Effect of Surfactants on Cathode Deposition of Tellurium from Alkaline Solutions

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Abstract

The effect of surfactants on the rate of the target reaction of tellurium precipitate from alkaline tellurium solutions and the side reaction of further reduction to ditelluride anions, and also current efficiency and morphology of cathode tellurium precipitates is examined on a graphite electrode pre-coated with tellurium sludges by the voltammetry method. Sodium lignosulphonate and polyvinyl alcohol have a weak effect on the rates of both cathode reactions and therefore on the morphology of tellurium precipitates, as demonstrated. Tetrabutyl ammonium hydroxide additive inhibits both reactions but simultaneously worsens the quality of cathode precipitate: there generated a powdery sludge that is partly poured out from the substrate and is almost completely rinsed away upon water washing.

The most efficient additive to obtain dense tellurium precipitates is OP-10 wetting agent. It substantially inhibits tellurium deposition and suppresses the side reaction of its dissolution in the virtually important range of potentials until the maximum current. At the same time, OP-10 significantly improves precipitate morphology and ensures obtaining fine-crystalline dense cathode tellurium precipitates.

Keywords: surfactants, rate of reactions, tellurium deposition, formation of ditelluride anions, alkaline solutions, surface morphology

INTRODUCTION

High purity tellurium and its alloys are widely used to produce photoconductive layers, and also piezoelectric and thermoelectric devices [1–3]. Herewith, the main procedure to obtain tellurium is electrolysis of alkaline tellurite solutions generated during hydrometallurgical processing of anode slimes from copper production [4, 5]. The cathode potential is gradually shifted to more negative values and inevitably reaches beyond the optimum limits, causing worsening of the quality of cathode precipitate because of the galvanostatic mode of electrolysis used in industry and a gradual reduction of the concentration of tellurite ions in the electrolyte over time. In turn, this contributes to capturing impurities from a solution and leads to a decrease in product purity.

Another significant issue of tellurium electrodeposition from concentrated alkaline solutions is the closeness and partial overlapping of potential ranges of the main (tellurium metal deposition) and side (soluble ditelluride anion formation) processes [6]. This also leads to a decrease in current efficiency with an increase in cathode potential and dramatic worsening of precipitate quality. Therefore the search for preparation conditions of cathode tellurium precipitates is a relevant task [7, 8]. The use

of surfactants may be quite promising among probable methods of selective impact on the rates of electrode reactions and the quality of cathode precipitates [9]. The positive effect of sodium lignosulphonate additive on morphology and thermoelectrical properties of tellurium precipitates from its nitric acid solutions was noted in [10]. Similar publications on the effect of surfactants on tellurium deposition process from alkaline electrolytes are not discovered by us. Therefore the goal of our work is the study of adsorption of some surfactants on the rates of the main and side reactions and morphology of cathode tellurium precipitates.

Considering the complex mechanism and kinetics of cathode processes in alkaline tellurite solutions in a wide range of potentials [11, 12], studies in this work will be limited by the range of potentials until the maximum diffusion current of tellurite ions that is of greatest interest during practical preparation of high purity tellurium.

EXPERIMENTAL

The kinetics of the target and side reactions of tellurium cathode deposition process was studied by the voltammetry method with potential linear sweep using IPC-compact programmable potentiostat (A.N. Frumkin Institute of Physical chemistry and Electrochemistry, IPCE RAS).

A mechanically updated graphite electrode (2 mm in diameter, the surface area of 0.031 cm^2) [13], at the end of which the tellurium precipitate with a thickness of 3 μm was applied to before each measurement from the base electrolyte by potentiostatic electrolysis ($E = -1.0$ V) was used as a working electrode. Cathode potentials were measured in relation to a saturated silver chloride reference electrode; platinum grid with an area of 1 cm^2 was used as an anode.

A solution containing 0.5 M TeO$_2$ (pure for analysis) and 4 M KOH (chemically pure) was used as a base electrolyte for pre-application of the tellurium precipitate and study of the kinetics of the target reaction. As surface-active additives, there have been studied the following substances: sodium lignosulphonate (SL, 2 g/L), polyvinyl alcohol (PVA, 10 % aqueous solution of PVA 18-88, 10 mL/L), tetrabutylammonium hydroxide (TBAH, 40 % aqueous solution, 10 mL/L) and OP-10 wetting agent (10 mL/L). Considering minor instability of freshly prepared solutions of surfactants, solutions aged for a day were used for measurements. The kinetics of the side reaction of ditelluride formation reaction was measured in background solution (4 M KOH).

Surface morphology of cathode precipitates was examined using a Hitachi TM-1000 scanning electron microscope (Japan). To approach real conditions of electrolysis, precipitate samples for this purpose (100 μm in thickness) were deposited onto a pre-prepared surface

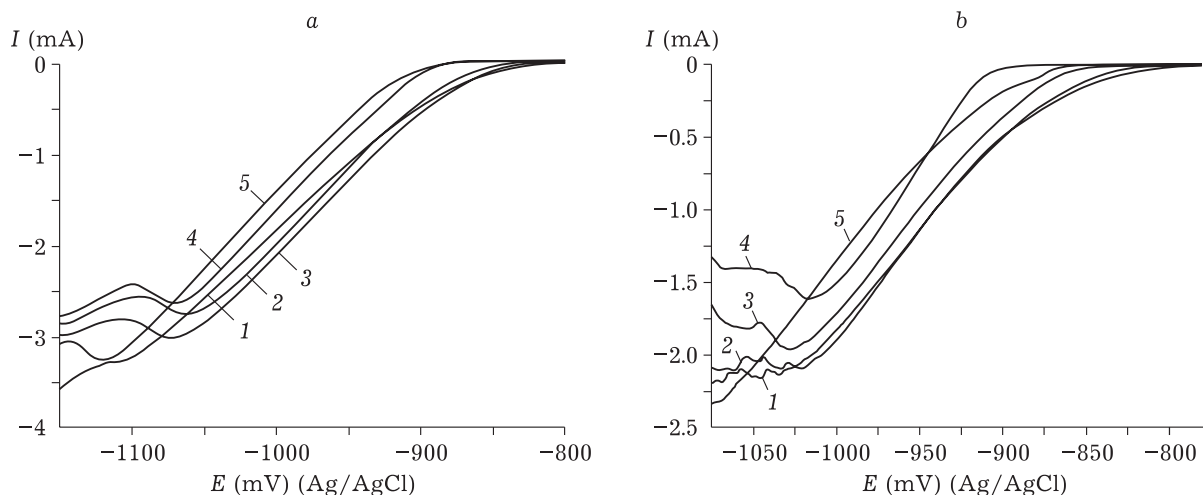Fig. 1. Cathode polarization curves of tellurium deposition from the pure solution 0.5 M K$_2$TeO$_3$ + 4 M KOH (curve *1*) and solutions with the addition of sodium lignosulphonate (*2*), PVA (*3*), OP-10 (*4*) and TBAH (*5*). The rate of the potential change, mV/s: 5 (*a*), 1 (*b*).

of vertical cathodes made of stainless steel in galvanostatic mode with fixed current density of 40 mA/cm^2, approximately equal to a half of the maximum current of the tellurium deposition process.

RESULTS AND DISCUSSION
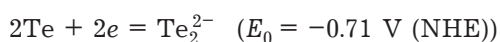
Effect of surfactants on tellurium deposition rate and cathode precipitate morphology

The progression of two reactions at the cathode is probable during tellurium electrodeposition from alkaline tellurite solutions in a range of potentials from the equilibrium value to the maximum current [6, 11]:

– target reaction (tellurite ion discharge to tellurium metal):

$TeO_3^{2-} + 3H_2O + 4e = Te + 6OH^-$

$(E_0 = 0.823 - 0.0886pH)$, V (NHE)
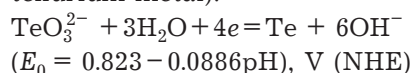
– and side reaction (reduction of metal tellurium to soluble ditellutide):

$2Te + 2e = Te_2^{2-}$ $(E_0 = -0.71$ V (NHE))

With a view to selecting the best conditions in demonstrating the effect of surfactants, measuring cathode polarization curves was carried out from base electrolyte and with surfactant additives with several potential scanning rates (1, 5 and 20 mV/s). As an example, Figure 1 gives the data for scan rates of 1 and 5 mV/s. It can be seen that herewith, the qualitative shape of polarization curves and their mutual location order for different surfactants remained almost unchanged. In addition, the value of the maximum discharge current of tellurite anions significantly increased with scan rate increase. Moreover, there was its minor shift to the negative potential range. The presence of surfactants with a scan of 20 and 5 mV/s almost did not affect the maximum current value (see Fig. 1, *a*). While with a scan rate of 1 mV/s (see Fig. 1, *b*), there is an increase in its values: the maximum current is reduced for PVA and OP-10, and a minor increase for
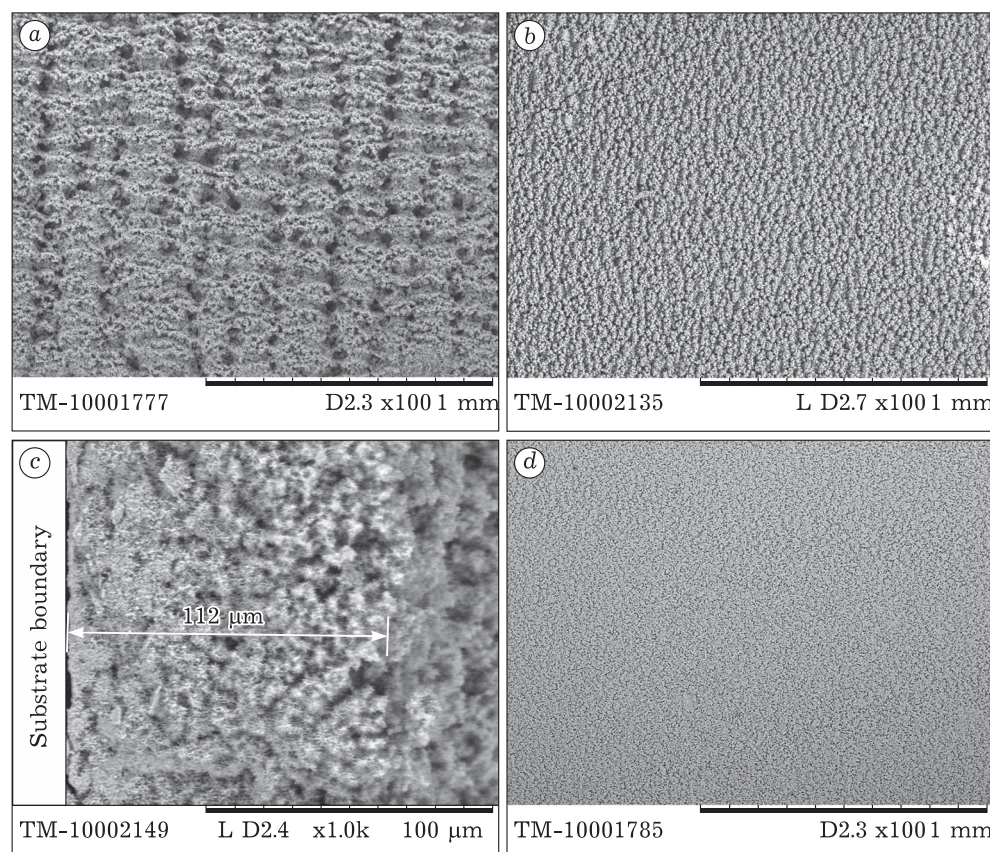

Fig. 2. Morphology of tellurium precipitates obtained from solutions: *a* – without surfactant addition; *b, c* – with the addition of 2 g/L of sodium lignosulphonate (*c* – cross section of this precipitate); *d* – with the addition of 10 mL/L of OP-10.

TBAH. Apparently, the effect of surfactants on the morphology and surface roughness of cathode precipitate begins to appear with low potential scan rate and long duration of curve survey. A quantitative gain of the effect of surfactants on tellurium deposition rate is most likely related to the same.

As it follows from the data of Fig. 1 the surfactants used by us, by tellurium deposition rate, may be divided into two groups: the effect of SL and PVA is relatively small, while OP-10 and TBAH additives lead to very significant inhibition of the process. For example, in the presence of OP-10, the deposition process is almost completely suppressed in a potential range to −900 mV, while there is a significant drop in current density in a wide range of potentials up to the maximum diffusion current. Considering this, it is logical to expect the effect of precisely these additives on the morphology of cathode tellurium precipitates.

Indeed, as can be seen from electron microscope images (Fig. 2) of the surface tellurium precipitate from a solution without additives already with a thickness of 100 μm has a quite rough porous structure with a large number of filamentous dendrites in precipitate surface and periodic (approximately 100−250 μm) vertical rows of pores (see Fig. 2, *a*). Perhaps, they are related to microconvective flows appearing during the deposition near vertical cathode surface. The presence of this porous structure may lead to worsening of washing out the cathode precipitate and decreasing its purity.

Sodium lignosulphonate additive improves tellurium cathode precipitate quality (see Fig. 2, *b*): rows of pore practically disappear; crystal size is reduced. Nevertheless, as can be seen from the image of the cross-section of this precipitate (see Fig. 2, *c*), it remains relatively dense in thin layers (20-40 μm). The amount and size of pores noticeably increase with an increase in layer thickness and thread-like dendrites are also generated in the surface. In addition, PVA additive has an effect close by nature on the morphology of cathode tellurium precipitates. However, out of alkaline electrolytes, OP-10 additive has the strongest smoothing effect on tellurium precipitate morphology (see Fig. 2, *d*): the sludge is obtained dense, uniform, and smooth. Not only periodically vertical rows of

pores but also thread-like dendrites in tellurium surface are absent.

From this standpoint, there have been acquired quite unexpected results on the morphology of tellurium precipitates in the presence of TBAH. It was found that even at the average thickness of precipitate 5−10 μm, a very tense powdery deposit that is partly crumbled away from the substrate and is almost completely washed away during washing away with water. Apparently, the noted gain of the maximum current is also related to a low amount of cathode tellurium precipitate. Considering the negative effect of this additive on the morphology of cathode tellurium, its further study is inappropriate.

Effect of surfactants on side reaction rate

According to the data of [6], in highly alkaline solutions (5 M KOH, rotating disk telluric electrode) the dependence of side reaction rate on the potential has a shape of a sharp peak with a maximum near $E = -1.0$ V. Figure 3 demonstrates experimental data regarding side reaction rate in the base electrolyte and the effect of surfactants on this process. From comparison the results for a pure solution (curve *1*) with the data of [6], it can be seen that they are quite close, considering the difference under measurement conditions (another alkali concentration, thinner cathode
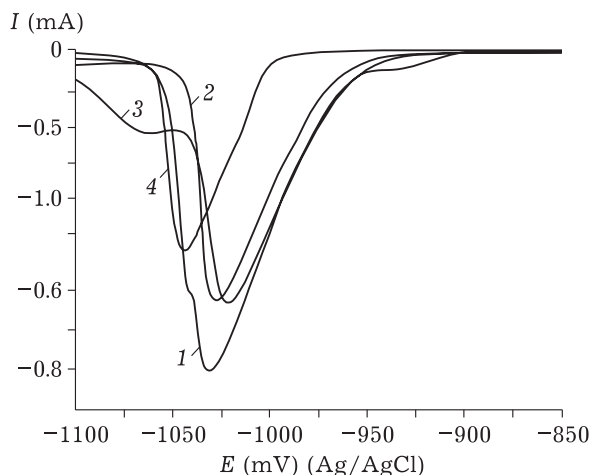
Fig. 3. Cathode polarization curves of the side reaction of the formation of soluble Te_2^{2-} ions in the pure solution 4 M KOH (curve *1*) and solutions with the addition of sodium lignosulphonate (*2*), PVA (*3*), OP-10 (*4*). The rate of the potential change is 1 mV/s.
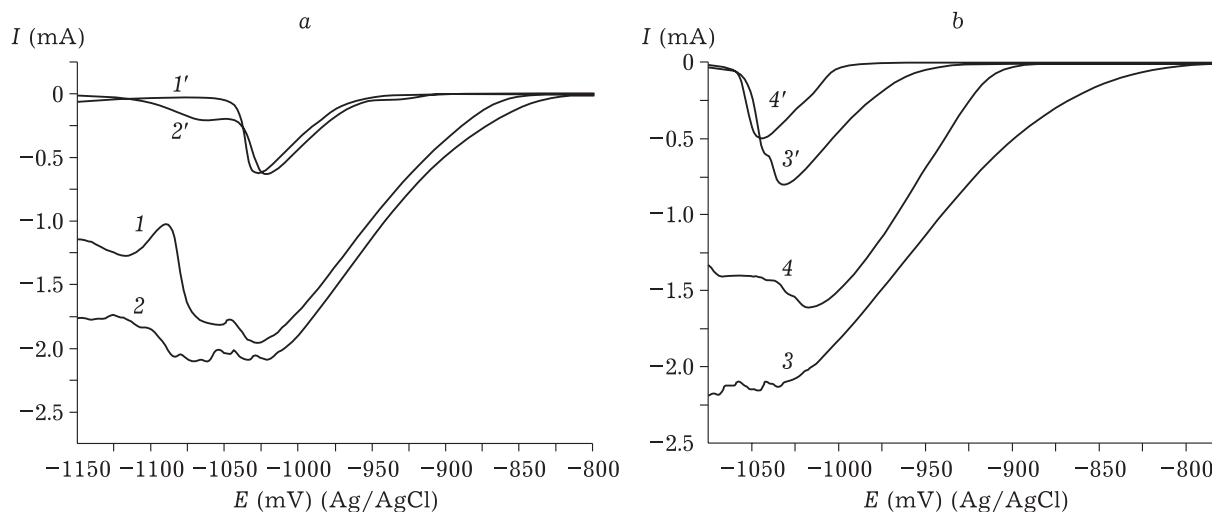
Fig. 4. Pairwise comparison of the rates of the taget (*1−4*) and side (*1'−4'*) reactions at different conditions of the precipitation: *a* − with the addition of PVA (*1, 1'*) and sodium lignosulphite (*2, 2'*); *b* − without surfactants (*3, 3'*) and with OP-10 (*4, 4'*) The rate of the potential change is 1 mV/s.

precipitate, the lack of solution stirring). As for the effect of surfactants, from the comparison of the data of Fig. 3 and 1, it can be seen that the effect of surfactants on both reactions is quantitatively similar: PVA and SL have little impact and only insignificantly inhibit tellurium dissolution rate. The current peak position is almost not shifted, while its value is reduced approximately by a quarter. On the contrary, OP-10 additive substantially shifts peak position and almost twice reduces its value. Apparently, this parallelism in the action of surfactants on both reactions is quite logical, as the chemical nature of the adsorbent (tellurium) and the range of adsorption potentials coincide.

In conclusion, *via* pairwise comparison of polarization curves of the target and side reactions (Fig. 4), the effect of the studied surfactants on the maximum rates of tellurium deposition (in other words, almost 100 % current efficiency) can be assessed. For this purpose, for each pair of curves (see Fig. 4), tellurium deposition currents (i_{max}) with the potential of the beginning of the side reaction were determined as the ratio to the maximum diffusion current of tellurite ions (i_{lim}) under these conditions and are equal to: 0.43 without surfactants, 0.53 for SL, 0.48 for PVA, and 0.90 for OP-10.

As it follows from the findings, the introduction of PVA and LS additives only insignificantly increases the relative rate of tellurium deposition. Unlike this, OP-10 additive almost entirely eliminates the effect of the side reaction in the most important range of potentials of tellurium deposition. Considering the positive effect of OP-10 on cathode precipitate morphology, precisely this additive could be recommended for deposition of dense cathode tellurium precipitates.

CONCLUSION

i) Sodium lignosulphonate (SL) and polyvinylalcohol (PVA) have a slight inhibiting effect on the rates of both reactions and, therefore, the morphology of tellurium precipitates.

ii) Tetrabutylammonium hydroxide (TBAH) additive leads to significant inhibition of both reactions and their shift towards the cathode side but, at the same time, dramatically worsens cathode precipitate quality, resulting in the formation of powdery tellurium precipitates poorly linked with the substrate and partly crumbled.

iii) The most efficient additive to prepare dense tellurium precipitates is OP-10 wetting agent. It significantly inhibits tellurium deposition and suppresses the side reaction of its dissolution in the practically important range of potentials until the maximum current. At the same time, OP-10 significantly improves precipitate morphology and ensures preparation of fine-crystalline dense cathode precipitates.

Acknowledgements

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