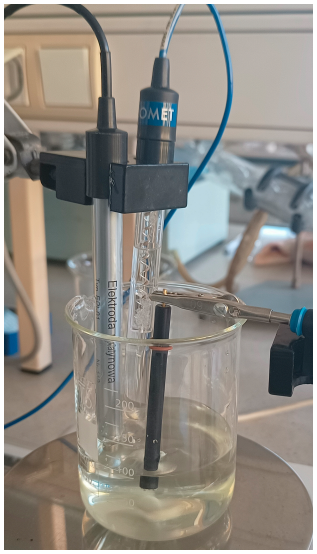


Figure 5. The setup used for electrolysis.

The reagents used for preparing samples of the photovoltaic panel for electrolysis were as follows:

- H_2O_2 (30% concentration, Merck);
- Concentrated HCl (high purity, 35–38%, ROMIL);
- HNO_3 (high purity, 67–69%, ROMIL);
- 1 M HCl—prepared in the laboratory by dissolving concentrated HCl in deionized water;
- 3 M HCl—prepared in the laboratory by dissolving concentrated HCl in deionized water;
- 1 M HNO_3—prepared in the laboratory by dissolving concentrated HNO_3 in deionized water;
- NH_4Cl (analytical grade, POCH);
- Indium beads, diam. 2–5 mm, 99.999% trace metals basis, Sigma Aldrich.

The laboratory equipment used for preparing samples of the photovoltaic panel for electrolysis is listed below:

- Ultrasonic bath with heating function up to 80 °C, SONOREX Bandelin;
- Muffle furnace with temperature gradient setting capability in the range of 30–1800 °C;
- Magnetic stirrer MS11 WIGO;
- Analytical balance Mettler Toledo XP 205.

The conditions for conducting the copper and indium electrolysis process are presented in Table 1.

Table 1. A compilation of conditions for conducting indium electrolysis from solutions after metal extraction from CIGS panel.

Potential [V]	Stirring Speed	Experiment Duration
−0.902	500 rpm	12–72 h, dependent on the concentration of In in the solution

3. Results and Discussion

3.1. Indium Content Analysis in Averaged Panel Samples Versus Samples from the Absorbing Layer

The first stage of laboratory research involved the characterization of the CIGS photovoltaic panel. Preparing the photovoltaic panel for analysis was very challenging due to its composition and diverse fractions, which could not be entirely homogenized in a planetary mill. The aim of grinding and disaggregation of the panel was not to obtain a perfectly homogeneous sample. The panel was prepared in the described manner to facilitate the approximate determination of the analyzed elements using ICP-MS. Additionally, efforts were made to simplify the panel preparation procedure and electrolysis to minimize costs, labor, and time.

Laboratory samples were obtained from the ground and averaged CIGS panel (as described in Section 2.1). These samples underwent mineralization, and after dilution, the content of In was analyzed using ICP-MS.

The obtained research results were compiled in Table 2. They are also presented graphically in Figure 6.

Table 2. Summary of indium content results in averaged panel samples (samples P1-P6). Analysis conducted using ICP-MS on acid-mineralized samples.

The Sample Designation	Indium [mg/g CIGS Panel]
P1	0.1233
P2	0.1525
P3	0.1339
P4	0.0877
P5	0.1461
P6	0.1480
The minimum value	0.0877
The maximum value	0.1525
The median	0.1400
The arithmetic mean	0.1319

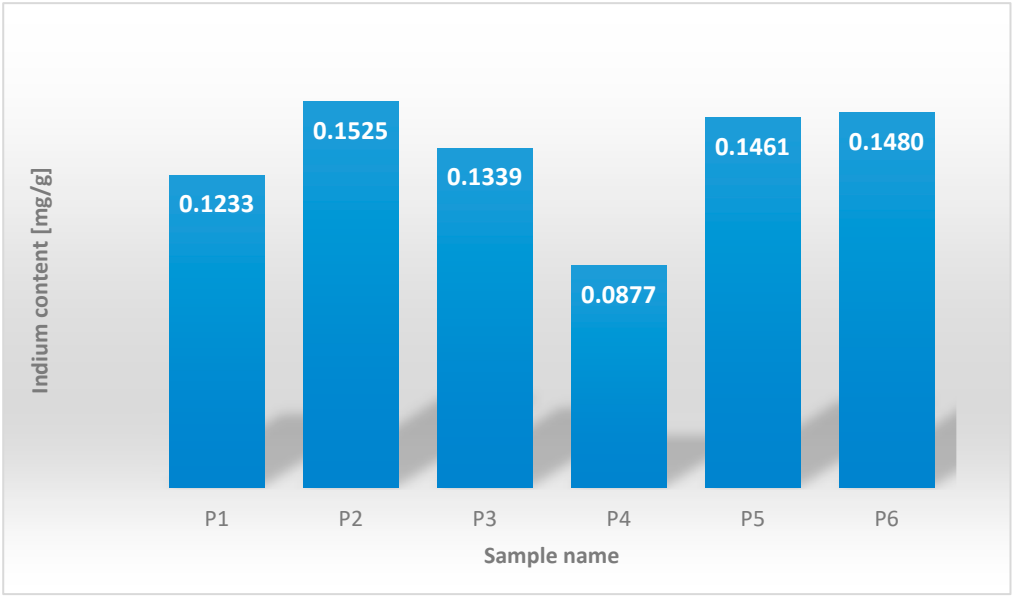


Figure 6. Summary of In content results in averaged panel samples (samples P1–P6). Analysis conducted using ICP-MS on acid-mineralized samples.

The research results indicate that the maximum content of indium in averaged panel samples is 0.152 mg/g. Taking into account the mass of a single panel, which is 1826 g, this allowed us to calculate that from one panel, potentially 277 mg of In can be recovered. The results indicate that the sample was not fully homogenized. To minimize costs and energy consumption associated with sample preparation, the disassembly and grinding of the CIGS panel were deliberately simplified. No thermal or aggressive chemical pretreatment was applied. Furthermore, in the analysis of In content, no outlier data points were removed. Instead, the results are presented as an approximate concentration range observed in the processed samples from the panel.

CIGS panels at the end of their life cycle are gaining increasing attention as an unconventional yet valuable source of critical raw materials. According to the literature, they contain indium in concentrations of approximately 100–300 ppm—levels that exceed those typically found in natural mineral deposits [8,9]. The concentration of indium obtained in our study (approximately 150 ppm) is consistent with the values reported in the literature, confirming the potential of CIGS panels as a significant secondary source of this element. Figures 7–9 depict the images and graphs obtained for the characterized ground and averaged panel sample, the macroscopic images of which are shown in Figures 2 and 3.

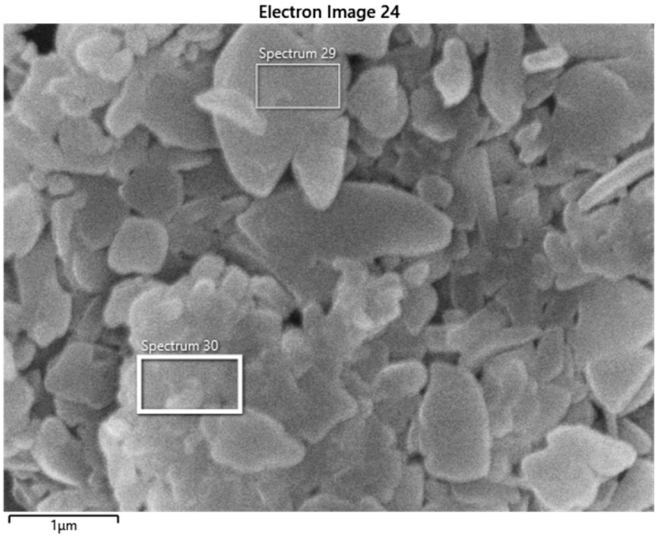


Figure 7. The image from the electron microscope of the averaged CIGS panel sample with marked points at Spectrum 29 and Spectrum 30, where elemental analysis was conducted.

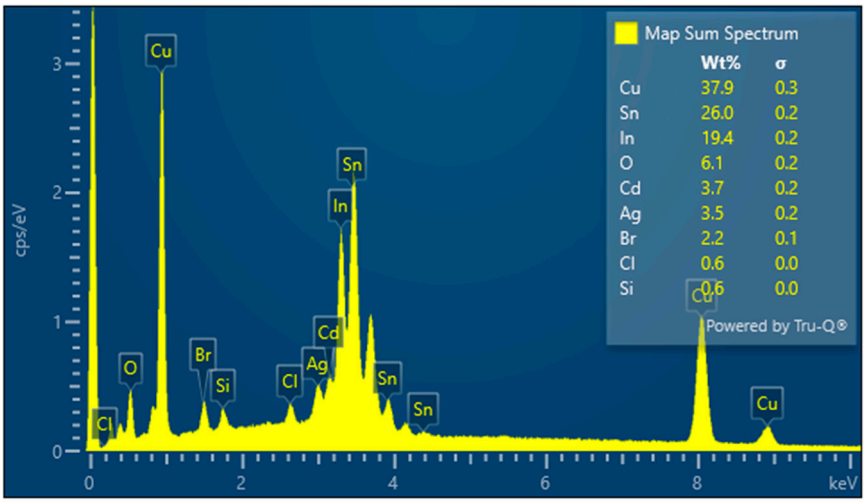


Figure 8. The result of the composition analysis at Spectrum point 29 for the averaged CIGS panel sample.

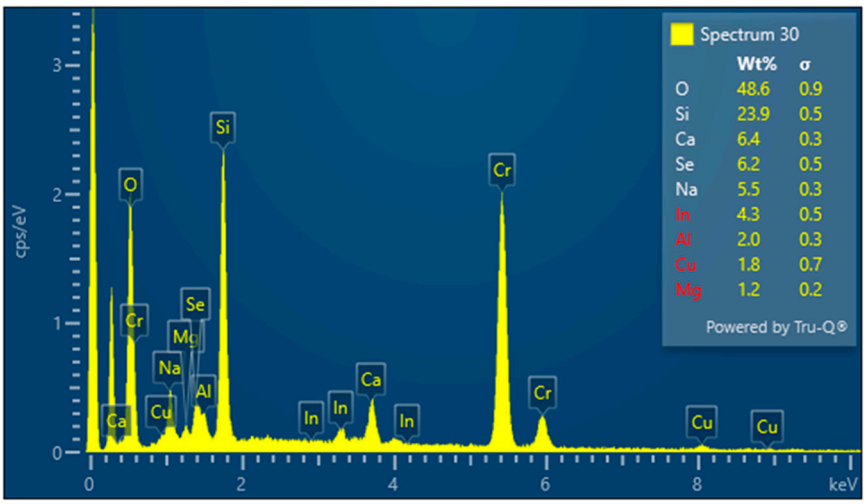


Figure 9. The result of the composition analysis at Spectrum point 30 for the averaged CIGS panel sample.

The results obtained from the analysis of SEM micrographs and compositional analysis for the averaged sample of the CIGS panel (Figures 7–9) confirmed the presence of metals such as Cu, In, and Se on the surface of the sample; however, their distribution was non-uniform. In Figure 9, large contents of Si were also observed, which resulted from the high content of glass comprising the casing of the investigated CIGS panel.

In addition to the characterization of averaged panel samples, investigations were also conducted for samples prepared from the absorbing layer. The absorption layer was not ground; instead, a small fragment of it was analyzed using electron microscopy.

Results obtained via electron microscope for the absorbing layer of the CIGS panel (depicted in Figure 4) are shown below (electron microscope image—Figure 10, and composition analysis results at selected points of the panel marked as Spectrum 7 and Spectrum 8—Figures 11 and 12).

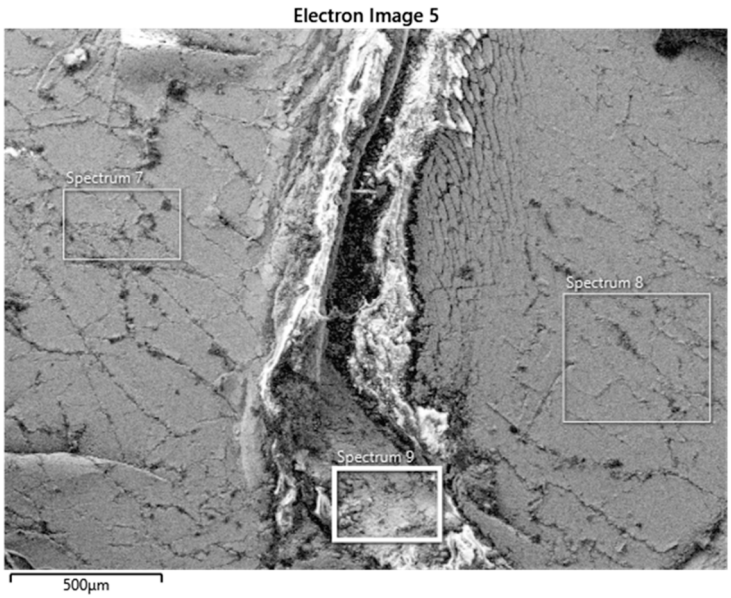


Figure 10. The electron microscope image of the averaged sample of the absorbing layer of the CIGS panel with marked points at Spectrum 7, Spectrum 8, and Spectrum 9, where elemental analysis was conducted.

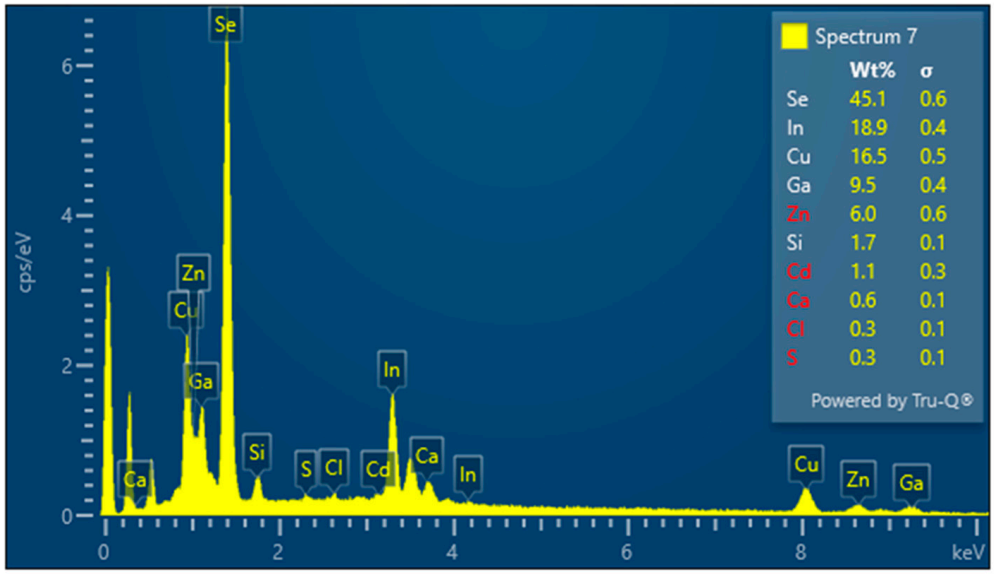


Figure 11. The result of the composition analysis at Spectrum point 7 for the sample of the absorbing layer of the CIGS panel.

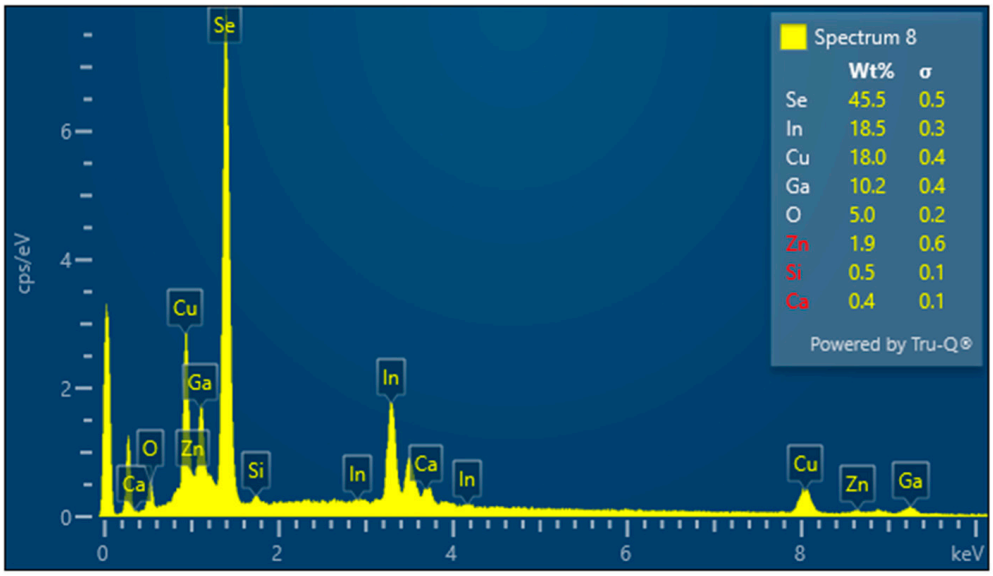


Figure 12. The result of the composition analysis at Spectrum point 8 for the sample of the absorbing layer of the CIGS panel.

The analysis of the electron microscope images and elemental analysis results presented in Figures 11 and 12 indicates that in the examined points of the absorbing layer of the panel, selenium, indium, copper, and gallium were present, and their distribution on the surface at the examined points was homogeneous (in the examined points, the surface % content of selenium, indium, gallium, and copper was marked at comparable levels, approximately 45%, 18–19%, 16–18%, and 9–10%, respectively).

These results confirm the assumption that metals such as In, Ga, and Cu are concentrated in the absorbing layer of the panel. The remaining part of the panel mainly consists of glass, which should be mechanically separated at the outset during the recycling process.

The absorbing layer sample from the panel was additionally subjected to analysis to determine its indium content. The acid-mineralized sample underwent total indium content determination using the ICP-MS method. The results of these analyses for the

absorbing layer samples (designated as PA1–PA6 in this publication) of the CIGS panel are summarized in Table 3 and visually depicted in Figure 13.

Table 3. Summary of In content results in the absorbing layer of the panel (samples PA1-PA4). Analysis conducted using ICP-MS on acid-mineralized samples.

The Sample Designation	Indium [mg/g of CIGS Panel]
PA1	0.039
PA2	1.757
PA3	1.145
PA4	2.293
The minimum value	0.039
The maximum value	2.293
The median	1.451
The arithmetic mean	1.309

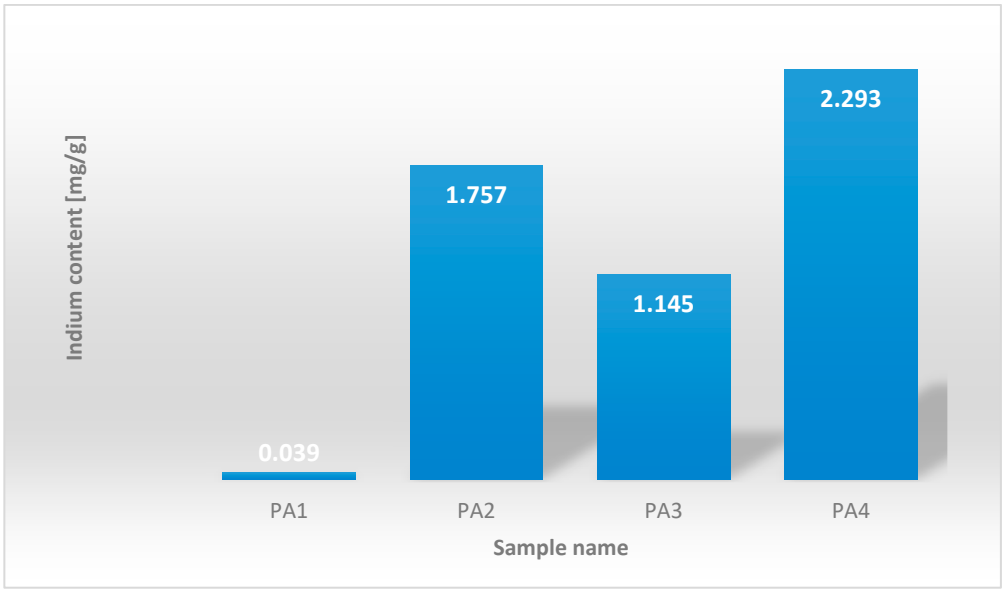


Figure 13. Summary of indium content results in the absorbing layer of the panel (samples PA1–PA4). Analysis conducted using ICP-MS on acid-mineralized samples.

The analysis of the data presented in Table 3 and depicted in Figure 13 revealed that in the absorbing layer of the panel, the determined contents for indium ranged from 0.039 to 2.293 mg/g (with a median of 1.45 mg/g). The results indicate incomplete homogenization of the sample. Nonetheless, the aim was to streamline the panel preparation process to minimize costs and energy consumption. Outliers were retained, and an estimated range of indium concentrations in samples from the absorbing layer of the panel was provided.

The indium contents in the absorbing layer of the panel were higher than those in the samples resulting from averaging the entire panel. Confirmation for the elemental analysis conducted using the ICP-MS method is provided by the results of the elemental analysis obtained from electron microscope images. The point analysis using electron microscopy also indicates that indium was concentrated in the absorbing layer of the panel.

These results allow us to conclude that a CIGS-type photovoltaic panel, where the absorbing part is encapsulated within a glass housing/structure, should be mechanically crushed during the recycling process to separate the glass from the absorbing part of the panel, which predominantly contains indium, a target for recycling.

After the mechanical separation of the panel parts concentrated with indium, an effective extraction and recovery method should be developed, as described in Section 3.2.

3.2. Preparation of Panel Samples for Electrolysis

The metal recovery process from a photovoltaic panel using electrolysis requires preliminary preparation. The photovoltaic panel was crushed and ground using a planetary mill, and the entirety was averaged (as described in Section 2.1). A representative sample was taken for analysis. A known mass of the sample was treated with a 3 M HCl solution, and indium were leached/washed using an ultrasonic bath at 80 °C. The leaching/washing process lasted for 4 h, with 30% H_2O_2 added to the mixture in four portions during washing. After the washing process was completed, the eluate was filtered into a 500 mL volumetric flask and topped up with deionized water. The indium content in the solution was determined using ICP-MS. Additionally, the pH of the solution was checked, ranging from 2 to 3.

To verify the efficiency of extraction conducted according to the procedure, extracts were prepared simultaneously from the CIGS panel and from the CIGS panel without (R1) and with the addition of a known amount of indium (R2), (Indium, beads, diam. 2–5 mm, 99.999% trace metals basis, Sigma Aldrich). A summary of key information regarding the preparation of metal extracts according to the procedure described for described method is provided in Table 4.

Table 4. The compilation of solutions prepared according to the described procedure is provided along with the results.

Solution Symbol	Preparation of the Solutions
R1	15 g of CIGS panel sample 460 mL of 3 M HCl 4 × 10 mL of H_2O_2 Mixed in an ultrasonic bath at 80 °C Washing time: 4 h The eluate was transferred to a 500 mL flask
R2	15 g of CIGS panel sample 1 g of indium 460 mL of 3 M HCl 4 × 10 mL of H_2O_2 Mixed in an ultrasonic bath at 80 °C Washing time: 4 h The eluate was transferred to a 500 mL flask

The obtained research results showed that the extraction process using 3 M HCl and H_2O_2 was effective. The studies demonstrated that as a result of this process, it is possible to extract up to 97% of indium from the panel into the solution.

3.3. Results for Samples Deposited on the Electrode

In Figure 14, photographs of the electrode with extracted indium from solutions prepared according to method described in Section 3.2 from a metal-enriched panel (solution R2) are presented. Additionally, electrolysis was conducted, resulting in the extraction of indium from the solution, which was the eluate from the CIGS panel (solution R1). In Figure 15, a photograph of the carbon electrode with extracted indium from solution R1 prepared from the CIGS panel is shown.

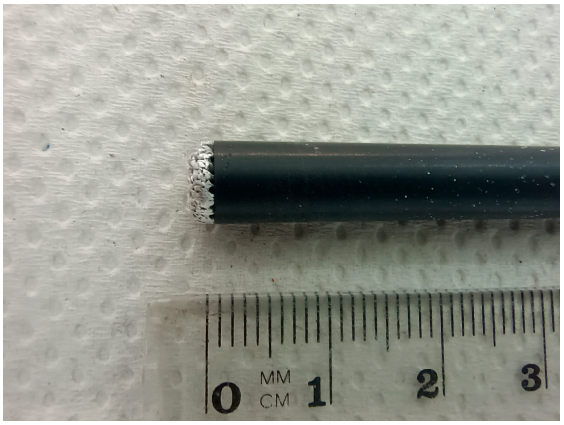


Figure 14. The carbon electrode with indium recovered from the solution during the electrolysis process. Optimization test results for the electrolysis parameters of indium from the solution with the addition of a known amount of indium (R2).

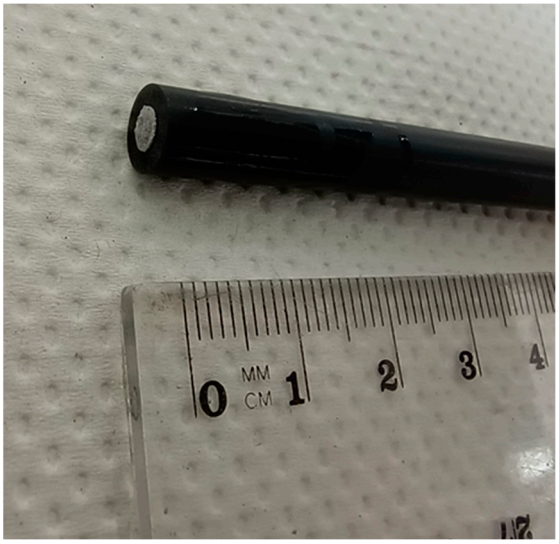


Figure 15. Carbon electrode with indium recovered from the solution during the electrolysis process without the addition of a known amount of indium (from the solution R1).

The samples deposited during the electrolysis process were examined using a scanning electron microscope. Figures 16–19 depict the results for solution R2, while Figures 20–22 show images taken for solution R1.

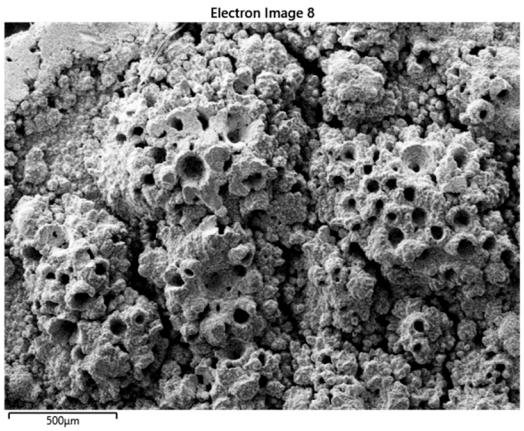


Figure 16. A photo from the electron microscope for the sample containing indium recovered from the solution with the addition of a known amount of indium during the electrolysis process (R2).

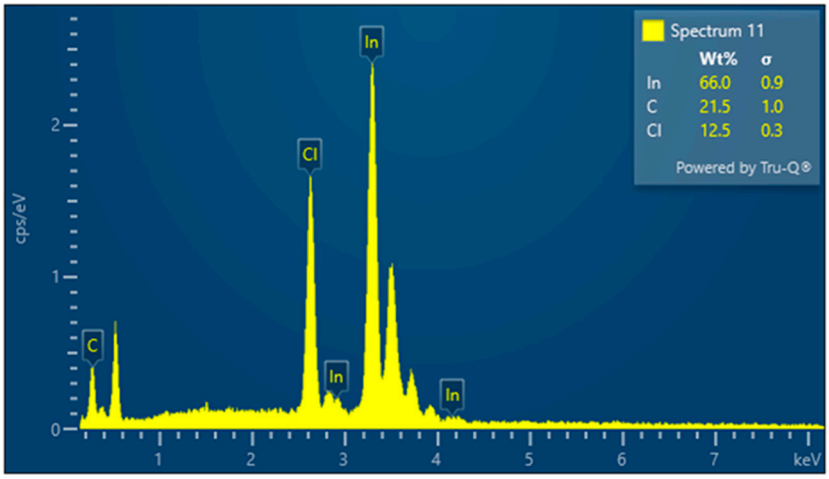


Figure 17. Result of the composition analysis at Spectrum 11 for the sample containing indium, recovered during the electrolysis process from the solution with the addition of a known amount of indium (R2).

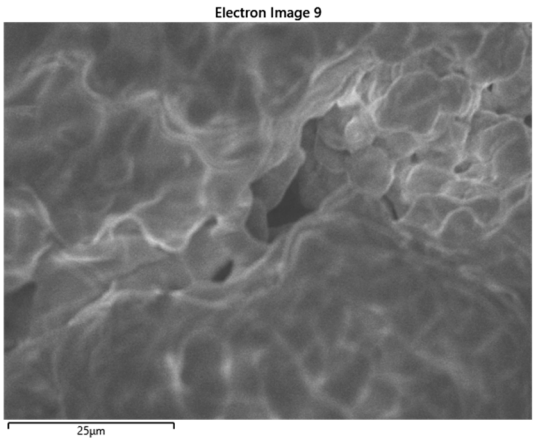


Figure 18. The image from the electron microscope at Spectrum 12 for the sample containing indium recovered during the electrolysis process from the solution with the addition of a known amount of indium (R2).

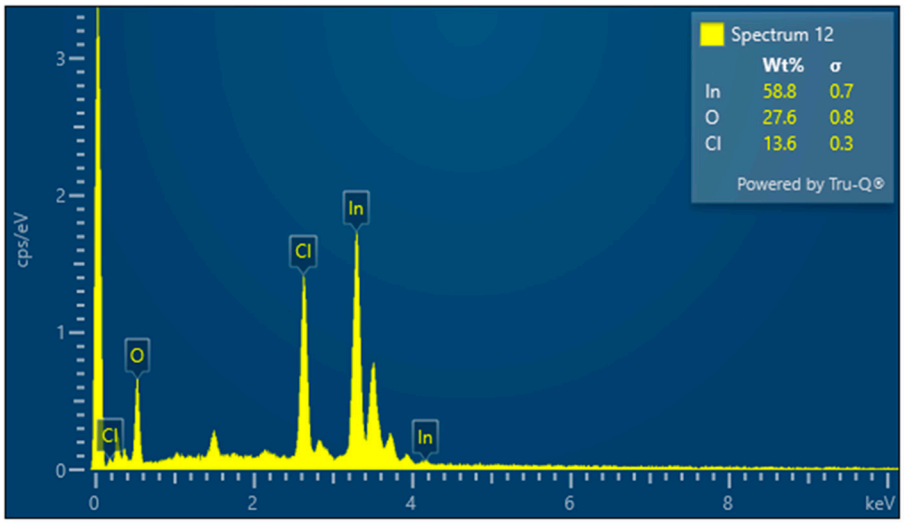


Figure 19. The result of the composition analysis at Spectrum 12 for the sample containing indium recovered during the electrolysis process from the solution with the addition of a known amount of indium (R2).

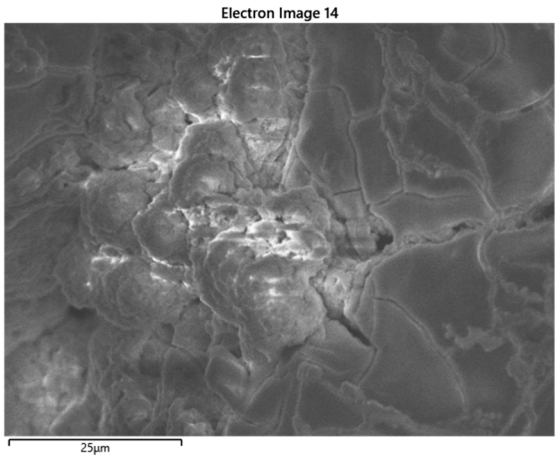


Figure 20. A scanning electron microscope image of the sample containing indium recovered from the solution without the addition of a known amount of indium during the electrolysis process (R1).

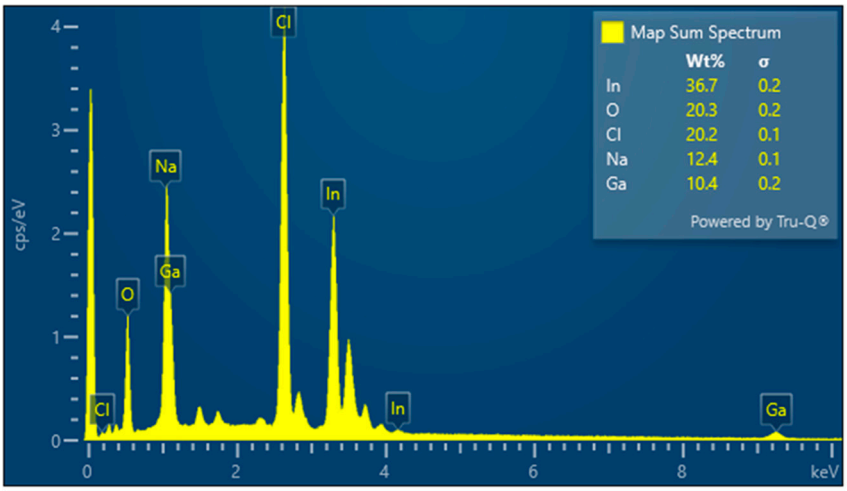


Figure 21. The result of the composition analysis for the sample containing indium recovered from the solution without the addition of a known amount of indium during the electrolysis process (R1).

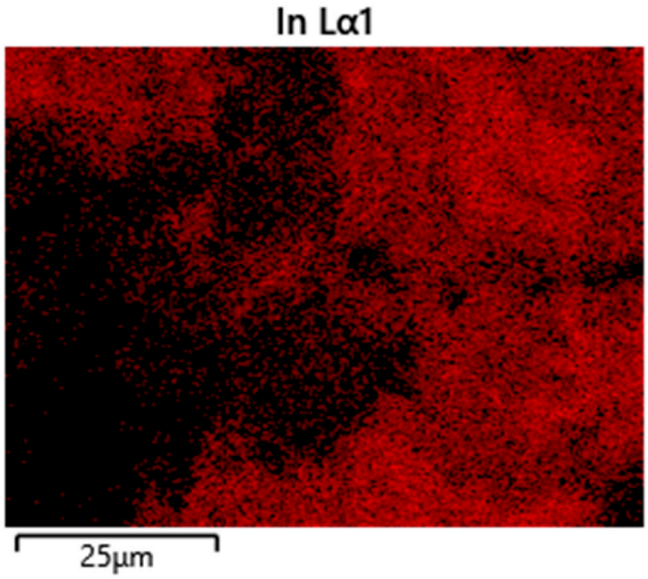


Figure 22. An example distribution of indium on the surface for the sample containing indium recovered from solution R1 during the electrolysis process.

The results presented in Figures 16–22 confirm that the electrolysis process employed successfully yielded indium (as shown in Figures 17, 19 and 21). Point analysis of the surface demonstrates that it constituted over 50% of the sample's composition at the examined point, with the remaining portion of the surface containing carbon, chlorine, and oxygen. Additionally, confirmation of the effectiveness of indium recovery in the electrolysis process is depicted in Figure 22, where an even distribution of indium in the examined sample obtained in process R1 can be observed.

Based on the obtained results, it can be concluded that the electrolysis method used in the metal recovery process is effective, allowing for selective recovery of metals (indium) from the solutions generated during the extraction process from the CIGS panel.

The electrolysis process for indium recovery from solution R1, which constitutes the liquid extract from CIGS panels prepared according to the procedure described in Section 3.2, was conducted under laboratory conditions at a temperature of 20–22 °C, as outlined in Table 1. The process lasted for 12–48 h, during which its effectiveness was monitored continuously. To confirm the effectiveness of the electrolysis process, samples were periodically taken from the solution undergoing electrolysis during the process. These samples were then analyzed using ICP-MS to assess the metal content. The obtained results are presented in Figure 23.

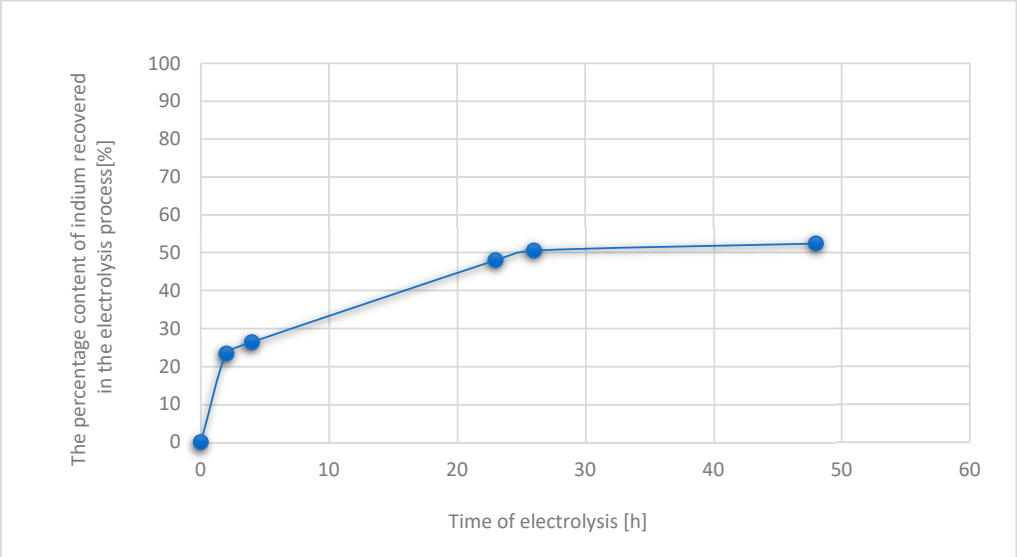


Figure 23. The graph depicting the relationship between indium recovery efficiency and electrolysis time.

Analysis of the results presented in Figure 23 indicates that in the electrolysis process applied in the study, up to 52% of the indium present in the solution was recovered within 48 h. The process was dynamic during the first 24 h, during which 50% of the indium was recovered from the solution. In the subsequent 24 h, only an additional 2% of the metal was recovered.

4. Conclusions

The dynamic advancement of photovoltaic technology has led to increased production, but it also raises concerns about the potential accumulation of waste. While photovoltaic panels are designed to operate efficiently for over 25 years, their lifespan eventually concludes, contributing to waste generation. Despite the environmentally friendly nature of photovoltaic energy production, capable of achieving zero CO_2 emissions during operation, the production process and disposal of panels can still pose environmental risks [31].

Recycling materials from used photovoltaic panels is paramount to mitigating their environmental impact. Indium, a crucial component in various photovoltaic panel types, particularly thin-film technologies like CIGS, plays a vital role in enhancing solar cell efficiency and performance. Moreover, indium is relatively scarce, with limited global reserves, underscoring the importance of its conservation and recycling to maintain a sustainable supply chain for photovoltaic production. Efficient recycling of indium from used photovoltaic panels serves to not only preserve this valuable resource but also reduce the environmental consequences associated with its extraction and processing. By implementing recycling processes for indium, reliance on new indium mining can be minimized, thereby mitigating environmentally disruptive practices. In essence, indium recycling is pivotal to advancing the sustainability of the photovoltaic industry and reducing its overall environmental footprint [32,33]. Based on the obtained results, it can be confirmed that the use of electrolysis in the metal recovery process demonstrates high efficiency, enabling selective recovery of these metals from the solutions obtained during the extraction from CIGS panels. In the conducted study, electrolysis allowed for the recovery of up to 52% of the indium present in the solution within 48 h. The dynamics of the process are particularly noticeable in the first 24 h, during which 50% of the indium was recovered from the solution. In the subsequent stage, i.e., the next day, an additional 2% of metal recovery was observed. These results suggest that electrolysis is an effective method for extracting metals from solutions obtained in the extraction process while enabling controlled selective recovery. This study presents a preliminary investigation into the electrolytic recovery of indium from CIGS photovoltaic panels using a simplified, low-energy process that does not require prior thermal treatment or the use of aggressive chemicals. Unlike many existing studies that rely on multi-step leaching and high-temperature pretreatment, the proposed method enables selective indium recovery through direct electrolysis in a diluted acidic medium. This approach minimizes chemical waste, reduces operational complexity, and demonstrates potential for scalability. While the findings are based on a single sample, they suggest that this method could offer a cost-effective and environmentally friendly alternative for indium recovery, particularly suited for small-scale or decentralized recycling operations. Most existing research on CIGS panel recycling adopts a holistic approach, aiming to recover multiple valuable elements such as copper, gallium, selenium, and components of the glass substrate. In contrast, this study focuses exclusively on indium due to its high economic value, limited natural availability, and strategic importance in the manufacturing of new thin-film photovoltaic devices. The primary objective of this work was to assess the feasibility of a selective electrolytic recovery process for indium as a first step toward a broader, modular multi-stage recovery system. Future research will aim to expand the method to include the recovery of additional critical metals and materials, with the ultimate goal of developing an integrated, environmentally responsible recycling pathway for the entire CIGS module.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CIGS	Copper indium gallium selenide panel
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
SEM	Scanning Electron Microscopy
SE	Secondary Electrons detector
BSE	Backscattered Electrons detector
TED	Transmission Electron Detector
LCDs	liquid crystal displays
LEDs	light-emitting diodes
RF	radio frequency

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