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ELECTROWINNING OF TELLURIUM FROM ACIDIC SOLUTIONS

OTRZYMYWANIE TELLURU METODĄ ELEKTROCHEMICZNĄ Z ROZTWORÓW KWAŚNYCH

The process of electrochemical deposition of tellurium was studied. Preliminary researches embrace the voltammetry and microgravimetric measurements. According to the results the electrolysis of tellurium was conducted under potentiostatic conditions. There was no deposition of tellurium above potential -0.1 vs. Ag/AgCl electrode in 25°C. The process of deposition is observed in the range of potentials -0.1 to -0.3 V vs. Ag/AgCl. The presence of tellurium was confirmed by XRF and XRD. The obtained deposits were homogenous and compact. Below potential -0.3 V vs. Ag/AgCl the Faradaic efficiency of the tellurium deposition decreased due to reduction of Te to H_2Te and hydrogen evolution.

Keywords: Tellurium, electrolysis, electrodeposition, cyclic voltammetry, electrochemical quartz microbalance

Przeprowadzono badania obejmujące możliwość otrzymywania telluru z roztworów kwaśnych metodą elektrochemiczną. Badania wstępne obejmowały analizę mechanizmu osadzania telluru z wykorzystaniem cyklicznej woltamperometrii oraz elektrochemicznej mikrowagi kwarcowej. Na podstawie otrzymanych wyników przeprowadzono proces elektrolizy w warunkach potencjostatycznych. W temperaturze 25°C powyżej potencjału -0.1 V względem elektrody chlorosrebrowej nie zachodzi proces osadzania telluru. W zakresie potencjałów od -0.1 do -0.3 V względem elektrody chlorosrebrowej następuje jego osadzanie na katodzie. Obecność tellury była potwierdzona metodami XRD i XRF. Osady otrzymane w omawianym zakresie parametrów charakteryzowały się zwartą i jednorodną budową. Poniżej potencjału -0.3 V względem elektrody chlorosrebrowej wydajność oraz szybkość procesu osadzania telluru ulegają obniżeniu w wyniku występowania reakcji konkurencyjnych: redukcji Te do H_2Te oraz wydzielania wodoru.

1. Introduction

Tellurium is one of the least frequently occurring elements in the earth. Its content in the earth crust amounts at ca. 0.005 ppm and is comparable with content of gold or platinum [1]. It accompanies ores of iron, silver, copper and lead and is a side product obtained during production of these metals [2, 3]. Recently, an intensive growth of interest in the above mentioned element has been observed due to its possible applications. First of all, tellurium is used as an alloy additive to steel, cast iron and non-ferrous metals alloys (copper, tin, lead). It improves mechanical properties of the alloys and also increases their resistance to corrosion. However, a particular attention is attracted by a possibility to synthesize tellurium-based semiconductor compounds, which can be used to produce solar cells (CdTe) or thermoelectric elements (Bi_2Te_3). That is why a demand of industry for pure tellurium is growing. It should also be indicated that at the same time there are attempts to find methods of recovering tellurium from semiconductor materials.

A process of tellurium production takes place mainly from copper refining slime or by recycling semiconductor materials. One of the processes enabling obtaining tellurium is electrolysis [3, 4]. Electrochemical techniques allow to obtain various materials from aqueous solutions and they exist within the area of contemporary hydrometallurgy activities. However, the number of parameters of electrolysis that can be changed requires intensive tests over the process of optimizing conditions of conducting it in order to achieve planned results. Modern analytical techniques, such as cyclic voltammetry or microgravimetry enable identification of areas in which electrochemical reactions responsible for obtaining the desired material take place. The techniques are widely applied in an analysis of the kinetics and mechanism of electrode reactions. The detailed analysis of the phenomena taking place during the process of electrodeposition by the electroanalytical techniques enable to achieving thin metallic [5-9] and alloy films [10-26] or semiconductor [27-35] layers. Unlike many popular techniques, the electrodeposition enable synthesis of thin layers in the nanometric size range and of strictly controlled

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morphology as a result of, so called, underpotential deposition (UPD) [36, 37].

The process of electrochemical obtaining tellurium can be performed both from acid and alkaline solutions. However, it is difficult due to electrochemical properties of tellurium and its very low solubility in aqueous solutions [38]. The electrochemical properties of tellurium in aqueous solutions are described in literature [38-40]. Because of the properties of tellurium, most of the values are calculated based on the thermodynamic data, and only some of them were experimentally proved.

The aim of the work is an analysis of the process of electrochemical obtaining tellurium form acid solutions. The tests were performed in sulphate solutions. The method of cyclic voltammetry was combined with an electrochemical microbalance and applied to identify reactions taking place on the electrode and to determine ranges of potentials in which its deposition occurs. Next, the results were confirmed by conducting electrolysis in selected potentiostatic conditions.

2. Experiment details

The electrolysis was conducted in a solution of TeO_2 concentration of 0.001 mol/dm^3. The solutions were prepared applying TeO_2 (analytical grade POCh) and H_2SO_4 (95% analytical grade POCh). Sulphuric acid (VI) was used to acidify the solution to pH=1. The electrolyte was made with the use of deionised water. Voltammetric and potentiostatic tests of tellurium deposition were performed applying a classical three-electrode electrochemical cell. The cell contained the reference electrode – a silver-silver chloride electrode, and the counter electrode was a platinum plate of 12 cm^2 in area. The cell was placed in a water jacket, and the electrolyte temperature was maintained by a thermostat (UTU-5 Remontar) with a precision of ±1°C.

The electrochemical cell used for the microgravimetric tests also contained three electrodes. The reference electrode was a silver-silver chloride electrode (sat. KCl), and the counter electrode was a platinum plate of 2.86 cm^2 in area. The working electrode was copper sputtered on the surface of a quartz resonator.

Either gold or copper was used as the working electrode. In chronoamperometric, voltammetric and microgravimetric tests the working electrode was a layer of gold sputtered onto a layer of a quartz plate (OMIG). The electrodes were kept in a desiccator and they did not undergo any additional operations before the experiment. The electrode area was 0.25 cm^2.

Deposition of coatings was conducted on copper plates placed in a Teflon holder. Each plate was polished mechanically and then chemically in a mixture of HNO_3 (analytical grade POCh), CH_3COOH (analytical grade POCh) and H_3PO_4 (analytical grade POCh) of components proportion 1:1:1. The solution was prepared with the use of concentrated acids. Before measurement, the electrodes were flushed with distilled water and acetone. The electrode area was 2.8 cm^2.

Electrochemical tests were performed using a potentiostat – galvanostat PAR273A. The potentiostat is equipped with an inbuilt integrator for counting charge flowing during measurement. Chronoamperometric and cyclic voltammetry tests as well as potentiostatic deposition of tellurium were conducted on it.

Microgravimetric tests were done with a quartz microbalance UELKO M106, additionally connected to the potentiostat. The obtained coatings underwent a phase analysis with the use of an X-ray diffractometer Rigaku MiniFlex applying filtered radiation CuKα. Elemental composition of coatings was defined by the X-ray fluorescence using a fluorescence spectrometer WD-XRF Rigaku Primini. Observation of cathodic deposits surface was performed with the use of a scanning microscope (Hitachi SU−70, Thermo Scientific).

3. Electrochemical studies

3.1. Voltammetry and microgravimetry

In order to analyse the mechanism and kinetics of electrochemical reactions taking place during electrolysis of telluric acid (IV), the initial tests included application of cyclic voltammetry. The process was performed in electrolyte containing 0.001 mol/dm^3 TeO_2 of pH=1. On the basis of the results the range of potentials of electrochemical reactions occurrence was determined. The voltammetric cycle was begun from the potential 1.0 V and it was changed towards more negative values up to reaching -0.8 V and then it was turned round and increased to the value of 1.0 V (Fig. 1).
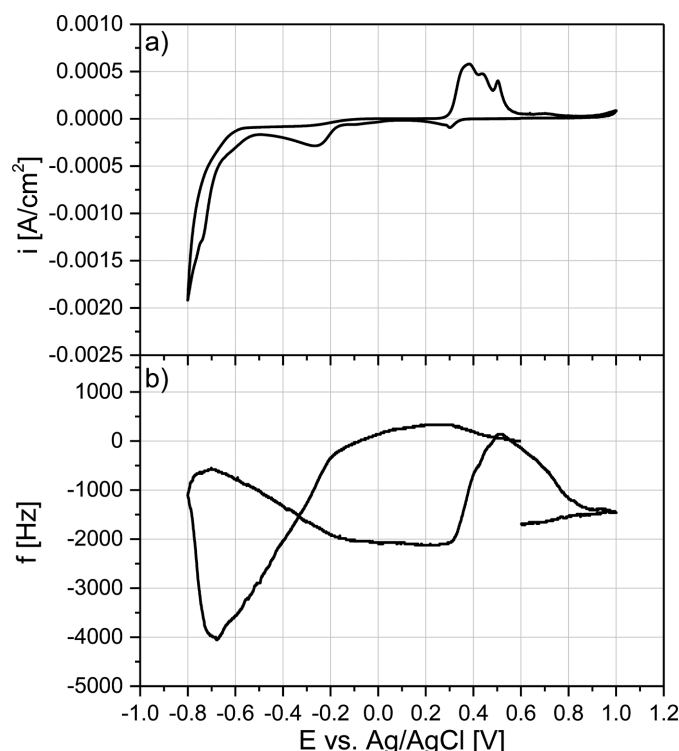

Fig. 1. a) Cyclic voltammogram made for a gold electrode in a solution of 0.001 mol/dm^3 TeO_2, pH=1; b) relation of frequency changes of the quartz resonator depending on changing potential of the working electrode during voltammetric tests

The obtained results show that the reduction process starts from potential 0.3 V when reduction of telluric acid to tellurium takes place following the reaction:

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te(s) + 2H_2O \qquad (1)$$
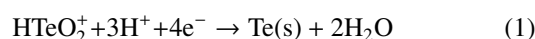
However, the process of tellurium reduction within the range of potentials is an effect of underpotential deposition [41-43]. The process is area limited and the potential determined here would not be suitable for conducting a process of electrolysis. Another peak occurs at potential -0.2 V. The peak is much bigger and probably it also follows the reaction (1). Below -0.5 V intensive evolution of hydrogen begins:

$$2H^+ + 2e^- = H_2 \tag{2}$$

The reduction of hydrogen ions can be a cause of other reactions taking place simultaneously:

$$HTeO^{2+} + 5H^+ + 6e^- \rightarrow H_2Te + 2H_2O \tag{3}$$

$$Te(s) + 2H^+ + 2e^- \rightarrow H_2Te \tag{4}$$
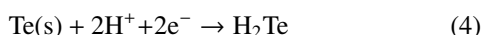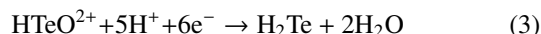
They can be responsible for a decrease of efficiency of the tellurium deposition process. When the potential is changed towards more positive values, anodic peaks responsible for solubility of previously deposited tellurium appear not until potential 0.3 V. Their complex shape indicates a complicated mechanism of tellurium solubility and a probable reaction of tellurium with the ground. Therefore, the results would confirm a possibility of occurrence of the underpotential deposition phenomenon. Solubility of tellurium can take place following the reaction:

$$Te(s) + 3H_2O \rightarrow H_2TeO_3 + 4H^+ + 4e^- \tag{5}$$
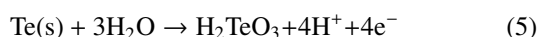
Parallel, there were conducted microgravimetric tests that make the analysis of the obtained results easier. The quartz microbalance indicates the potentials range at which the flowing charge is also accompanied by a change of the electrode mass and confirms a character of electrode processes taking place (adsorption, underpotential deposition, overpotential deposition). A decrease in the resonator frequency results from an increase of the electrode mass described by the Sauerbrey equation [44]:

$$\Delta f = -\frac{\Delta m f_0^2}{A (\mu\rho)^{\frac{1}{2}}} \tag{6}$$

where: Δm – electrode mass change [g], f_0 – basic frequency of quartz resonator, A – electrode area, μ – rigidity modulus [Pa], ρ – density [g/cm3].

Analysing the voltammogram in combination with the results from the quartz microbalance (Fig. 1), it can be noticed that initially the resonator frequency increases which corresponds to a decrease of the electrode mass. The processes are characteristic for a gold electrode in sulphate solutions within the above presented potentials. The effect results from a process of sulphate ions desorption. From potential 0.3 V the quartz resonator frequency stabilizes and then from potential 0.2 V it begins to fall down. The results indicate a growth of the electrode mass. A cathodic peak corresponds to the growth at potential 0.2 V on the voltammogram. After exceeding potential -0.2 V, a much more intensive increase of the electrode mass takes place, which is connected with occurrence of another peak on the voltammogram. The increase is also connected with deposition of tellurium (1). After exceeding potential -0.7 V, the frequency begins to rise rapidly, which

indicate the dissolution of previously deposited tellurium (4) and a decrease of the electrode mass. When the potential is turned round at -0.8 V and changed towards more positive values, the electrode mass decrease lasts until potential -0.7 and then it begins to increase again. The increase results from deposition of tellurium following the reaction (1). After exceeding potential -0.2 V, the resonator frequency stabilizes. From potential 0.3 V another decrease of the electrode mass is noticed as well as parallel occurrence of anodic current. It is when tellurium solubility takes place following the reaction (5). It is intriguing to observe a mass increase taking place afterwards when the potential exceeds the value of 0.5 V. The increase can result from precipitation of insoluble tellurium oxides.

3.2. Chronoamperometry and microgravimetry

On the basis of voltammetric experiments combined with microgravimetric ones a potential range where the electrode mass increased was selected. Next, chronoamperometric tests were done within the selected range in order to confirm the obtained results (Fig 2). The process was performed in electrolyte containing 0.001 mol/dm³ TeO₂ of pH=1. Duration of the measurement was 60 s.
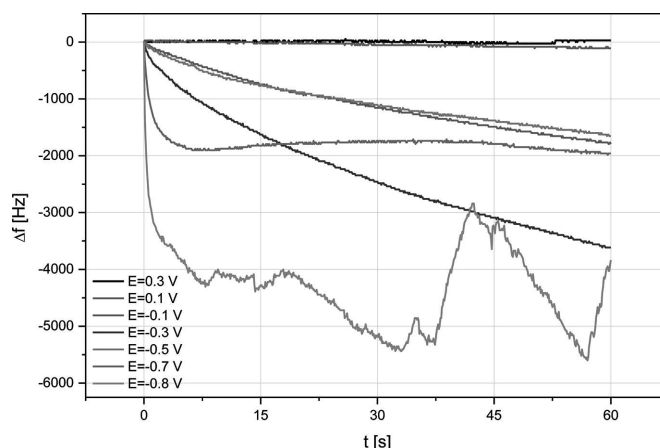

Fig. 2. Relation of a change of quartz resonator frequency and time during chronoamperometric tests for a gold electrode in a solution of 0.001 mol/dm³ TeO₂, pH=1. A value of the working electrode potential in relation to the silver-silver chloride electrode Ag/AgCl

It can be noticed that for more positive potentials: 0.3 and 0.1 V, the electrode mass increase is slight. The results are in accordance with former voltammetric measurements, where within the selected potential ranges the mass increase was also small. Only when the electrode gets polarised below potential 0.1 V, significant changes of the mass electrode can be observed. In case of polarising the electrode with potential from -0.1 to -0.5 V a continuous growth of the electrode mass can be observed. The results are also in accordance with voltammetric tests where within the discussed range of potentials the electrode mass growth was the highest. On the other hand, when potential -0.7 V is applied, an intensive increase of the electrode mass is noticed only for the first few seconds of the process duration. Later, the process of tellurium deposition gets inhibited. Comparing the obtained results with voltammetric tests, it can be stated that it is caused by occurrence of competitive electrochemical reactions (3) and (4). The highest

mass growth was observed at potential -0.8 V. However, it should be noticed that it was not a regular increase of the electrode mass. The diagram features irregular increases and decreases of mass. It can result from different electrochemical reactions taking place at the same time (1), (2), (3) and (4).

Chronoamperometric tests in combination with electrochemical quartz microbalance also allow to compare efficiencies of the tellurium deposition process depending on the applied parameters. Estimation of the process efficiency is possible when the results are presented in the system f(q)= Δf (Fig. 3). Then, on the basis of the slope of obtained curves, it is possible to determine in which case the process will take place with the highest efficiency. Controversial results were obtained for the process of tellurium deposition at potentials 0.3 and 0.1 V. The summary charge flowing during the process duration was positive which indicates occurrence of anodic processes. However, the size of the flowing charge was very small (Fig. 3). It should be stressed that within the above mentioned potentials range we face phenomena of underpotential deposition of tellurium, adsorption and desorption of sulphate ions and charging a double electrical layer. All the phenomena decide about the summary electrical charge flowing through the system and a total change of the electrode mass change. Therefore, it can be assumed that within the discussed potentials range no efficient deposition of tellurium takes place. The most intensive process of tellurium deposition takes place at potential -0.8 V, but only for the first few seconds of the process duration. Next, the intensity lowers due to occurring competitive reactions (2), (3) and (4). A process of electrolysis at potential -0.7 V looks alike. Also here, the process of deposition is very intensive only at the beginning, decreases to zero later, and even dissolution of the previously deposited tellurium takes place. The results obtained after polarisation of the gold electrode with potentials -0.1, -0.3 and -0.5 V seem to be very advantageous from the point of view of conducting the process of tellurium deposition. The highest efficiency was observed within this range of potentials. However, it should be noticed that the highest mass growth was registered when potential -0.3 V was applied. The mass growth was stable for the whole duration of the process.
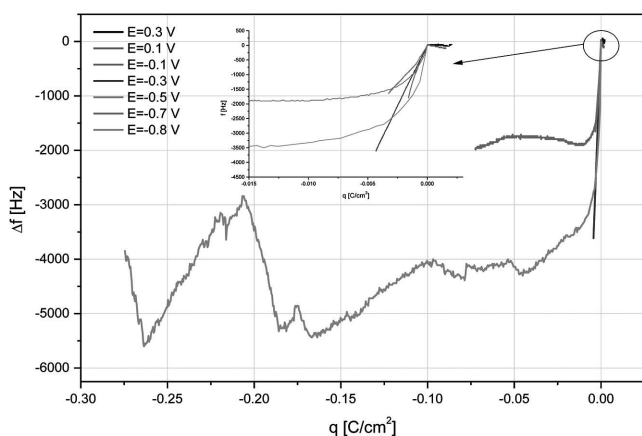
3.3. Tellurium electrolysis

On the basis of the obtained results an electrolysis process was conducted for selected parameters. The electrolysis process was conducted on specifically prepared copper plates. The process duration was one hour in each of the cases. The obtained results reflect the previous voltammetric and chronoamperometric tests combined with microgravimetric ones (Fig. 4). The highest efficiency accompanied by the highest mass growth was observed for potential 0.3 V. Applying higher potentials causes both lowering of the tellurium deposition velocity and lower efficiency. For potentials lower than -0.3 V a systematic decrease of tellurium deposition velocity is observed as well as lowering of the process efficiency. On the basis of a thermodynamic analysis and previous electrochemical tests, it can be stated that the above effects result from occurrence of competitive reactions (2), (3) and (4).
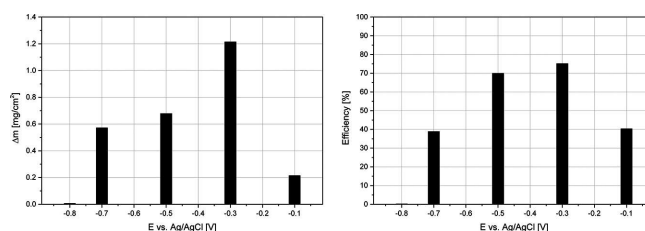

Fig. 4. An increase of the copper electrode mass obtained during the electrolysis process conducted in a solution of 0.001 mol/dm^3 TeO$_2$, pH=1 depending on the applied potential; b) efficiency of the tellurium electrolysis process conducted in a solution of 0.001 mol/dm^3 TeO$_2$, pH=1 depending on the applied potential

4. WDXRF and XRD analysis

The obtained samples were analysed with the method of X-ray fluorescent spectroscopy method and they underwent a phase analysis with the X-ray diffraction method to prove the presence of tellurium in the deposit. On the basis of the results obtained during an elemental analysis with the XRF method the presence of tellurium on copper fields was confirmed.
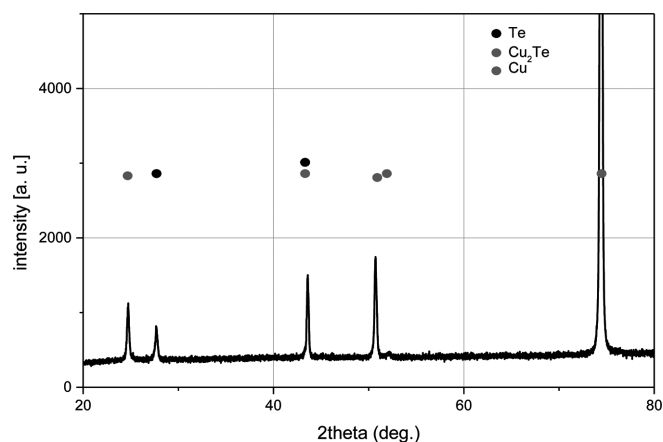

Fig. 5. The phase diffractogram for a sample obtained at potential -0.1 V

In case of the phase analysis the peaks typical for tellurium were also observed on the samples (Fig. 5). However, it

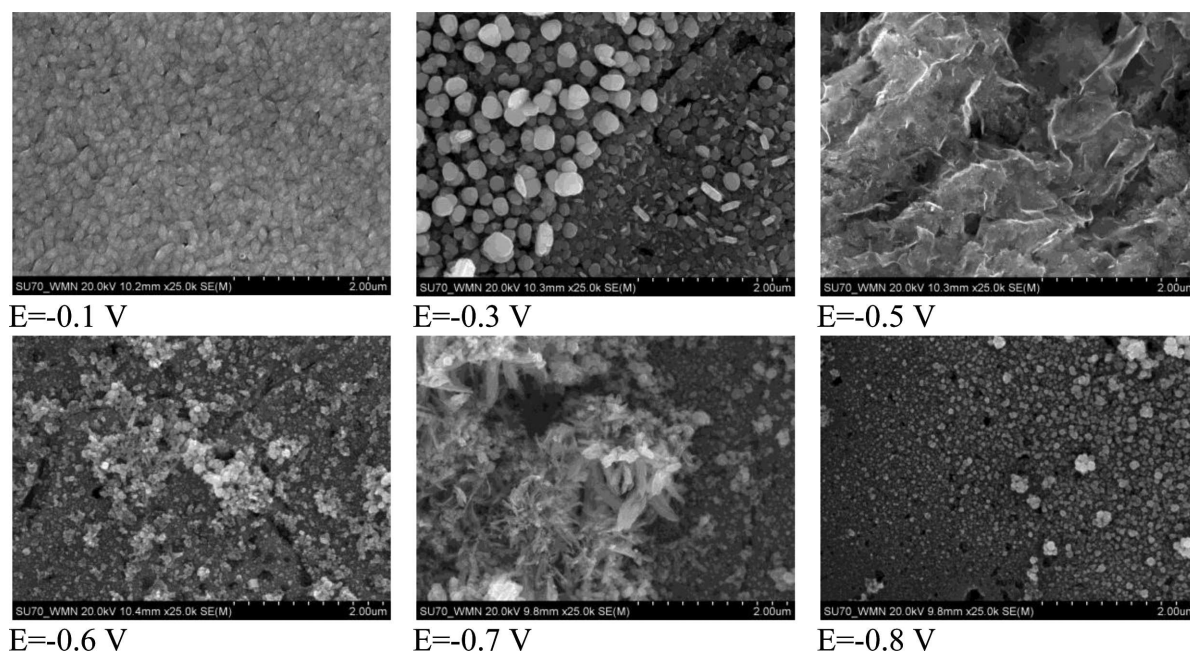Fig. 3. Relation of a change of quartz resonator frequency and time during chronoamperometric tests for a gold electrode in a solution of 0.001 mol/dm^3 TeO$_2$, pH=1. A value of the working electrode potential in relation to the silver-silver chloride electrode Ag/AgCl

Fig. 6. Morphology of cathodic deposits obtained at different potentials from a solution of 0.001 mol/dm^3 TeO$_2$, pH=1

should be added that there appeared also peaks corresponding to the Cu$_2$Te phase. Occurrence of copper telluride is connected with a reaction between the deposited tellurium and the copper plate.

Morphology of the obtained deposits was examined with the use of the electron scanning microscope (Fig. 6). It can be observed that compact deposits were obtained for samples at potentials -0.1 and -0.3 V. Whereas, further lowering of the potential favoured creation of porous structures with typical dendritic burls.

5. Conclusions

Due to a low solubility of tellurium in aqueous solutions, it was not possible to apply concentrations higher than 0.001 mol/dm^3. Velocity and efficiency of the electrolysis process depends on the used potential. Depending on the applied potential different electrode reactions can take place during electrolysis. The mechanism of electrode reactions decides about velocity and efficiency of the tellurium electrolysis process and also about the deposit morphology. Above the potential -0.1 V the process of tellurium deposition does not take place. The reaction of tellurium reduction following the reaction (1) and its deposition on the cathode occurs within the potentials range from -0.1 to -0.3 V.

The deposits obtained within the discussed concentrations range were characterised by compact and homogeneous structure. The highest efficiency of the tellurium electrolysis process was obtained for potential -0.3 V. Below potential -0.3 efficiency and velocity of the tellurium deposition process get lower as a result of appearance of competitive reactions (2), (3) and (4). A lower mass growth was observed and the samples featured porous structure and numerous dendritic burls.

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