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Effect of Alkali Concentration on the Rates of the Target and Side Cathode Reactions Involved in the Electrolysis of Tellurite Solutions

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Abstract

The effect of KOH concentration on the rate of the target reaction of metal tellurium deposition from alkaline tellurite solutions and on the rate of the side reaction of tellurium dissolution was studied by means of voltammetry with the linear potential scanning on a graphite electrode coated with tellurium deposit. It was established that KOH only weakly (with a change by 5–10 %) affects the rates of the target and side reactions within the range of alkali concentrations 2–4 M, which is used for the production of tellurium. The reasons for a decrease in the rates of the target and side reactions at low alkali concentrations were considered. It was shown that the target and side cathode reactions have the diffusion-determined nature in the range of alkali concentrations 0.5–4 M with tellurium deposition and 0.1–4 M with tellurium dissolution. The side cathode reaction of Te dissolution has a one-electron mechanism, and it requires 20 % of the amount of electricity used for tellurium deposition.

Keywords: tellurium, ditelluride anion, alkaline tellurite solutions, electrolysis, reaction rate, limiting current

INTRODUCTION

The efficiency of any technological process is to a high extent dependent on the optimal parameters of its mode, which allows a substantial improvement in energy and resource-saving, and in the ecological safety of the production. This is also true for the industrial production of tellurium.

Tellurium and its alloys, for example, the tellurides of cadmium, lead, copper, etc. are widely used in electronics for the production of photoconductive layers, as well as piezo- and thermoelectric layers. The application of tellurium in ferrous and non-ferrous metallurgy and other branches of industry is also known [1–8].

The main industrial method of obtaining tellurium is electrolysis of alkaline tellurite solutions

formed during hydrometallurgical processing of anodic slime from copper production [6–8].

During galvanostatic preparation of metal tellurium from alkaline tellurite solutions using insoluble anodes, permanent changes of the cathode potential and the concentration of “free” potassium hydroxide (excess KOH with respect to the stoichiometrically necessary amount for the dissolution of TeO_2) occur in solution with a decrease in tellurium concentration. Taking into account the relatively small difference of equilibrium potentials of the target reaction of Te deposition on the cathode and the side reaction of its cathode dissolution with the formation of ditelluride Te_2^{2-} , the above-indicated changes in electrolysis conditions may affect the relations between the partial reactions and lead to a decrease

in the yield as a function of current and to worsening of the quality of cathode deposit, which is important for obtaining high-purity tellurium.

Previously we studied the relations between the currents of the indicated target and side reactions for KOH concentration (C mol/L) equal to 4 M, and determined the potential region within which mainly the target process alone occurs [9]. The goal of the present investigation is to study the effect of C_{KOH} within the range 0.1–4 M on the rates of the target and side reactions during the electrolysis of tellurite solutions.

EXPERIMENTAL

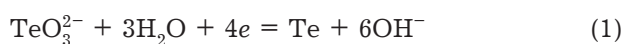
The investigation was carried out with a mechanically renewed graphite electrode [10], with the end having an area of 0.03 cm^2 , onto which a layer of metal tellurium ($15 \mu\text{m}$) was preliminarily deposited from the electrolyte containing 0.5 M TeO_2 and 4 M “free” KOH, at the fixed potential (-0.95 V) with the control of deposit thickness relying on the quantity of electricity that passed through. The rates of cathode reactions were measured by means of linear voltammetry at the rate of potential scanning 1 mV/s , using an IPC-compact potentiostat (IPCE RAS, Russia). The auxiliary electrode was made of platinum wire with an area of 1 cm^2 . The cathode potential was measured with respect to the saturated silver chloride reference electrode Ag/AgCl. Experiments were carried out with a thermostated three-electrode cell 50 cm^3 in volume at $25 \text{ }^\circ\text{C}$.

The effect of the alkali on the rate of cathode target reaction of tellurium deposition was studied in the solution containing 0.5 M TeO_2 and 0.5–4 M “free” KOH. The electrolyte was prepared using distilled water, TeO_2 of Ch. reagent grade (pure), and KOH of Ch. D. A. reagent grade (analytically pure). Dissolution was carried out at a temperature of $70 \text{ }^\circ\text{C}$ for 2 h. The effect of alkali concentration on the rate of the side reaction of cathode dissolution of metal tellurium was studied in the solution containing 0.1–4 M KOH in the absence of tellurium.

RESULTS AND DISCUSSION

Effect of KOH concentration on the rate of target reaction

The target cathode reaction of tellurium deposition from the alkaline tellurite solutions looks like [1, 2]



The equilibrium potential with respect to the normal hydrogen electrode is

$$E_0 = 0.823 - 0.0886\text{pH}, \text{ V}$$

It was established that within the alkali concentration range $C_{\text{KOH}} = 2\text{--}4 \text{ M}$, which is of practical interest for obtaining tellurium from alkaline tellurite electrolytes, alkali concentration has a weak effect on the rate of the target reaction. The limiting current (I_{lim}) varies by 5–10 %, and the corresponding potential shifts to the negative side by 15 mV (Fig. 1, a).

However, at lower alkali concentrations ($C_{\text{KOH}} < 2 \text{ M}$), the rate of the target reaction starts to decrease more substantially. For instance, at $C_{\text{KOH}} = 0.5 \text{ M}$ the value of I_{lim} of tellurium deposition decreases by 10 %, its potential shifts to the negative side by 30 mV (see Fig. 1, b). Most probably, this occurs as a consequence of a decrease in the concentration of tellurite ions (TeO_3^{2-}) because of the incomplete dissolution of TeO_2 . The consumption of electricity (Q) for tellurium deposition is practically independent of alkali concentration and is approximately 1000 mC (see Fig. 1, b).

The cathode deposition of metal tellurium from alkaline tellurite solutions is controlled by the diffusion of TeO_3^{2-} anion to the cathode surface, which is confirmed by the typical linear dependence of the limiting current density I_{lim} on the rate of cathode potential scanning (V , mV/s) raised to a power of 0.5 (Fig. 2, a). The values of I_{lim} were obtained from polarization curves (see Fig. 2, b).

Effect of KOH concentration on the rate of the side cathode reaction

In alkaline tellurite solutions, along with the target reaction of the deposition of metal tellurium, the side reaction of the dissolution of this metal proceeds on the cathode, which is accompanied by the formation of ditelluride anion Te_2^{2-} [1, 2]:



The equilibrium potential of this reaction (with respect to the normal hydrogen electrode) is $E_0 = -0.71 \text{ V}$.

Both cathode reactions proceed at close potential values, so with inevitable increase in the potential during electrolysis in the galvanostatic mode, the yield as a function of current decreases for the target reaction, and at the same time the quality of the deposit worsens [9].

The effect of KOH concentration within the range 0.1–4 M on the rate of the side reaction of the cathode dissolution of tellurium was investigated. It was established that, unlike for the tar-

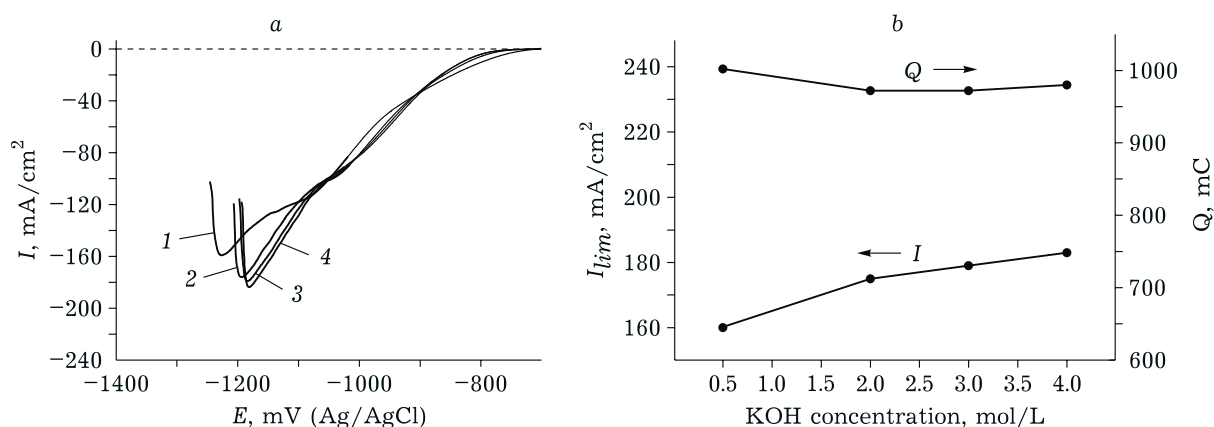


Fig. 1. Effect of the concentration of "free" KOH on the cathode voltammograms (a), limiting current (I_{lim}) and consumption of electricity (Q) during tellurium deposition (b). Electrolyte: 0.5 M TeO₃ + x M KOH. KOH concentration, x , mol/L: 1.5 (1); 2 (2); 3 (3); 4 (4). Potential scanning rate 1 mV/s.

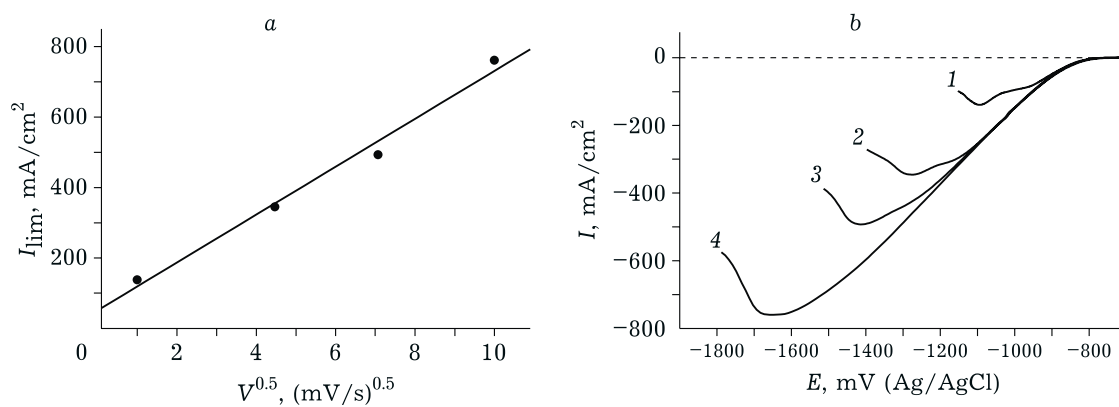


Fig. 2. Effect of the cathode potential (V) scanning rate on the limiting current (I_{lim}) (a) and voltammograms (b) during tellurium deposition. The solution: 0.5 M TeO₂ + 4 M KOH. Potential scanning rate, mV/s: 1 (1); 20 (2); 50 (3); 100 (4).

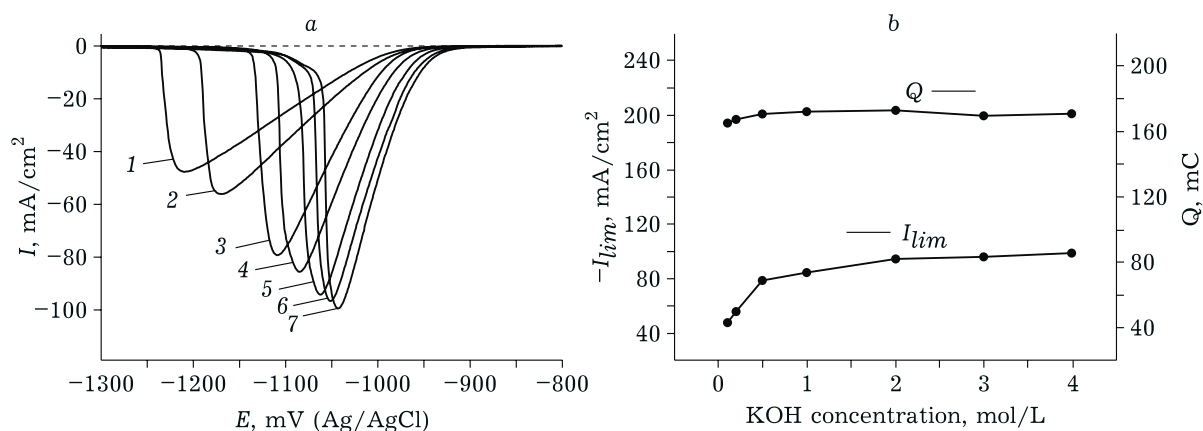


Fig. 3. Effect of KOH concentration of the behaviour of voltammograms (a), consumption of electricity (Q) and limiting current (I_{lim}) (b) during the cathode dissolution of tellurium. KOH concentration, mol/L: 0.1 (1); 0.2 (2); 0.5 (3); 1 (4); 2 (5); 3 (6); 4 (7). Potential scanning rate 1 mV/s.

get reaction, the appearance of voltammograms of the side reaction is substantially dependent on alkali concentration (Fig. 3, a). In all cases, these voltammograms are the curves with the maxi-

mum, after which the current drops down almost to zero with further potential scan. A decrease in the concentration of the alkali leads to a monotonous decrease in the height of the peak on the

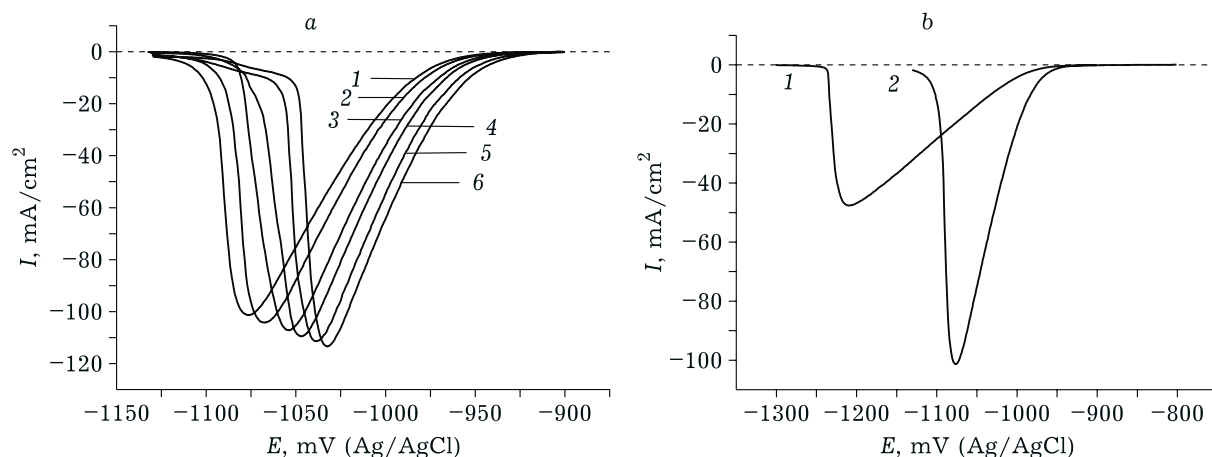


Fig. 4. Effect of base electrolyte (2 M KCl) on the cathode dissolution of tellurium in the alkaline electrolyte: *a* – x M KOH + 2 M KCl; KOH concentration, x , mol/L: 0.1 (1); 0.5 (2); 1 (3); 2 (4); 3 (5); 4 (6); *b* – 0.1 M KOH (1); 0.1 M KOH + 2 M KCl (2). Potential scanning rate 1 mV/s.

polarization curve and its shift to the higher cathode potential region. The amount of consumed electricity Q remains practically the same (200 mC) (see Fig. 3, *b*) and is equal to one fourth of the charge consumed for the deposition of tellurium 15 μm thick on the graphite electrode (870 mC). So, the polarization curves under consideration confirm the single-electron mechanism of the cathode dissolution of metal tellurium according to equation (2).

On first glance, the data presented in Fig. 3, *a* lead us to a conclusion that the rate of the side reaction (2) decreases substantially in the region of low KOH concentrations ($C_{\text{KOH}} < 0.5$ M). However, more detailed analysis shows that a decrease in KOH concentration is accompanied not only by a substantial decrease in the concentration of OH^- but also by a decrease in another value which is essential for voltammetry: the electrical conductivity χ of the solution (Table 1) [11]. If a decrease in the conductivity of the solution is compensated by the introduction of the base electrolyte (2 M KCl) with high conductivity ($\chi = 20.2$ ($\text{Ohm} \cdot \text{m})^{-1}$), the effect of KOH concentration on the rate of the side reaction within the alkali concentration range of the highest significance for tellurium production (2–4 M) disappears almost completely (Fig. 4, *a*).

In the solutions with low KOH concentration ($C_{\text{KOH}} < 0.5$ M) in the presence of the base electrolyte, the rate of the cathode side reaction of tellurium dissolution increases substantially in comparison with the rate in the solution without the base electrolyte. For instance, at $C_{\text{KOH}} = 0.1$ M the limiting diffusion current is 100 mA/cm^2 , while in the solution without the base electrolyte

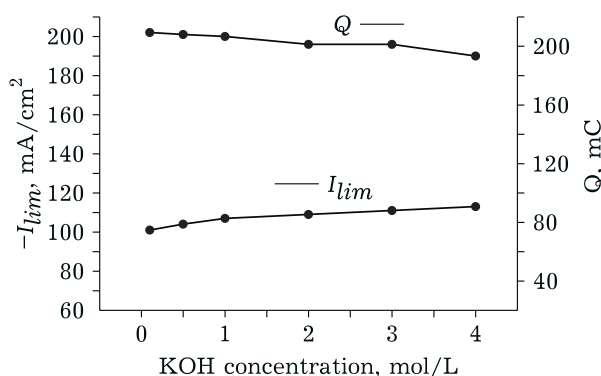


Fig. 5. Effect of KOH concentration of the consumption of electricity (Q) and limiting current (I_{lim}) during the cathode dissolution of tellurium in the alkali containing the base electrolyte (2 M KCl).

it is 50 mA/cm^2 (see Fig. 4, *b*). The corresponding potential shifts substantially to the positive region by 130 mV. The very fact that the rate of the side reaction of tellurium dissolution increases by a factor of 2 in the presence of the base electrolyte suggests that the conductivity of the solution rather than the concentration of OH^- has a decisive effect on the rate of the side reaction. This is also confirmed by the fact that the alkali has almost no effect on the limiting diffusion currents of Te dissolution and the consumption of electricity in KOH solutions with the base elec-

TABLE 1

Electric conductivity of solution (χ) for different KOH concentrations [11]

KOH concentration, M	0.1	0.5	1	3	4
χ , ($\text{Ohm} \cdot \text{m})^{-1}$	2.13	9.85	21	44.8	54.9

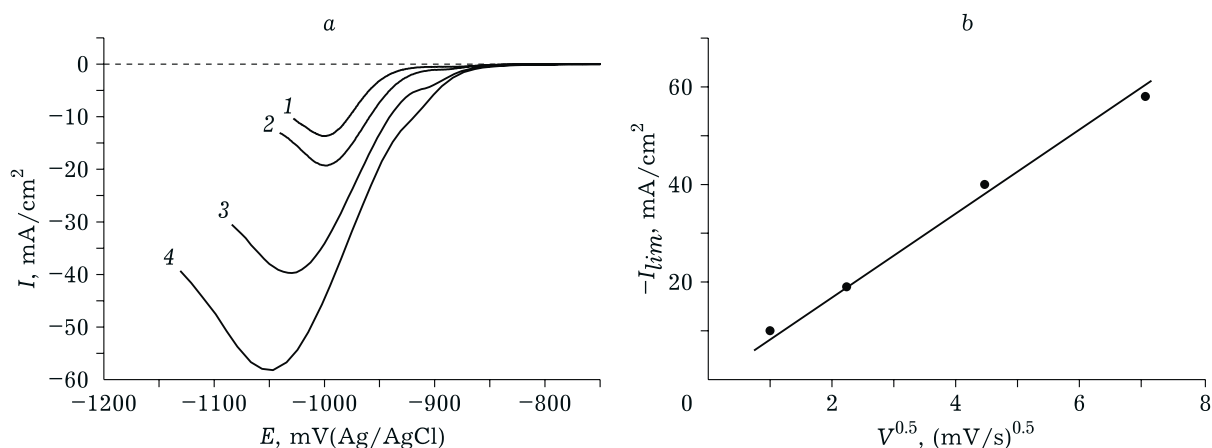


Fig. 6. Voltammograms (a) at different potential (V) scanning rates, mV/s : 1 (1); 5 (2); 20 (3); 50 (4) and limiting current (I_{lim}) of the cathode dissolution of tellurium depending on $V^{0.5}$ (b) in 4 M KOH.

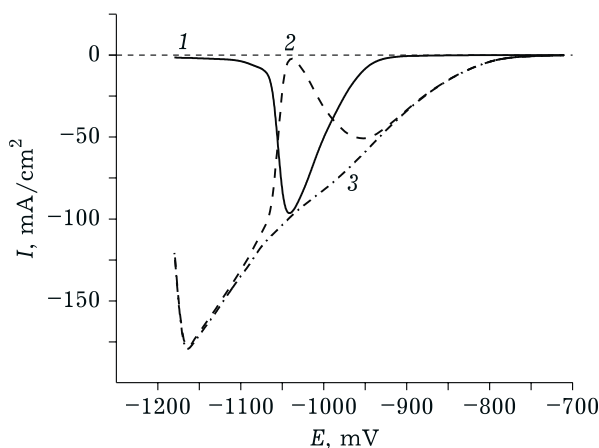


Fig. 7. Relations between the currents of the partial cathode reactions: 1 – the partial curve of tellurium dissolution in 4 M KOH; 2 – calculated partial curve of tellurium deposition from the solution of 0.5 M $\text{TeO}_2 + 4$ M KOH; 3 – experimental curve of tellurium deposition from the solution of 0.5 M $\text{TeO}_2 + 4$ M KOH.

trolyte, unlike for the solutions containing no base electrolyte (Fig. 5).

The effect of the rate of potential scan (V) on the cathode dissolution of metal tellurium in KOH was investigated. Polarization curves (Fig. 6, a) and the values of I_{lim} derived from these curves (see Fig. 6, b) allowed us to determine the limiting stage of the side cathode reaction. One can see in these data that an increase in the rate of cathode potential scan leads to a substantial increase in the rate of tellurium dissolution. The dependence of limiting currents I_{lim} on scanning rate raised to the 0.5 power ($V^{0.5}$) is linear. This directly suggests that the rate of the side cathode reaction of tellurium dissolution is limited by the diffusion of ditelluride anion into the volume of the electrolyte.

The effect of the side reaction on tellurium deposition may be estimated from the relations between the currents of partial cathode reactions shown in Fig. 7. One can see that within the potential range $-900 \dots -1100$ mV the side reaction of dissolution causes a substantial decrease in the rate of the target reaction of tellurium deposition. It follows from the data shown in Fig. 1, b and Fig. 3, b that the target reaction accounts for $\sim 80\%$, while the side reaction of tellurium dissolution accounts for $\sim 20\%$ of total electricity consumption.

So, the studies allowed us to evaluate the effect of KOH concentration on the rates of the target and side cathode reactions and to determine the working range of alkali concentration for the recovery of metal tellurium from tellurite solutions. This result is of practical interest from the viewpoint of resource saving and an increase in the ecological safety of this technological process.

CONCLUSION

Within the concentration range of 2–4 M, the “free” potassium hydroxide only weakly affects the rates of the target reaction of tellurium deposition and the side reaction of its cathode dissolution: these rates change by 5–10%. A decrease in the rate of the target reaction at KOH concentration below 2 M is caused by a decrease in TeO_3^{2-} concentration due to the incomplete dissolution of tellurium dioxide. A decrease in the rate of the side reaction within the range of KOH concentrations 0.1–1 M is caused by the low electric conductivity of the solution.

Within the studied range of KOH concentrations, the target reaction of tellurium deposition

and the side reaction of its dissolution have diffusion-driven nature. The side reaction of tellurium dissolution obeys the single-electron mechanism.

During the cathode deposition of tellurium, the target reaction accounts for 80 %, while the side reaction of tellurium dissolution accounts for 20 % of the total consumption of electricity. Results of the investigation allow optimization of the working mode of electrolytic extraction of tellurium from alkaline tellurite solutions.

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REFERENCES

- 1 Wu T., Zhang M., Lee K.-H., Lee C.-M., Lee H.-K., Choa Y., Myung N. V., Electrodeposition of compact tellurium thick films from alkaline baths, *J. Electrochem. Soc.*, 2017, Vol. 164, No. 2, D82–D87.
- 2 Zhong J., Wang G., Fan J., Li Q., Kiani M., Zhang J., Yang H., Optimisation of process on electrodeposition of 4N tellurium from alkaline leaching solution, *Hydrometallurgy*, 2018, Vol. 176, P. 17–25.
- 3 Lee T., Lee S., Lee E., Sohn S., Lee Y., Lee S., Moon G., Kim D., Kim Y., Myoung J., Wang Z., High-power density piezoelectric energy harvesting using radially strained ultrathin trigonal tellurium nanowire assembly, *Advanced Materials*, 2013, Vol. 25, No. 21, P. 2920–2925.
- 4 LaLonde A. D., Pei Y., Wang H., Snyder H., Lead telluride alloy thermoelectrics, *Materials Today*, 2011, Vol. 14, No. 11, P. 526–532.
- 5 Abad B., Rull-Bravo M., Hodson S. L., Xu X., Thermoelectric properties of electrodeposited tellurium films and the sodium lignosulfonate effect, *Electrochimica Acta*, 2015, Vol. 169, P. 37–45.
- 6 Kindyakov P. S., Korshunov V. G., Fedorov P. I., Kislyakov I. P., Chemistry and Technology of Rare and Scattered Elements [in Russian], K. A. Bolshakov (Ed.), 2nd edition, Moscow: Vysshaya Shkola, 1976. 320 p.
- 7 Buketov E. A., Malyshev V. P., Recovery of Tellurium from Copper Electrolyte Slimes [in Russian], Alma-Ata, Nauka: 1969. 208 p.
- 8 Soshnikova L. A., Kupchenko M. M., Processing of Copper Electrolyte Slimes [in Russian], Moscow: Metallurgiya, 1978. 499 p.
- 9 Belobaba A. G., Masliy A. I., Effect of surfactants on cathode deposition of tellurium from alkaline solutions, *Chemistry for Sustainable Development*, 2018, Vol. 26, No. 1, P. 7–12.
- 10 Kletenik Yu. B., Aleksandrova T. P., Submicron regeneration of the surface of indicator electrodes. Graphite electrode [in Russian], *Zhurn. Analit. Khimii*, 1997, Vol. 52, No. 3, P. 280–284.
- 11 Handbook on Electrochemistry [in Russian], A. M. Sukhotin (Ed.), Leningrad, Khimiya: 1981. 488 p.