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Study of an Opportunity of Using Solid Electrodes for Express Determination of Tellurium in Alkaline Solutions

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Abstract

Tellurium reduction in alkaline solutions in the concentration range of tellurite ions of 0.001–1 M was studied by a voltammetric method on updated solid indicator electrodes (Au, Pt, Ni and graphite). It was detected that a change in the form of the cathode current-voltage curve was observed for all electrodes at constant alkali concentrations and an increase in the tellurium concentration in solutions above 0.2–0.3 M. It was found that a change in the ratio of hydroxide and tellurite ions concentrations could be one of the probable causes for this. An opportunity of using the studied electrodes for express control of the tellurium concentration in the alkaline electrolyte used to obtain high purity tellurium was demonstrated.

Key words: tellurium, cathode reduction, alkaline electrolyte, solid indicator electrodes, electroanalysis

INTRODUCTION

Tellurium is a rare element with some unique properties that drive its application. Metallurgical enterprises manufacturing cast iron, steel, lead alloys, where technical tellurium is used as a dopant, are the major consumers of tellurium. Higher quality tellurium is used as a component of semiconductors for electronics, space technology, and solar energetics. The application range of its compounds constantly broadens. Lately, the demand for tellurium increases both in industries and new spheres of use of its compounds. In this regard, much attention is given to manufacture of high purity tellurium.

Anode slimes of electrolytic refining of copper are the major raw materials to obtain tellurium. The complexity and diversity of the chemical composition of slimes and the current traditions at plants determine the availability of many technological schemes of tellurium extraction [1–6]. Tellurium in almost all schemes is preliminarily transferred to an aqueous solution of its salt or solid dioxide, and then reduced to the elementary condition by the known methods. Thus, the technological scheme of tellurium preparation at the MMC “NORILSK NICKEL” [7] includes the following basic operations: leaching of tellurium-containing raw materials with a sulphuric acid solution, tellurium cementation by nickel powder, leaching of the cementate in aqueous caustic, TeO_2 precipitation and electrochemical isolation of the metal from an aqueous TeO_2 solution, refining fusion. (The same technology is used at the Sibkhimtekhnologiya JCS (Berdsk, Russia).)

Tellurium electrodeposition from alkaline solutions is well studied [8, 9]. As a rule, cathode tellurium is increased during 5–7 days. Since a decrease in the tellurium concentration during electrolysis leads to a decrease of the yield on current efficiency and worsening of the quality of the cathode precipitate, the stripped solution is periodically reinforced. In this regard, the need for express control of the tellurium concentration arises during electrolysis. At least, this is compulsory for timely decision making about reinforcing the solution, as well as for determining the residual tellurium content and correct selecting the completion time of the electrolysis process. In our opinion, voltammetric method is the most promising for solving this task.

The present work is devoted to the study of tellurium reduction on solid indicator electrodes to assess an opportunity of their use in electroanalysis of alkaline tellurium electrolytes.

EXPERIMENTAL

All studies were carried out using an electrochemical sensor equipped with a three-electrode electrochemical cell [12], a device for mechanical updates of the solid indicator electrode and an IPC-Micro potentiostat combined in a single housing. Gold, platinum or nickel wire with a diameter of 0.5 mm, as well as a rod with a diameter of 2 mm of spectral graphite powder impregnated with epoxy resin and polyethylene polyamine were an indicator electrode. The lateral surface of the electrode is isolated from solutions by a cured epoxy shell. The electrode end updated by cutting of a thin surface layer directly in the analyzed solution before each measurement was the working surface of the electrode. A silver chloride electrode was used as a comparison electrode, a graphite rod with a large surface – as auxiliary. The built-in potentiostat ensured the assignment of the potentiometric mode to obtain the current-voltage curve, registering of the potential and current run through the electrodes flowed by transmission of information to the computer. Current-voltage curves were recorded with a sweep rate of 20 mV/s. The values of the potentials, including the standard equilibrium, are given in the article relatively saturated silver chloride electrode.

The studies were carried out in the supporting solution of KOH contained different tellurium concentrations, KOH concentration varied from 0.4 to 8 mol/L. A solution of tellurium with a concentration of 1 mol/L was prepared by dissolving a sample weight of TeO_2 in 4 M KOH solution when heating in a water bath (temperature of 70–80 °C) with stirring for 2 h. This process corresponds to the reaction

$$TeO_2 + 2KOH = K_2TeO_3 + H_2O \quad (1)$$

If the solution was of grey colour because of tellurium dioxide not dissolved, it was filtered off, and the tellurium concentration was determined by dichromatometric titration [13]. Lower concentration solutions were prepared by sequential dilution of 4 M KOH solution.

RESULTS AND DISCUSSION

Gold, platinum, nickel and graphite electrodes were selected as indicator electrodes. There are literature data about electrochemical reduction of Te(IV) using these electrodes in acid and neutral solutions [14–17]. Works on tellurium reduction using the selected electrodes were not found by us. The most known data on Te(IV) reduction in alkaline solutions were obtained using dropping mercury [18–21] and tellurium [8, 9] electrodes. According to these studies, the following reactions are probable in alkaline solutions:

$$TeO_3^{2-} + 3H_2O + 4\bar{e} = Te + 6OH^- \quad E^0 = -0.81\ V \quad (2)$$

$$2Te + 2\bar{e} = Te_2^{2-} \quad E^0 = -1.07\ V \quad (3)$$

$$Te + 2\bar{e} = Te^{2-} \quad E^0 = -1.36\ V \quad (4)$$

$$Te_2^{2-} + 2\bar{e} = 2Te^{2-} \quad E^0 = -1.67\ V \quad (5)$$

Cathode current-voltage curves for gold and platinum electrodes in a pure solution of 4 M KOH in the presence of various tellurium concentrations are given in Figs 1, 2. It can be seen that the currentless potential of the studied electrodes in an alkaline solution is close to zero. The cathode current does not change during cathodic polarization up to approximately –0.85 V. The maximum recovery current of Te(IV) to Te^0 by equation (2) is observed at more negative potentials in solutions with the tellurium concentration of 0.1–0.2 M (see Figs. 1, 2,

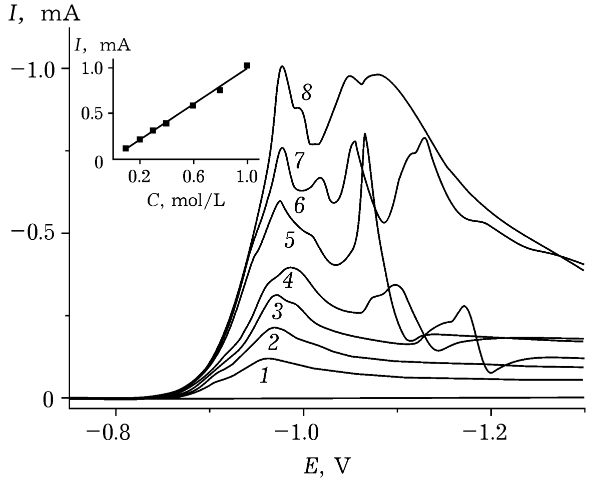

Fig. 1. Current-voltage curves of Te(IV) reduction using a gold electrode. Here, and in Figs. 2–4: background is 4 M KOH solution; in the insertion: calibration dependence; Te(IV) concentration (M): 0 (*1*), 0.1 (*2*), 0.2 (*3*), 0.3 (*4*), 0.4 (*5*), 0.6 (*6*), 0.8 (*7*), 1.0 (*8*).

curves *2*, *3*). A change in the form of the current-voltage curve happens and additional peaks appear in a more negative region of potentials occur with an increase in the tellurium (IV) concentration. Herewith, the position of the first cathode peak is preserved, and its value almost linear depends on the concentration of tellurite ions in a solution. It was found that current-voltage curves obtained using gold and platinum electrodes were well reproduced.

It is established that the current-voltage curves obtained on gold and platinum electrodes are well reproduced. The calibration dependences on these electrodes come out of zero and linear in a wide range of concentrations (0.001–1 mol/L).

A similar character of current-voltage curves in 4 M KOH solution containing different concentrations of tellurite ions was also observed in a nickel electrode, however, the reproducibility of current-voltage curves for this electrode does not meet analysis requirements. In this regard, Te(IV) reduction using a nickel electrode was not studied in detail.

Current-voltage curves of reduction of tellurite ions using a graphite electrode substantially differ from dependencies for metal electrodes. Cathodic curves registered using an updated graphite electrode in 4 M KOH solutions containing 0.01–0.1 M Te(IV) are given in Fig. 3. One can see that a reduction wave of Te(IV) with the distinct limiting current is observed in the region of potentials from −0.9 to −1.4 V. A small maximum, the value of which has only a weak dependence on the tellurium concentration in a solution, is noticeable at the limiting current of the wave at the potentials near −1.5 V. Such a form of the current-voltage curve is preserved up to the tellurium concentration of 0.2 mol/L. It was found that limiting current values was linearly dependent on the tellurium concentration in a solution in a range of 0.01 to 0.2 M.

The closeness of the half-wave potential and the standard potential of the reaction is worth

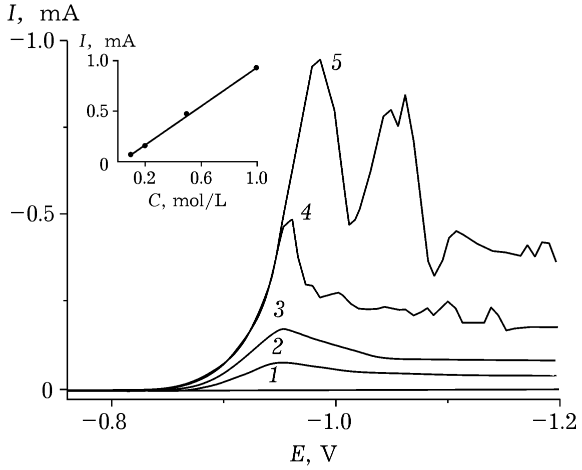

Fig. 2. Current-voltage curves of Te(IV) reduction using a platinum electrode. Te(IV) concentration (M): 0 (*1*), 0.1 (*2*), 0.2 (*3*), 0.5 (*4*), 1.0 (*5*).

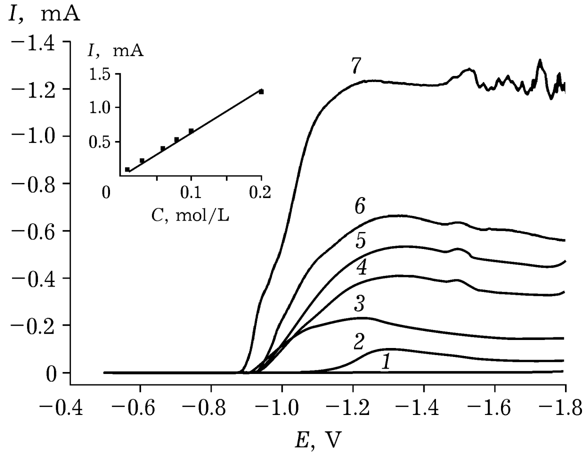

Fig. 3. Current-voltage curves of Te(IV) reduction using a graphite electrode. Te(IV) concentration (M): 0 (*1*), 0.01 (*2*), 0.03 (*3*), 0.06 (*4*), 0.08 (*5*), 0.1 (*6*), 0.2 (*7*).

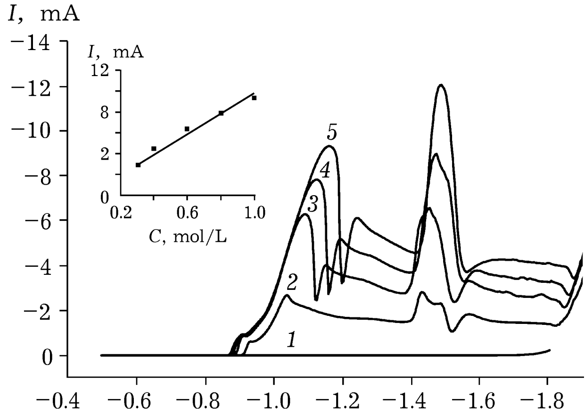

Fig. 4. Current-voltage curves of Te(IV) reduction using a graphite electrode. Te(IV) concentration (M): 0 (*1*), 0.3 (*2*), 0.6 (*3*); 0.8 (*4*), 1.0 (*5*).

noting. Apparently, the limiting current does not reflect the joint occurrence of processes along reactions (2) and (3). Data of work [18] that present direct and alternating current polarograms of tellurium (IV) reduction in a region of potentials from −0.8 to −1.5 V also speak in favour of this. A typical polarographic wave was obtained in the first case. Two peaks in this region of potentials are observed in the alternating current polarogram: the first peak, the potential of the maximum of which coincides with the half-wave potential of the direct current polarogram, accounts to Te(IV) reduction to metal tellurium, the second peak is more negative and corresponds to the formation of telluride ions.

It was found that a change in the form of the current-voltage curve and the appearance of additional peaks were observed in the graphite electrode, like metal electrodes with the fixed concentration of KOH (4 M) and an increase in the tellurium concentration above 0.2 M (Fig. 4). However, unlike metal electrodes, the form and the region of potentials of the primary analytical signal in graphite electrode is not preserved. Nevertheless, the value of the current for a peak in a region of potentials of −1.0 to −1.2 V is reproduced well and is linear dependent on the tellurium concentration in a solution in a range of 0.3 to 1.0 M.

Thus, the value of the limiting current is used in a graphite electrode as an analytical signal in a region of tellurium concentrations of 0.01 to 0.2 M, at higher concentrations – a peak in the region of potentials between −1.0 to −1.2 V. Calibration dependencies for these regions of tellurium concentrations are demonstrated in Figs. 3, 4.

One may assume that the change observed by us in the form of the current-voltage curve with an increase in the tellurium concentration is due to a decrease in the concentration of a free alkali in a solution. To clarify this issue current-voltage curves of solutions with the fixed concentration of tellurite ions and different concentrations of KOH were obtained. Cathodic current-voltage curves on an example of 0.1 M and 0.4 M solutions of Te(IV) are presented in Fig. 5. One can see that the alkaline concentra-

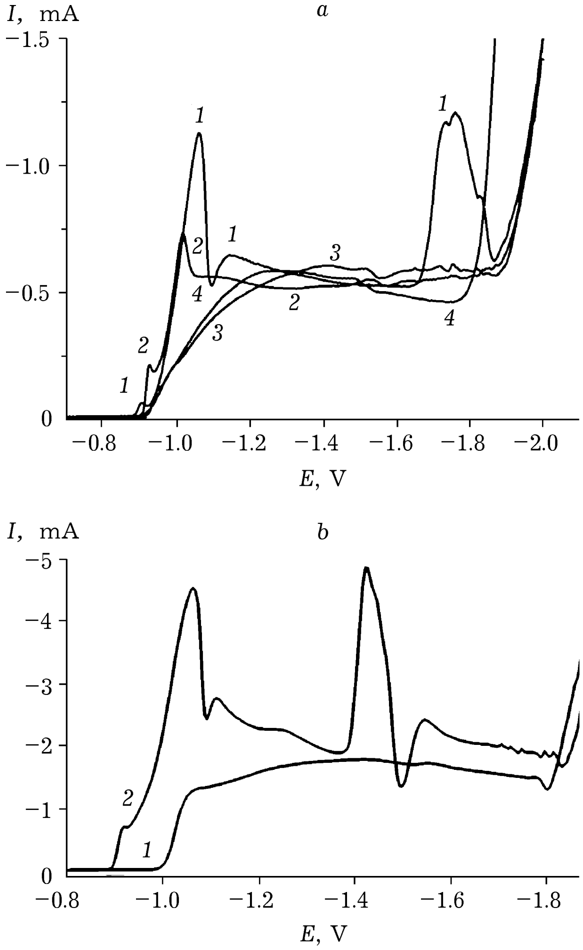

Fig. 5. Effect of KOH concentration on the form of the current-voltage curve: *a* – Te(IV) concentration is 0.1 M; KOH concentration (M): 0.4 (*1*), 1.0 (*2*), 2.0 (*3*), 4.0 (*4*); *b* – Te(IV) concentration is 0.4 M; KOH concentration (M): 8.0 (*1*), 4.0 (*2*).

TABLE 1

Effect of the concentration of alkali on the form of current-voltage curves

$C_{TeO_3^{2-}}$, M	C_{KOH}, M	$C_{KOH}/C_{TeO_3^{2-}}$	Form of cathodic curves
1	4	4	Curve with maxima
0.5	4	8	The same
0.4	4	10	The same
0.4	8	20	Current-voltage wave
0.3	4	13	Curve with maxima
0.2	4	20	Current-voltage wave
0.1	4	40	The same
0.1	2	20	The same
0.1	1	10	Curve with maxima
0.1	0.4	4	The same

tion affects both the form of the current-voltage curve and the value of the current. Thus, during tellurium (IV) reduction from a 4 M KOH solution containing 0.1 M Te(IV), a wave is observed (see Fig. 5, *a*, curve *4*). Reducing the alkali concentration to a value ≤2 M leads to the appearance of peaks in the region of potentials from −0.9 to −1.1 V and more negative than −1.6 V (curves *1, 2*). On the contrary, if the cathodic curve of a solution of tellurium with a concentration of 0.4 M in a solution of 4 M KOH represents a curve with maxima (see Fig 5, *b*, curve *2*), then it has the form of a wave (curve *1*) in a solution of 8 M KOH. The value of the current of the analytical signal drops with an increase in the alkali concentration. Thus, it can be seen from the curves obtained that their form is directly associated with the ratio of the concentration of an alkali and tellurium in a solution.

A similar dependence of the value of the limiting current on the alkali concentration in a solution was also observed for a tellurium electrode [8, 9]. The difference in the limiting current values ($i_{1/c}$) of tellurium in solutions with low and high alkali concentrations is associated by the authors with differences in the nature of tellurium-containing particles in these solutions.

The results of carried out analysis of the entire collection of the resulting current-voltage curves for a graphite electrode are summarized in Table 1. As can be seen, the current-voltage curve takes the form of a wave in more concentrated solutions by alkali (the ratio of hydroxide and tellurite ions ≥20), and a curve is observed in less concentrated. Thus, the observed modifications are due to an excess of an alkali in a solution.

Dependencies of the current from the concentration of Te(IV) for a graphite indicator electrode were used to control the content of Te(IV) in alkaline electrolytes. Analysis was carried out in electrolyte samples (without dilution and additional sample preparation) selected in different times of electrolysis. Determining correctness was checked by comparison of the obtained results with dichromatometric titration results [13]. The results are presented in Table 2. The table data demonstrate that the results are compatible. The accuracy of the current-voltage method is lower than that of dichromatometric but quite satisfactory for quick assessment of the content of tellurium in the electrolyte with the purpose of rapid intervention into the technological process.

CONCLUSION

Cathodic reduction of tellurium in alkaline solutions using updated solid electrodes (Au, Pt, Ni, and graphite) was studied with the aim to

TABLE 2

Determining results of Te(IV) in alkaline electrolytes (n = 3, P = 0.95)

Sample No.	Te(IV) concentration, g/L			
	Dichromatometry		Voltammetry	
	C±δ	S_r	C±δ	S_r
1	62.1±0.9	0.0057	58±4	0.0273
2	28.1±0.6	0.0093	30±2	0.0237
3	6.0±0.2	0.0144	6.8±0.6	0.0383

find a method of express control of the tellurium concentration in alkaline electrolytes used for the preparation of high purity tellurium.

It was demonstrated that with the fixed alkali concentration (4 M) and an increase in the tellurium concentration above 0.2–0.3 M, a change in the form of the cathodic current-voltage curve related to a change in the ratio of tellurite and hydroxide ions concentrations was observed.

It was found that platinum, gold and graphite electrodes could be used for assessment of the tellurium concentration in alkaline electrolytes by current-voltage techniques of analysis.

REFERENCES

1 Hoffmann E., *J. of Metals*, 41, 7 (1989) 33.

2 Bol'shakov K. A. (Ed.), Khimiya i Tekhnologiya Redkikh i Rasseyannykh Elementov, part III, Vyssh. Shkola, Moscow, 1976.

3 Kudryavtsev A. A., Khimiya i Tekhnologiya Selena i Tellura, Vyssh. Shkola, Moscow, 1961.

4 Lebed' A. B., Proizvodstvo Selena i Tellura na OAO Uralelektromed' JSC, Izd-vo Ural. Un-ta, Yekaterinburg, 2015.

5 Ha Y.-C., Sohn H.-J., Jeong G.-J., Lee C. K., Rhee K.-I., *J. Appl. Electrochem.*, 3 (2000) 315.

6 Rhee K.-I., Lee C. K., Yoo C.-S., Kim T.-H., Sohn H.-J., EPD Congress "The Recovery of Tellurium from Copper Anode Slimes" (Proceedings), 1997, pp. 495–496.

7 Kislenko E. A., Ter-Oganesyants A. K., Anisimova N. N., Dyl'ko G. N., Luchitskiy S. L., *Tsv. Metally*, 12 (2006) 48.

8 Alekperov A. I., *Usp. Khim.*, 43, 4 (1974) 585.

9 Abrarov O. A., Bigelis V. M., Elektroosazhdeniye Tellura, Fan, Tashkent, 1976.

10 Aleksandrova T. P., Skvortsova L. I., Bek R. Yu., Vays A. A., Simp. "Teoriya i Praktika Elektroanaliticheskoy Khimii" (Treatises), Tomsk, 2010, p. 59.

11 Aleksandrova T. P., Bek R. Y., Skvortsova L. I., Vais A. A., *Electroanal.*, 23, 5 (2011) 1073.

12 RU Pat. No. 2408877, 2011.

13 Sharlo G., Metody Analiticheskoy Khimii. Kolichestvennyy Analiz Neorganicheskikh Soyedineniy, Khimiya, Moscow, 1965.

14 Nguyen Van Ngac, Vittori O., Quarin G., *J. Electroanal. Chem.*, 167 (1984) 227.

15 Traore M., R. Modolo, Vittori O., *Electrochim. Acta*, 33, 7 (1988) 991.

16 Montiel-Santillan T., Solorza O., Sanchez H., *J. Solid State Electrochem.*, 6 (2002) 433.

17 Dergacheva M. B., Statsyuk V. N., Fogel' L. A., *Electrochim.*, 37, 6 (2001) 734.

18 Schmidt H., Stackelberg M. V., *J. Polarograph. Soc.*, 8, 3 (1962) 49.

19 Lingane J. J., Niedrach L. W., *J. Am. Chem. Soc.*, 71, 1 (1949) 196.

20 Lingane J. J., Niedrach L. W., *J. Am. Chem. Soc.*, 70, 12 (1948) 4115.

21 Panson A. J., *J. Phys. Chem.*, 67, 10 (1963) 2177.