RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

April 1974

Translated from *Uspekhi Khimii*, **43**, 585-611 (1974)

U.D.C. 541.13 ; 546.23 ; 546.24

Electrochemistry of Selenium and Tellurium

A.I.Alekperov

The review deals with the principal advances in the electrochemistry of selenium and tellurium. Problems concerning the kinetics and mechanisms of the cathodic reduction of selenium and tellurium to different valence states and their anodic oxidation in aqueous and non-aqueous solutions are discussed.
The practical applications of electrochemistry in the isolation, refining, and determination of small amounts of the two elements are described.
The bibliography includes 178 references.

CONTENTS

I.	Introduction	235
II.	Electrochemical behaviour of selenium and tellurium electrodes in electrolytes of different compositions	236
III.	Cathodic and anodic deposition of selenium and tellurium	239
IV.	Polarography of selenium and tellurium	246

I. INTRODUCTION

Selenium and tellurium belong to the class of rare elements which are widely employed in various branches of modern engineering. These elements have many specific properties. As their purity improves, new properties are discovered and the scale and specific features of their applications are extended.

With expansion of the field of their applications, there arises the necessity for an intense investigation of the chemical and physicochemical properties and also of the technology of the preparation of pure and ultrapure selenium, tellurium, and their compounds.

The present state of the chemistry and technology of the preparation of pure and ultrapure selenium and tellurium have been described in monographs by Chizhikov and Schastlivyi[1,2], Kudryavtsev[3], Nazarenko and Ermakov[4], Bagnoll[5], and Yukhtanov[6] and in reviews[7,8].

The first study on the electrochemistry of tellurium was published at the beginning of the 19th century. Almost 100 years later the study of the electrochemical behaviour of selenium was begun. Subsequently, isolated papers, frequently containing contradictory data, appeared from time to time. Systematic study of the electrochemical properties of selenium and tellurium began in the 1950's–1960's in connection with their large-scale applications in modern engineering. Extensive data have now accumulated, a systematic account of which requires a separate review.

II. ELECTROCHEMICAL BEHAVIOUR OF SELENIUM AND TELLURIUM ELECTRODES IN ELECTROLYTES OF DIFFERENT COMPOSITIONS

1. OXIDATION-REDUCTION POTENTIALS OF SELENIUM AND TELLURIUM

Selenium

Apart from the metallic state, selenium can exist in the −2, +2, +4, and +6 states of oxidation. For the most stable states, the oxidation-reduction potentials can be represented schematically as follows[9]:

$$H_2Se \xrightarrow{-0.40} Se \xrightarrow{+0.74} H_2SeO_3 \xrightarrow{+1.15\delta} SeO_4^{2-}: \text{ acid solutions,}$$

$$Se^{2-} \xrightarrow{-0.92} Se \xrightarrow{-0.366} SeO_3^{2-} \xrightarrow{+0.05\delta} SeO_4^{2-}: \text{ alkaline solutions.}$$

The standard potential of the selenium–selenous acid system has been determined[10] by direct measurement of the equilibrium constant of the reaction

$$Se(\text{hexagonal}) + 2I_2(\text{cryst.}) + 3H_2O \rightleftarrows H_2SeO_3 + 4H^+ + 4I^-$$

and a value of +0.74 V† was adopted.

In view of the fact that a state of equilibrium is reached for the above system, it was concluded that the selenium–selenous acid system is reversible.

The steady-state potential of the selenium electrode in selenous acid solutions corresponds to the equilibrium potential of the selenium–selenous acid system[11]. The equilibrium state of the selenium–selenous acid system is also reached in solutions containing tin(II) chloride. The reduction of selenous acid by $SnCl_2$ permits the calculation of the equilibrium constant for the reaction[12]

$$H_2SeO_3 + 2SnCl_2 + 4HCl = 2SnCl_4 + Se + 3H_2O\ .$$

Titrations of selenous acid solutions with tin(II) chloride at different hydrochloric acid concentrations established[13] that in 2–8 M HCl the potential of the Se/SeO_3^{2-} system is +0.74 V. Hence it follows that in the above HCl concentration range selenium in solution in the SeO_2–HCl system exists preferentially as selenous acid.

Tellurium

It dissolves in alkalies and acids with oxidising properties. It forms compounds in both positive (Te^{2+}, Te^{4+}, and Te^{6+})‡ and negative (Te^{2-}, Te_2^{2-}) valence states. Tellurium(IV) compounds are the most stable. In the quadrivalent state tellurium forms numerous complexes[4]. In 2.5 M hydrochloric acid solution the tellurium complex has the composition H_2TeCl_6.[14] As stated by Iofa et al.,[15] in 3.5–7 M HCl there exist at least four different complex tellurium ions which are interconverted as the hydrochloric acid concentration is varied.

The potential of the tellurium electrode in hydrochloric acid solutions of tellurium(IV) was first measured by Reichinstein[16] and Kazarnovskii[17]. With increase of hydrochloric acid concentration from 0.05 to 4.5 M, the potential of the tellurium electrode also rises. It assumes the highest value (+0.567 V) in 2.5 M HCl. It was adopted[16,17] as the equilibrium standard potential of the Te/Te^{4+} system. This is not quite correct, since the authors made not altogether justified assumptions, namely that $TeCl_4$ is completely dissociated into Te^{4+} and Cl^- and that the activity coefficient is unity.

The introduction of a correction by Yakovleva and Andreev[18] in the calculation of the standard potential of the tellurium electrode in hydrochloric acid solutions cannot also be regarded as entirely justified. The authors state that, since there are no literature data for the activity coefficients of Te^{4+} ions and it is difficult to determine them, they can be assumed equal to the activity coefficients of $[Fe(CN)_6]^{4-}$ ions. The activity coefficient of an electrolyte is known to depend on the interaction between the ions with formation of ionic association complexes. Evidently the electrostatic and specific interactions between different ions must differ and hence one cannot assume the identity of the activity coefficients of different ions.

Thus +0.576 V should not be regarded as a standard potential but as an experimental or apparent potential observed in the Te/Te^{4+} system when the concentration ratio in the latter corresponds to the stoichiometry of the electrochemical reaction

$$Te^{4+} + 4e \rightleftarrows Te\ .$$

By measuring the equilibrium potential in the deposition of tellurium from hydrochloric acid solutions by tin(II) chloride, it was established[13] that at hydrochloric acid concentrations in the range 2–3 M the apparent reduction potential is almost independent of acid concentration and amounts to +0.584 V. With further increase of acid concentration, the reduction potential falls.

The surface of the tellurium electrode is rapidly oxidised, the oxide film having a significant influence on the electrode potential. The electrodes treated in an atmosphere of hydrogen at −200°C and then heated to 400°C in a high vacuum exhibit a potential in buffer solutions (free from O_2) which corresponds to the Te/TeO_2 system (in the pH range 2–12).[19]

Schuhmann[20] obtained the following data by direct measurements of the potential of the tellurium–tellurous acid system:

$$Te + 2H_2O = TeO_2(\text{solid}) + 4H^+ + 4e, \qquad \varphi = +0.529\ V,$$

$$Te + 2H_2O = TeOOH^+ + 3H^+ + 4e, \qquad \varphi = +0.559\ V.$$

With increase of pH, the potential of the tellurium electrode shifts in alkaline solutions and assumes a negative value. The e.m.f. of the cell Te(solid) | TeO_2(solid) | buffer solution ‖ calomel electrode at 25°C and in the pH range 2.2–8 is described by the equation $\varphi = 0.349 - 0.058$ pH.[21] Under these conditions, the electrode can be used as an indicator electrode in acidimetric titrations.

In 1 M NaOH solution the potential of the Te/TeO_3^{2-} system is −0.395 V (s.c.e.)§.[18] The sharp change of the potential of the tellurium electrode in alkaline electrolytes is due to the reaction $3Te + 6NaOH = Na_2TeO_3 + 2Na_2Te + 3H_2O$.

As a result of this reaction, the composition of the electrolyte near the electrode probably changes, Te^{2-} ions appear and create completely different conditions at the tellurium electrode. Another cause of the fall of the electrode potential as the concentration of alkali is altered may be a change in the composition and structure of the tellurite ions.

† The standard potentials are quoted relative to the hydrogen electrode.

‡ The valence indices characterise the degree of oxidation and not the ionic structures.

§ s.c.e. = saturated calomel electrode.

The standard potential of the TeO_3^{2-}/TeO_4^{2-} system in alkaline solutions was obtained on the basis of the oxidation of tellurite with hypoiodate[9]:

$$Te_2O_3^{2-} + 2OH^- = TeO_4^{2-} + H_2O + 2e.$$

It was found that $\varphi = +0.4$ V.

Thus the potentials of tellurium systems can be represented schematically as follows:

$$H_2Te \xrightarrow{-0.72} Te \xrightarrow{+0.529} TeO_2(solid) \xrightarrow{+1.026} H_6TeO_6(solid) \text{ acid solutions,}$$

$$Te^{2-} \xrightarrow{-1.14} Te \xrightarrow{-0.57} TeO_3^{2-} \gtrless^{+0.46} TeO_4^{2-} \text{ alkaline solutions.}$$

More detailed information about the carefully adjusted potentials of tellurium systems and the variation of the potential of the tellurium electrode with pH is given by Pourbaix[22].

2. ELECTROLYTIC REACTIONS AT SELENIUM AND TELLURIUM ELECTRODES

Selenium

Comparison of the conductivities in the S, Se, Te series shows that the conductivity of sulphur is very low, tellurium resembles metals as regards its conductivity, and selenium exhibits semiconductor properties. Semiconductor properties and photosensitivity have a marked influence on the electrochemical behaviour of selenium.

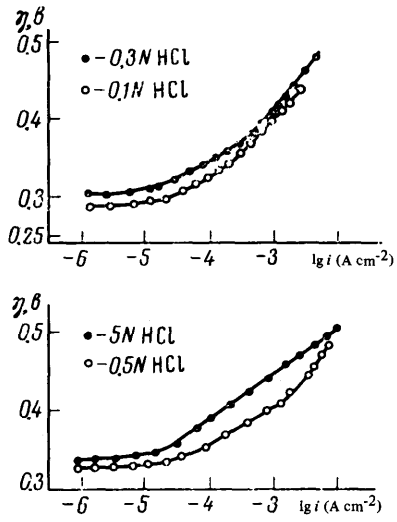


Figure 1. Polarisation curve obtained with the tellurium electrode in hydrochloric acid solutions[29].

In the polarisation of selenium with n- and p-type of conduction in 0.1 N sulphuric acid solution, Gobrecht et al.[23] noted that polarisation of n-type selenium hardly changes on illumination and is determined mainly by the ohmic resistance of the electrode. Illumination of p-type selenium lowers appreciably the cathodic polarisation. Anodic polarisation decreases much less on illumination. The different effects of illumination on the cathodic and anodic processes show that the decrease of the cathodic polarisation in the given case does not occur solely due to a decrease of the ohmic resistance of selenium under the influence of light. The high cathodic polarisation is evidently caused by the fact that in the cathodic reduction of hydrogen ions free electrons are involved, the concentration of which in p-type selenium may be very low.

A high cathodic polarisation in the dark and its decrease on illumination were noted in the electrolytic deposition of selenium at a selenium electrode from selenous acid solutions[24] and also from weakly and strongly acid solutions of selenium dioxide[25].

After the application of an external e.m.f. to the electrodes of the electrolytic cell consisting of two selenium electrodes immersed in 57% H_2SeO_3, the cathode acquires a high sensitivity to illumination, amounting approximately to 1000 ma lm^{-1}.

It is believed[26] that such high light sensitivity of a photoelectric cell of this kind is due to the formation on the surface of the selenium electrode of a blocking layer by adsorbed hydrogen atoms (a solid solution of hydrogen in selenium) generated by the reduction of H+ ions at the electrode.

The photoelectric effect at the selenium electrode (gold foil coated by red selenium) in aqueous hydrochloric acid solution has been investigated[27].

Tellurium

When a tellurium electrode is immersed in 0.1 N H_2SO_4 or 0.1 N NaOH solutions at low current densities (5×10^{-6}–1×10^{-5} A cm^{-2}), a sharp potential jump towards lower positive values associated with a fall of IR is observed in the initial stage of the cathodic polarisation. The subsequent slow variation of the potential (before attaining a steady value) is associated with the reduction of the oxide film, the formation of a double layer, the reduction of H^+ ions, and the formation of hydrogen molecules on the electrode surface.

In the anodic polarisation the rapid initial increase of the potential is associated with the ionisation of H_2 formed in the cathodic polarisation. The subsequent slow change of the potential is a consequence of the evolution of oxygen accompanied by the oxidation of the metal[28]. When the surface of the electrode is completely covered by oxides, the potential acquires a constant value and changes only with current density.

The $\eta - \lg i$ polarisation curves (the variation of the hydrogen overvoltage η with $\lg i$), measured with the aid of a tellurium electrode in 0.05–5 N H_2SO_4, in buffer solutions at pH 3–13, and in 0.1 N NaOH have two linear sections with slopes of about 0.04 V and about 0.12 V. On this basis, it has been suggested that[28] in the above media the evolution of hydrogen on tellurium takes place via an electrochemical mechanism.

In hydrochloric acid solutions the slope of the $\eta - \lg i$ curves varies with the acid concentration (Fig. 1). In solutions at hydrochloric acid concentrations below 0.3 N the $\eta - \lg i$ curves consist of two linear sections with slopes $\upsilon_1 \simeq 0.04$ V and $\upsilon_2 \simeq 0.12$ V. It was suggested[29] that in these solutions the evolution of hydrogen at tellurium proceeds via an electrochemical mechanism in which the formation of hydrogen molecules from H^+ and adsorbed hydrogen atoms is the rate-determining stage. In more concentrated hydrochloric acid solutions the $\eta - \lg i$ curve has a single linear section with a slope of 0.06 V.

In order to account for the change in slope in more concentrated hydrochloric acid solutions, it was suggested[29] that the evolution of hydrogen at tellurium proceeds via a "dual mechanism", i.e. there may be two rate-determining stages proceeding at very similar rates.

In the derivation of the kinetic equation for the possible stages in the cathodic evolution of hydrogen at tellurium, the authors calculated the slopes of the $\eta - \lg i$ curves for different mechanisms on the basis of the theoretical concept of Bockris and Potter[30]. The results showed that, in more concentrated hydrochloric acid solutions at low current densities, the evolution of hydrogen at tellurium can proceed via a dual electrochemical-catalytic mechanism with two different rate-determining stages having similar rates.

At low current densities ($1 \times 10^{-5} - 5 \times 10^{-4}$ A cm^{-2}) in hydrochloric acid solutions the evolution of hydrogen at a tellurium electrode proceeds via a slow discharge mechanism. On further increase of current density (to 1×10^{-2} A cm^{-2}), cathodic dissolution begins with formation of tellurium hydride[31].

As at mercury[33] and other electrodes[34,35], in the electrochemical reduction of $Fe(CN)_6^{3-}$ at the tellurium electrode[32] a decrease of the concentration of the indifferent electrolyte (KCl) near the zero-charge point [$\varphi = -0.30$ V (s.c.e.)] entails a decrease of the current on the $i - \varphi$ curves owing to the effect of the electrical double layer on the kinetics of the electrochemical reaction. An increase of the concentration of the indifferent electrolyte leads to a gradual removal of inhibition of the reaction and at a concentration of 0.1 N the inhibition is completely removed. Chloride and bromide ions do not have an appreciable influence on the kinetics of the electrochemical reduction of $K_3[Fe(CN)_6]$ at tellurium, while iodide ions sharply inhibit the reaction.

3. ANODIC AND CATHODIC DISSOLUTION OF SELENIUM AND TELLURIUM

Selenium

In the anodic polarisation of the selenium electrode in neutral and acid solutions vigorous anodic dissolution of selenium takes place. Depending on the electrolysis conditions and the composition of the electrolyte, the anodic reaction product can be selenous acid or a mixture of selenous and selenic acids. In selenous acid solutions the acid itself becomes concentrated, the anodic reactions occurring without appreciable inhibition with an apparent yield close to 100%.[25]

An important factor in the refining of selenium is the preparation of selenous acid, which is synthesised by the combustion of technical selenium in a stream of oxygen with subsequent dissolution of the resulting selenium dioxide in distilled water. The data obtained[25] suggest that the electrochemical method (anodic dissolution of selenium or interaction of electrically regenerated chlorine with powdered selenium in a single bath) may be promising for the synthesis of selenous acid.

The high resistance of selenium (10^5–10^{11} Ωcm) hinders the use of pure selenium as the material of anodes. For this reason, anodes consisting of a mixture of selenium and graphite have been employed. The most suitable ratio is Se : graphite = 3 : 1.

Measurements of polarisation curves with the aid of the selenium–graphite anode in different electrolytes have shown that at low current densities the anodic curves are the same to a first approximation as the curves obtained in the anodic dissolution of thin selenium films. At high currents (> 10 mA cm^{-2}) there is a linear relation between current density and polarisation.

The form of the polarisation curves shows that the principal reason for the high polarisation is the ohmic potential drop in the electrode itself, and in the electrolyte in the case of H_2SeO_3 solutions, which have a low conductivity.

Selenous acid is synthesised by the reaction of electrically regenerated chlorine with selenium without an inert current-conducting material. A mixture of HCl and NaCl solutions has been employed as the electrolyte with a current density at the anode (graphite) of 30–40 mA cm^{-2}; the cathode consists of a PVC fabric membrane impregnated with titanium. The resulting acid contains small amounts of H_2SeO_4.

In the anodic polarisation of the selenium electrode containing Br_2, HBr and $HBrO_3$ appear as impurities[36] in the solution in addition to H_2SeO_3.

By electrolysing selenous acid at the anode, it is possible to prepare selenic acid and its salts:

$$H_2SeO_3 + H_2O - 2e \rightarrow H_2SeO_4 + 2H^+ .$$

The method of anodic oxidation of selenous acid was proposed for the synthesis of selenic acid and its salts free from admixtures of other elements[37–39].

A separate study on the cathodic distribution of selenium has apparently not been made. However, it has been noted[37] that in the electrolysis of KOH solutions with selenium as the cathode and platinum as the anode, polyselenide ions of the type Se_n^{2-} are formed, in which n may be 4.4.

Tellurium

In the electrolysis of alkaline solutions using tellurium electrodes tellurium dissolves both anodically and cathodically. The cathodic dissolution results in the formation of Te^{2-} and Te_2^{2-} ions.

The formation of Te_2^{2-} ions in the cathodic polarisation of tellurium in alkaline solutions was pointed out a long time ago by Le-blanc[40] and Müller and Nowakowsky[41], who observed that in the electrolysis of solutions of alkalies using the tellurium electrode a gas was not evolved at either electrode, both dissolving. In the electrolysis of a KOH solution, the solution at the cathode becomes red (polytellurides are formed). The anode dissolves tellurium in an oxidation state close to four, the Te^{4+} ion passing into the solution; most of these ions react with OH^- ions, forming TeO_3^{2-}. Under the conditions where the solution contains simultaneously positive and negative tellurium ions, the equilibrium $3Te \rightleftharpoons 2Te^{2-} + Te^{4+}$ is established. In concentrated alkaline solutions with a measurable amount of products the equilibrium in this reaction is displaced to the right and on dilution of the solution the reaction proceeds in the opposite direction.

The main product in the cathodic dissolution of tellurium in solutions at pH < 9 are Te^{2-} ions, while at pH > 12 the product is Te_2^{2-} ions. In the pH range 9–12 a mixture of Te^{2-} and Te_2^{2-} is formed in the solution. According to the literature[42,43], the overall reaction in the dissolution of the tellurium cathode can be represented as follows:

$$Te + 2(n-1)H^+ + ne = (n-1)H_2Te + \frac{2-n}{2}Te_2^{2-} .$$

The number of electrons n per atom of dissolving tellurium is 2 in acid solutions and 1 in alkaline solutions.

It has been noted[44] that in alkaline solutions the steady-state potential φ_{st} of the tellurium electrode changes very slowly with time, reaching 0.15 V in 1 N KOH and 0.08 V in 0.1 N NaOH. After a preliminary cathodic polarisation of the electrode, φ_{st} is −0.75 V and gradually shifts towards less negative values. This shift takes place as a result of the spontaneous oxidation of Te_2^{2-} (formed from the tellurium electrode in the cathodic polarisation) to Te and TeO_3^{2-}.

The polarisation of the tellurium electrode in NaOH solutions[45] and $Ba(OH)_2$ and NH_4OH solutions[46] was investigated by Awad. In 0.005–0.01 N NaOH at current densities of 1×10^{-6}–1×10^{-3} A cm^{-2} the $\eta - \lg i$ curves have a single linear section with a slope of about 0.1 V. In more concentrated solutions (up to 5 N NaOH) there are two sections with the slopes $\upsilon_1 \simeq 0.04$ V and $\upsilon_2 \simeq 0.1$ V. It is suggested that at low NaOH concentrations the rate-limiting stage in the cathodic process is the discharge of Na^+ ions. At current densities of 1×10^{-4}–1×10^{-2} A cm^{-2} in 0.5–5 N NaOH solutions the $\eta - \lg i$ curves are to some extent located at potentials more positive than that of the normal hydrogen electrode. In the region near the cathode the solution becomes red, indicating the formation of polytellurides.

Comparison of the experimental slopes with the calculated value (0.06 V) obtained in accordance with the reaction $2Te + 2e \rightarrow Te_2^{2-}$ suggests that a direct formation of Te_2^{2-} by this reaction is impossible.

Therefore Awad[46] postulated that the cathodic dissolution of tellurium proceeds in stages with participation of the electrolyte cation according to the following mechanism:

$$Te + Na^+ + e \rightarrow NaTe ,$$
$$NaTe \rightarrow Te + Na^+ + e ,$$
$$NaTe + Te + e \rightarrow Te_2^{2-} + Na^+ .$$

Awad[46] believes that in $Ba(OH)_2$ and NH_4OH solutions the multistage process can be represented in the following manner on the assumption that tellurium is present as diatomic species:

$$M^+ + Te_2 + e \rightarrow MTe_2 , \quad (1)$$
$$MTe_2 + M^+ + e \rightarrow M_2Te_2 , \quad (2)$$
$$M_2Te_2 + Te_2 + e \rightarrow M_2Te_4^- , \quad (3)$$
$$M_2Te_4^- + e \rightarrow 2M^+ + 2Te_2^{2-} . \quad (4)$$

In 0.5 N NH_4OH and 0.005 and 0.01 N $Ba(OH)_2$ solutions the rate of dissolution is controlled by the discharge of the electrolyte cation, i.e. stage (2) is rate-determining. At high $Ba(OH)_2$ concentrations, the rate is determined by the electrochemical reaction, i.e. stage (4) is slow. However, Awad's experimental data do not confirm his ideas concerning the stoichiometric numbers of the above reactions. The order of the reaction with respect to sodium ions in the double layer is inconsistent with the experimental data. Therefore Komandenko and Rotinyan[47] believe that the formation of Te_2^{2-} probably proceeds without involvement of the alkali metal cation via the mechanism

$$Te + OH^- + e \rightarrow TeOH^{2-} ,$$
$$TeOH^{2-} + Te + e \rightarrow Te_2OH^{3-} \quad \text{slow stage},$$
$$Te_2OH^{3-} + Te + e \rightarrow Te_3OH^{4-} ,$$
$$Te_3OH^{4-} + Te + e \rightarrow 2Te_2^{2-} + OH^- .$$

One can also assume that the polytelluride is formed as the result of the reaction of the Te^{2-} ion with elemental tellurium on the surface of the electrode. However, polarisation data alone, which were used to establish the mechanism of cathodic dissolution of tellurium, are insufficient. It is also necessary to establish the nature of the intermediates and to determine the current yield of the most stable product which accumulates and is responsible for the slow stage. It is therefore difficult at present to give a definite preference for a particular mechanism.

The cathodic dissolution of tellurium is used in some cases for the preparation of hydrogen tellurides[37].

The anodic behaviour of tellurium has been investigated in acid[48–51] and in alkaline[40,52,53] solutions. On the basis of polarisation measurements, Fishman et al.[50] and Awad[51] suggest that the Te^{4+} ion is formed in anodic polarisation. However, the physicochemical properties of tellurium compounds and also experimental data[48] provide adequate grounds for the belief that in acid solutions the primary anodic product is Te^{2+}. Apart from its electrochemical reaction, Te^{2+} subsequently undergoes disproportionation, and, in weakly acid electrolytes, hydrolysis.

In 1.5–3 N NaOH solutions at a current density of 10–40 mA cm^{-2} the anodic dissolution of tellurium proceeds with a 100% current yield. At higher concentrations of alkali the current yield exceeds 100%.

When lower concentrations of alkali are employed, an insoluble form of tellurous acid is formed on the surface of the anode, which markedly increases the resistance.

The anodic process proceeds via the overall reaction $Te + 4OH^- - 4e \rightarrow H_2TeO_3 + H_2O$,[52] which consists of a series of consecutive stages:

$$Te + OH^- - e \rightarrow TeOH ,$$
$$TeOH + OH^- - e \rightarrow TeO + H_2O ,$$
$$TeO + OH^- - e \rightarrow TeOOH ,$$
$$TeOOH + OH^- - e \rightarrow H_2TeO_3 .$$

III. CATHODIC AND ANODIC DEPOSITION OF SELENIUM AND TELLURIUM

1. DEPOSITION FROM AQUEOUS SOLUTIONS

Selenium

Depending on the composition of the electrolyte and the electrolysis conditions, selenium may be deposited in the form of red amorphous and grey hexagonal modifications or their mixture. The electrolytic deposition of red amorphous selenium is carried out in acid and weakly alkaline selenous acid electrolytes[54–56]. The electrolysis is performed at 20–40°C and a current density of 10–20 mA cm^{-2}.

With the development of xerography towards the end of the 1950's, interest was aroused in methods for the preparation of films of amorphous selenium on a metallic base. In order to obtain fairly strong films of red amorphous selenium in the electrolysis of selenous acid and its salts, Graham et al.[57] investigated the effect of the pH of the medium wetting the reactants, the material of the electrode, temperature, and illumination on the structure and electrophysical properties of the deposits. The electrolysis was performed in two baths: (1) acid bath: 350 g of SeO_2 per litre of water, pH 0.8; (2) alkaline bath: 211 g of SeO_2 per litre of dilute NaOH solution, pH 8.

Citric acid was employed as the wetting agent. Selenium was deposited on platinum, bright nickel, black nickel, gold, copper, silver, chromium, and lead electrodes. The electrolysis was carried out in the temperature range 5–40°C and under illumination ranging from moderate to very intense from three 500 W lamps focussed on the surface of the electrode. The most satisfactory coatings were obtained on platinum and nickel. However, the resulting red amorphous selenium deposits proved to be unsuitable for xerography. According to the authors, this is due to the high impurity content in the electrolytic amorphous selenium.

The preparation of selenium coatings by electrolysis was also reported by Krusenstiern and Meier [58].

In acid solutions selenium is deposited on iron, nickel, and copper with and without external polarisation. In neutral solutions without external polarisation it is deposited only on iron. In alkaline solutions selenium is deposited on the above metals only when external polarisation is applied. In all cases the rate of deposition of selenium depends on the nature of the metal [59].

It has been noted [25] that in the electrolysis of 2 M H_2SeO_3 (temperature 20–40°, current density 0.03–0.06 mA cm^{-2}), 2 M $KHSeO_3$ (pH ~ 7), and 2 M H_2SeO_3 + 2 M KCl (current density 2.5 mA cm^{-2}) solutions grey hexagonal selenium is deposited on platinum and nickel cathodes.

In the temperature range 45–70°C at a current density of 10–30 mA cm^{-2} a mixture of grey hexagonal and red amorphous selenium is deposited on the cathode. At elevated temperatures (70–100°C) grey hexagonal selenium (the so called metallic selenium) is deposited on the cathode [60].

The addition of H_2SO_4 and HNO_3 to the electrolyte up to a concentration of 1.2 *N* lowers the potential in the bath from 3.5 to 2.5 V but does not have an appreciable influence on the nature of the electrolytic selenium [61]. In the electrolysis of selenium-containing solutions the acidity of the electrolyte has a marked influence on the cathodic process [25]. A grey, fairly loose deposit of elemental selenium, which is weakly attached to the metallic base, is formed on the cathode from 2 M H_2SeO_3 solutions. At low current densities the current yield of selenium is 45–50%.

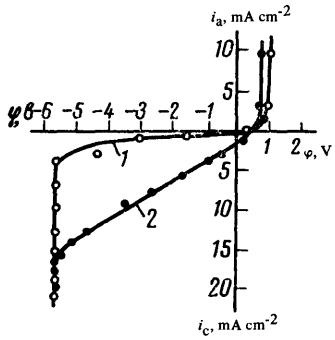


Figure 2. Cathodic–anodic polarisation curves for a 2 M H_2SeO_3 solution: 1) in the dark; 2) under illumination [25].

The cathodic process is accompanied by a high polarisation, which falls appreciably when the surface of the electrode is illuminated (Fig. 2). At high current densities the polarisation is affected by the semiconductor properties of the selenium deposited on the electrode. The high potential gradient in the surface layer of selenium leads to the electrical breakdown of the surface layer. Under the breakdown conditions, vigorous evolution of hydrogen takes place on the electrode. The current yield of selenium falls to 20–25%.

When the surface of the cathode is illuminated, the electrode potential shifts towards positive values and the electrical breakdown of the surface barrier does not occur, the discharge of H^+ diminishing sharply and the current yield of selenium coming close to the theoretical value [62].

Von Hippel and Bloom [63] deposited grey hexagonal selenium from a sulphuric acid electrolyte containing 840 g of SeO_2 per litre of 18 *N* H_2SO_4 and recommended that grey selenium be electrodeposited at 90°C, a temperature which promotes the maximum rate of formation of nuclei. Dense and homogeneous deposits of selenium firmly adhering to the metallic base were obtained on the cathode. Analogous results were achieved also when H_2SeO_4 was employed instead of H_2SO_4. Von Hippel and Bloom [63] recommend that highly acid electrolytes (18 *N* H_2SO_4 + 150 g $litre^{-1}$ SeO_2 at 55–120°C) be employed to coat various articles made of nickel, silver, antimony, and steel. The surface of the cathode was initially coated with the corresponding metal selenide.

A 9 : 1 selenium–graphite mixture was employed as the material of the anode. Under these conditions, the loss of selenous acid in the cathodic reaction is compensated by its formation by the anodic oxidation of selenium. The resulting grey hexagonal selenium coatings can be used in the manufacture of rectifiers and photocells. Selenium coatings obtained by electrolysis in highly acid electrolytes have a distinct texture [64].

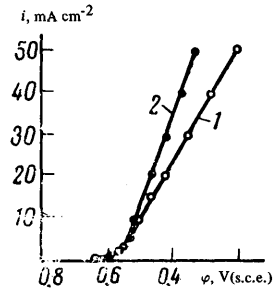


Figure 3. Cathodic polarisation curves for a solution of 840 g of SeO_2 in 1 litre of 18 *N* H_2SO_4; 1) in the dark; 2) under illumination [66].

The electrolytic deposition of the grey hexagonal modification of selenium on a platinum cathode at 95°C from concentrated sulphuric acid containing selenium dioxide has been reported [65].

The cathodic reduction of selenium in highly acid electrolytes (SeO_2 + 55–60% H_2SO_4 or H_2SeO_4) is accompanied by a relatively low polarisation.

At low current densities the polarisation of the selenium electrode hardly changes under illumination. The effect of illumination on the polarisation of the selenium electrode in concentrated sulphuric and selenic acid electrolytes begins to have an appreciable effect at current densities in excess of 10 mA cm^{-2}. The slight

decrease of cathodic polarisation (Fig. 3) under illumination is probably associated with a decrease of the ohmic resistance of selenium under the influence of light.

The $\eta - \lg i$ polarisation curves for the cathodic deposition and anodic dissolution of selenium, measured in concentrated sulphuric and selenic acid electrolytes at low current densities (1×10^{-4}–1×10^{-2} A cm^{-2}), have a single linear section with a slope of 0.7 V (Fig. 4). The exchange current found from the intersection of the anodic and cathodic curves is 1.4×10^{-4} A cm^{-2}.

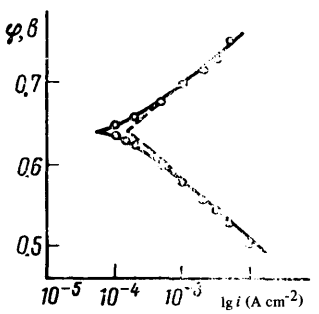


Figure 4. Cathodic–anodic polarisation curves for the solution of 840 g of SeO_2 in 1 litre of 18 N H_2SO_4.[66]

Thus in highly acid solutions the inhibition of the cathodic reaction associated with the depletion of the surface layer of selenium in free electrons, which is characteristic of weakly acid electrolytes, is not observed. The exchange current in highly acid electrolytes is higher by approximately 2 powers of 10 than in weakly acid solutions. The current yield of selenium in concentrated sulphuric and selenic electrolytes is close to 100%.

It is believed[63] that the electrochemical reduction of selenous acid in concentrated sulphuric and selenic acid electrolytes proceeds with participation of the $(H_3SeO_3)^+$ cation, which is formed in accordance with the equilibria

$$H_2SeO_3 \leftrightarrows H^+ + HSeO_3^-, \quad H_2SeO_3 + H^+ \rightleftarrows (H_3SeO_3)^+ .$$

Its concentration increases with the acidity of the electrolyte.

The absence of inhibition in the electrochemical reduction of selenium in concentrated sulphuric and selenic acid solutions is attributed by other workers[66] to the fact that the free electrons involved in the cathodic process are generated in a sufficient amount on the surface of the electrode. Possibly the products of the interaction of selenium with fairly concentrated acids of the H_2SeO_4 and H_2SO_4 type behave as electron generation centres. Despite the fact that there is no direct proof of the formation of these products and there are no data concerning their nature and properties, the polarisation and capacitance measurements as well as the properties of selenium in concentrated solutions[3] suggest that preference should be given to this explanation.

Elemental selenium dissolves readily in concentrated sulphuric acid with formation of $SeSO_3$. The electrolytic reduction of $SeSO_3$ in 98% sulphuric acid solutions proceeds via the reaction

$$SeSO_3 + 6H^+ + 6e \rightarrow Se + S + 3H_2O^{67,68} .$$

The current yield is nearly theoretical. Since $SeSO_3$ is frequently formed in the course of the manufacture of sulphuric acid (when the raw material contains selenium), the electrolytic reduction of $SeSO_3$ can be used for the quantitative separation of selenium from sulphuric acid.

The technology of the electrolytic preparation of selenium from the anodic sludge in the copper refining industry has been described[69]. The sludge is roasted with Na_2CO_3, leached with water, and the solution is saturated with boric acid, filtered, and the pH adjusted to 8–9 by the addition of an aliphatic polybasic alcohol (for example 2-amino-2-methylpropane-1,3-diol). This solution serves as the catholyte, aqueous NaOH or Na_2CO_3 being employed as the anolyte. Selenium is evolved at a potential of 4.5–6 V. The cathode can also be made of iron, copper, titanium, and aluminium and the anode can be made of materials resistant to NaOH solutions.

Selenium is deposited from solutions of alkali metals by hydrogen selenide via the reaction

$$HSe^- + OH^- - 2e \rightarrow Se + H_2O .$$

The anodic oxidation of sodium selenide has been used to coat the plates of rectifiers[70]. The electrolysis was performed at elevated temperatures and a maximum current density of 10 mA cm^{-2}. However, owing to the instability of the selenide solutions, the anodic deposition of selenium has not found wide scale application.

In the electrolysis of alkaline solutions of a selenite, the selenide is formed on the cathode via the reaction $SeO_3^{2-} + 3H_2O + 6e \rightarrow Se^{2-} + 6OH^-$ and can be used for the deposition of selenium on the anode. This process is complicated by the chemical reactions

$$2HSe + {}^1/_2O_2 = 2Se + H_2O, \quad SeO_3^{2-} + 2HSe^- + H_2O = 3Se + 4OH^- .$$

The colloidal selenium formed as a result of this reaction interacts with the selenide and forms polyselenides which are not involved in the electrochemical reaction and merely reduce the concentration of the selenide in the electrolyte. Under certain conditions, sodium selenide is formed in the cathodic compartment in the electrolysis of sodium selenite solutions[71].

2. CATHODIC DEPOSITION OF TELLURIUM FROM ACID SOLUTIONS

In the electrolysis of acid tellurium-containing solutions, coarsely crystalline or fine-grained tellurium deposits are formed on the cathode depending on the electrolysis conditions and the composition of the electrolyte. Spongy deposits are mainly produced in the electrolysis of weakly acid solutions of tellurium. TeO_2, the formation of which is associated with the hydrolysis of tellurium chloride near the electrode, has been found in the spongy tellurium deposits[72].

The best electrolytes for the electrolytic deposition of tellurium from acid solutions are hydrochloric acid solutions. The high positive potential of the Te/Te^{4+} system and the high solubilities of TeO_2 and $TeCl_4$ in hydrochloric acid solutions are extremely favourable for the electrolytic deposition of pure tellurium. The electrochemical behaviour of tellurium in hydrochloric acid solutions has been investigated[25,31,72–76].

Müller and Schlosser[73], who were the first to achieve the electrochemical deposition of tellurium from hydrochloric acid solutions (300 g litre^{-1} Te + 200 g litre^{-1} HCl), noted that pure tellurium is deposited on platinum and titanium cathodes at 30°C.

For the deposition of tellurium with a purity not less than 99.99%, the limiting permissible concentrations of impurities in solution such as selenium, silver, mercury, and gold should not exceed 5 mg litre^{-1} and those of impurities such as aluminium, iron, magnesium, and calcium, and others should not exceed 70–100 mg litre^{-1}.[25] The electrolysis conditions are as follows: $(0.5–2.0) \times 10^{-3}$ M TeO_2 or $TeCl_4$ + $(2.5–5) \times 10^{-3}$ M HCl electrolyte, current density 15–20 mA cm^{-2}, 25–30°C. Such electrolytes can be prepared by the anodic dissolution of technical tellurium in hydrochloric acid solutions[48].

Chlorine in the form of $TeCl_2$ remains in all the tellurium deposits as a mechanical impurity[72]. An increase of the acidity of the solution, the presence of alkali metal chlorides in the electrolyte, and an increase of current density lead to an increase of the $TeCl_2$ content.

A change in the electrolyte temperature has an appreciable influence on the mechanism of the cathodic deposition of tellurium and on the nature of the deposits. A fine-grained grey deposit is formed on the cathode at 25–50°C and current densities of 10–15 mA cm^{-2}. At 75 to 90°C and a current density of 20 mA cm^{-2}, coarse-grained dark-grey deposits are formed, their current yield in relation to Te^{4+} falling from 99% at 25°C to 89% at 90°C.

The formation of $TeCl_2$ is associated with a multistage mechanism of the reduction of Te^{4+} ions by Te^{2+}. Some of the Te^{2+} ions near the electrodes react with Cl^- ions to form $TeCl_2$, which is deposited on the surface of the cathode together with a freshly formed layer of elemental tellurium. Other Te^{2+} ions undergo further electrochemical reaction and disproportionation: $2Te^{2+} = Te + Te^{4+}$.

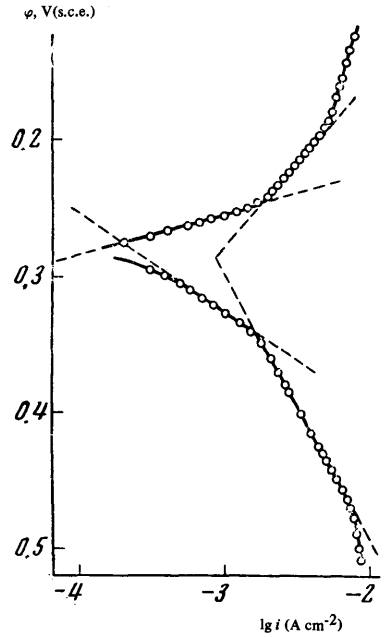


Figure 5. Cathodic–anodic polarisation curves obtained in 2 M HCl + 0.05 M $TeCl_4$ solution[74].

Vigorous formation of Te^{2+} ions and their disproportionation are observed in the anodic polarisation of the tellurium electrode in hydrochloric acid solutions. After the start of electrolysis, the electrolyte near the anode becomes greenish-yellow, then assumes a red tint, and is converted into a dirty-grey turbid suspension, black crystals (pure elemental tellurium) being formed after approximately 30–40 min.

Te^{2+} ions in the solutions after anodic polarisation were detected directly by treatment with an oxidant ($K_2Cr_2O_7$).

The study of the kinetics of the decrease in the amount of Te^{2+} ions in solution after the anodic polarisation of tellurium had ceased and chemical analysis of the solid mass established that (1) Te^{2+} is formed in the anodic dissolution of tellurium in hydrochloric acid solutions; apart from being involved in an electrochemical reaction, Te^{2+} ions subsequently disproportionate and are also deposited in the form of $TeCl_2$ on the surface of the anode; (2) the disproportionation reaction is a second-order process.

The cathodic polarisation curves measured with the aid of the tellurium electrode in hydrochloric acid solutions of tellurium(IV) show the onset of a limiting current, which increases with the concentration of tellurium in the electrolyte, temperature, and the rate of stirring. At an HCl concentration of 2.5–5 M the limiting current varies linearly with the concentration of tellurium in the electrolyte[74]. In this acidity range tellurium is present in solution in the form of the complex ions $TeCl_6^{2-}$.

As the acidity of the electrolyte diminishes, the chlorine in the complex ion is gradually replaced by H_2O or OH^-, tellurous acid is precipitated, and the concentration of Te^{4+} ions in solution falls.

The initial sections of the polarisation curves (Fig. 5) for 2.5–5 M HCl + 0.02–0.25 M Te solutions at 25–50°C show a break and two linear sections with different slopes; $b_{c1} = 0.035$ V, $b_{c2} = 0.12–0.14$ V, $b_{a1} = 0.066–0.070$ V, and $b_{a2} = 0.15–0.20$ V. The exchange currents are $i_{0.1} = 2 \times 10^{-4}$ A cm^{-2} and $i_{0.2} = 1 \times 10^{-3}$ A cm^{-2}.

Comparison of the results of the polarisation measurements with the direct detection of Te^{2+} ions permits the assumption that the cathodic deposition and anodic dissolution of tellurium in hydrochloric acid electrolytes proceed in stages.

The most probable mechanism of the process can be represented in the following form[25]:

$$TeCl_6^{2-} \rightleftarrows TeCl_2^{2+} + 4Cl^-, \quad (1)$$

$$TeCl_2^{2+} + e \rightleftarrows TeCl_2^+, \quad (2)$$

$$TeCl_2^+ + e \rightarrow TeCl_2 \quad (3)$$

$$\text{or } TeCl_2^{2+} + 2e \rightarrow TeCl_2, \quad (4)$$

$$TeCl_2 + e \rightarrow TeCl_2^-, \quad (5)$$

$$TeCl_2^- + e \rightleftarrows Te^0 + 2Cl^- \quad (6)$$

$$\text{or } TeCl_2 + 2e \rightarrow Te^0 + 2Cl^-. \quad (7)$$

If there is only one slow stage in reactions (1)–(7), the sum of the apparent transfer coefficients should be equal to the number of electrons involved in the overall reaction, i.e. $\alpha' + \beta' = 4$, which is not observed experimentally. Therefore one must postulate that the cathodic deposition and anodic dissolution of tellurium in hydrochloric acid solutions occur by more than one slow stage.

The formation of Te^{2+} ions and the increase of their concentration during electrolysis suggest that the slow stage may be reaction (5). On the other hand, reaction (3), whose product can disproportionate and also remain in the solid state apart from being involved in an electrochemical reaction, presumably also has a slow stage.

If one supposes that reactions (3) and (5) and reactions (5) and (3) are slow in the cathodic and anodic processes respectively and that the preceding electrochemical stages are reversible, then, using the characteristics of multistage processes and the proposed reaction mechanism, the following kinetic equations may be derived:

$$i_c = k_{-3}[TeCl_6^{2-}][Cl^-]^4 \exp[-(1+\alpha_3)F\varphi_c/RT],$$

whence $\alpha' = 1 + \alpha_3$, $\beta' = 1 + \beta_5$, $\alpha' + \beta' < 4$, and

$$i_a = k_{+5}[Cl^-]^2 \exp[(1+\beta_5)F\varphi_a/RT].$$

Thus $\alpha' + \beta''$ must be four, which is in fact observed experimentally.

Electrodeposition from tellurium solutions containing tellurium sulphate mixed with ammonium hydrogen tartrate was carried out by Pellini[77]. According to Gallo[78], Pellini's method[77] is unsuitable for the electrochemical deposition of relatively large amounts of tellurium and the electrolysis of pyrophosphate electrolytes is recommended. The electrolytic deposition of tellurium on a lead cathode from a $TeO_2 + HF + H_2SO_4$ electrolyte has been described[79]. However, owing to the corrosive nature of the electrolyte, the method has not found any practical application. It is occasionally recommended for the deposition of thin tellurium films on various metallic surfaces[80]. The conditions governing the electrolytic deposition of tellurium from media described by Mathers and Turner[79] were recently reinvestigated[81] and it was found that a dense deposit of tellurium with a metallic lustre and having a purity of 99.98% is formed on the cathode.

There are data[82] showing that in the electrochemical deposition of tellurium from sulphuric acid electrolytes in an ultrasonic field the limiting permissible current density for the formation of high-grade tellurium deposits is appreciably increased. In sulphuric acid solutions tellurous acid is reduced to elemental tellurium, while telluric acid is not reduced. This property can be used to separate tellurous and telluric acids[54].

The polarisation curves measured with the aid of the tellurium electrode in sulphuric acid electrolytes suggested[83] that the cathodic and anodic processes proceed in stages.

It was established, using buffer solutions in the pH range 7–10, by potentiostatic measurements[84] that at cathodic potentials the tellurium is in a state of cathodic passivation, while at anodic potentials the active state is followed by a state of secondary passivation.

The first studies of the electrochemical behaviour of ultrasmall amounts (10^{-10} M) of tellurium were made by Ghosh–Mazumder and Haissinsky[85]. The authors employed a mixture of tellurium-129 and tellurium-127 isotopes in the form of quadrivalent ions. The experiments were performed in HCl, HBr, and H_2SO_4 media or in solutions of the corresponding salts. With increase of the acidity of the medium, the tellurium deposition potential shifts towards positive values. The nature and state of the electrode surface have an appreciable influence on the tellurium deposition potential. The electrodes can be arranged in the following sequence in terms of the tellurium deposition potential:

platinised Pt > smooth Pt > Pd > Au > Ru.

Tellurium was electrochemically deposited also from nitric acid (0.5–1 M HNO_3) electrolytes at a maximum tellurium concentration of 1.5 g litre^{-1} using platinum electrodes and a current density of 1.2–1.8 mA cm^{-2}.[25] A deposit of grey tellurium firmly adhering to the electrode surface is formed on the cathode; its current yield is close to 100% and appreciable evolution of hydrogen is not observed.

At current densities of 3–5 mA cm^{-2} the deposition of tellurium on the cathode occurs with the evolution of hydrogen and the current yield of tellurium falls to 80%. The tellurium deposited by electrolysis from nitric acid solutions is purer than that deposited from hydrochloric acid electrolytes. In the electrolysis of hydrochloric acid solutions of tellurium the formation of hydrogen telluride is observed only when tellurium is deposited from solutions with very low tellurium concentrations under limiting current conditions at 0–10°C. The mechanism of the formation of H_2Te involves the reaction $Te^{2-} + 2H^+ \rightarrow H_2Te$.[86] Telluride ions are formed initially and then diffuse from the cathode and interact with hydrogen ions migrating to the surface of the cathode. When H_2Te is formed, the evolution of hydrogen ceases; Te^{2+} ions are probably adsorbed on the surface of the cathode and act as a "poison" for the evolution of hydrogen.

The electrolytic method is also used to prepare tellurides[2]. In the electrolysis of sodium sulphate solutions using an anode made of a metal whose telluride is to be obtained and tellurium as the cathode, the products are tellurides. Copper and nickel tellurides have been synthesised in this way. In the synthesis of zinc tellurides, a zinc plate was used as the anode and the cathode consisted of a tellurium–platinum alloy. Nitric and sulphuric acids serve as the electrolyte.

The conditions of the electrolytic deposition of tellurium–silver alloys from nitric acid electrolytes and of tellurium–cadmium alloys from cyanide electrolytes have been described by Klochko and Medvedeva[87] and by Trusova and Chizhikov[88] respectively. The conditions governing the joint electrodeposition of tellurium–copper[89] and tellurium–chromium[90] have also been described.

Using a tellurium cathode and an anode made of other metals in a 1 M $NH_4OH + CH_3COOH$ solution at pH 4.5, CuTe, SnTe, ZnTe, PbTe, and Bi_2Te_3 were synthesised electrolytically[91].

It has been reported[92] that Ag_2Se and Ag_2Te are formed respectively on a silver cathode in the electrolysis of 0.01 M SeO_2 and TeO_2 solutions in 1 M H_2SO_4 at 25°C and a current density up to 0.05 mA cm^{-2}. The electrolysis of acidified $CuSO_4 + H_2SeO_3$,[93,94] $H_2TeO_3 + H_2SeO_3$,[95] $AgNO_3 + H_2SeO_3$,[96] $Bi(NO_3)_3 + H_2SeO_3$,[97] and $CdSO_4 + H_2SeO_3$[98] solutions results in the formation of the corresponding metal selenides on platinum, copper, silver, cadmium, and tellurium cathodes.

The formation of selenides has also been noted[99] in the electrolysis of H_2SO_4, Na_2SO_4, and KNO_3 solutions using a selenium cathode and an anode made of copper, nickel, cadmium, and certain other metals.

3. CATHODIC DEPOSITION OF TELLURIUM FROM ALKALINE ELECTROLYTES

For the electrodeposition of tellurium from alkaline solutions, the electrolyte is usually prepared by dissolving TeO_2 in sodium hydroxide solution.

Apart from simple tellurites of the type Na_2TeO_3, the existence of sodium polytellurites of the type $Na_2Te_3O_7$, $Na_2TeO_5.3H_2O$, and $Na_2TeO_9.5H_2O$ was established in the TeO_2–Na_2O–H_2O system[100]. The reduction of tellurium at the cathode in such solutions is a fairly complex process, the final product of which is elemental tellurium.

A Japanese patent[101] reports the formation of tellurium by the electrolysis of alkaline electrolytes.

In the Soviet Union the preparation of tellurium on an industrial scale was achieved by Gaev et al.[102] The electrolysis was carried out in an electrolyte containing 100 g litre^{-1} of tellurium and 160 g litre^{-1} of free sodium hydroxide. Tellurium is deposited on the cathode in powder form and its purity is 99.5%. Tellurium with a lower impurity content can be obtained by employing a purer electrolyte.

Electrolytic units for the electrolytic isolation of tellurium have been organised in many copper-electrolytic and metallurgical works[103-106], where selenium and tellurium-containing waste accumulates.

At low current densities the electrodeposition of tellurium proceeds with chemical polarisation, while at high current densities concentration polarisation obtains[107]. The cathodic polarisation curves show a limiting current ($i$lim) (Fig. 6). With increase of the concentration of alkali in the electrolyte, the limiting current falls.

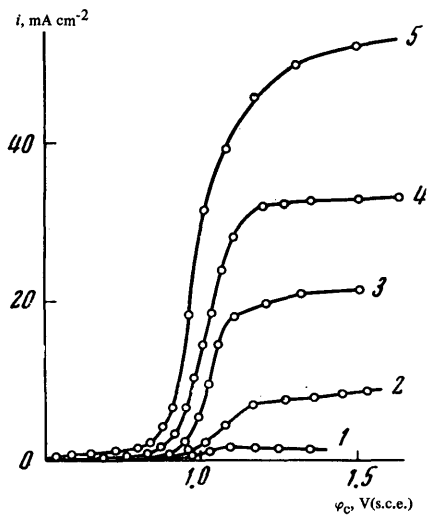


Figure 6. Cathodic polarisation curves for a 4 M NaOH solution containing different concentrations of tellurium (M): 1) 0.016; 2) 0.064; 3) 0.16; 4) 0.25; 5) 0.41.[25]

In an electrolyte with a high concentration of alkali $i$lim varies linearly with the tellurium concentration in the electrolyte and on dilution (in the absence of an excess of alkali) the increase of $i$lim with the concentration of tellurium is faster than would be expected for a direct proportionality. The difference between the values of $i$lim for tellurium in solutions with low and high concentrations of alkali has been attributed[108] to the different nature of the tellurium-containing species being discharged in concentrated and dilute solutions of alkali. In concentrated solutions of alkali the $\varphi - \lg i$ polarisation curves have a single linear section at relatively high current densities (Fig. 7). At low current densities the cathodic curves show a decrease of potential characteristic of the spontaneous dissolution of the metal[109].

Depending on the concentration of alkali in the electrolyte, the overall electrode reaction can be represented as follows:

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

$$HTeO_3^- + 2H_2O + 4e = Te + 5OH^-\ .$$

Bearing in mind that in a solution with a high excess of alkali the dominant species are the $[Te(OH)_6]^{2-}$ ions[18], which dissociate via the reaction $[Te(OH)_6]^{2-} \rightleftharpoons Te(OH)_3^+ + 3OH^-$,[109] it follows that, according to the hypothesis put forward[108,109], the electrodeposition of tellurium presumably corresponds to the overall electrode reaction $Te(OH)_3^+ + 4e \rightarrow Te + 3OH^-$, which proceeds in stages via the mechanism

$$Te(OH)_3^+ + e \rightarrow Te(OH)_3\ ,$$

$$Te(OH)_3 + e \rightarrow Te(OH)_3^-\ ,$$

$$Te(OH)_3^- + e \rightarrow Te(OH)_3^{2-}\ ,$$

$$Te(OH)_3^{2-} + e \rightarrow Te^0 + 3OH^-\ .$$

The rate-determining stage is the generation of the last electron. The slope of the linear sections of the $\varphi - \lg i$ curves calculated on the basis of the theory of multistage reactions using kinetic equations is satisfactorily consistent with the experimental results.

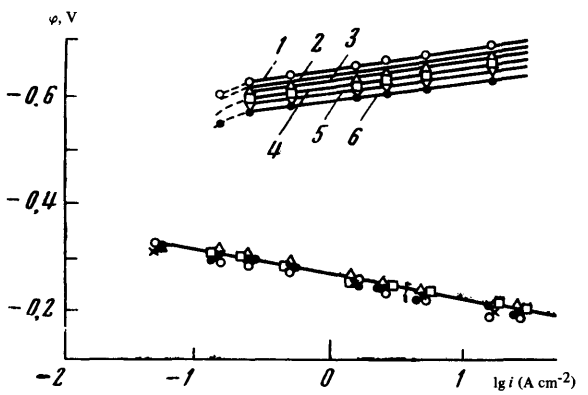


Figure 7. Cathodic–anodic polarisation curves for a 2.5 M NaOH solution containing different concentrations of tellurium (M): 1) 0.0075; 2) 0.015; 3) 0.03; 4) 0.06; 5) 0.12; 6) 0.188.[109]

In the electrolysis of thiotelluride (Na_2TeS_2) solutions tellurium is deposited on the cathode and elemental sulphur on the anode and polytellurides are formed[110]. The accumulation of polysulphides in the electrolyte leads to a decrease of the current yield of tellurium owing to the dissolution of tellurium on the cathode in the polysulphide.

In the course of the electrolysis of alkaline solutions containing tellurium and selenium, tellurium is deposited on the cathode and selenium remains in solution. Optimal conditions have been found whereby the concentration of tellurium in alkaline selenium-containing solutions can be reduced to 5×10^{-5}%.[111] Alkaline electrolytes have also been used in the refining of tellurium[112,113]. All the tellurium deposits obtained by the electrolysis of alkaline or acid solutions containing alkali metal ions contain an admixture of the latter in an amount of 0.01–0.05%.

4. CATHODIC DEPOSITION AND ANODIC DISSOLUTION OF SELENIUM AND TELLURIUM IN NON-AQUEOUS ELECTROLYTES

The conductivities of alcohols, acetic acid, and ethylene glycol increase sharply when $SeCl_4$ or $TeCl_4$ are dissolved in them. The high conductivities of the solutions have been attributed[114] to the presence of H^+ and Cl^- ions formed as the result of the dissociation of HCl produced by the reaction

$$SeCl_4\,(TeCl_4) + nCH_3OH \rightleftarrows Se\,(Te)\,Cl_{4-n} \cdot (OCH_3)_n + nHCl\ .$$

In the electrolysis of alcoholic, acetic acid, and ethylene glycol solutions of $SeCl_4$ or $TeCl_4$, selenium or tellurium is deposited on the cathode. Depending on the electrolysis conditions, primarily on temperature, the selenium deposits can be amorphous or crystalline. Crystalline selenium deposits are obtained from electrolytes heated to 45–60°C. However, under such conditions the nature of the electrolyte changes during electrolysis with formation of an organoselenium compound. Selenium is not electrodeposited from such solutions. Intermediate reduction products were not detected in the cathodic selenium deposits. The current yield of selenium does not exceed 15%. When the electrolyte contains 10% of aromatic hydrocarbons, the current yield of selenium rises to 27%.[115]

As in aqueous hydrochloric acid solutions, the cathodic deposition of selenium in the above solvents proceeds with a high overvoltage, which falls appreciably when the surface of the electrode is illuminated.

At temperatures of 5–10°C and current densities of 5–10 mA cm^{-2}, deposits of metallic tellurium firmly adhering to the surface of the electrode are formed on graphite and titanium cathodes in 0.5–1 M $TeCl_4$ solutions in acetic acid[116], alcohols, and ethylene glycol[25].

A cryptocrystalline tellurium deposit was formed on a platinum cathode in mixed aqueous alcoholic hydrochloric acid electrolytes (water content not greater than 2%) at a current density of 10–20 mA cm^{-2} and a temperature of 15–20°C. Black velvety cathodic deposits are obtained at current densities in the range 10–20 mA cm^{-2}.

Chlorine was detected in all the electrolytic tellurium deposits. Its content depends on the electrolysis conditions and the nature of the electrolyte. The greatest amount of chlorine (up to 7%) remains in deposits which were isolated from acetic acid solutions and the smallest amount (down to 0.04%) was found in deposits from ethylene glycol electrolytes. The chlorine in the electrolytic tellurium deposits is present as a mechanical admixture of tellurium dichloride[25].

Polarisation measurements made with the aid of the tellurium electrode in $TeCl_4$–CH_3OH or $TeCl_4$–C_2H_5OH solutions yield reproducible results (Fig. 8).[117] The cathodic curves show a limiting current section. The limiting current i_{lim} increases with the concentration of tellurium (curves *2*–*4*), temperature, and rate of stirring of the electrolyte, and decreases both with increase of the concentration of chloride ions as a result of the addition of HCl or LiCl to the electrolyte (curves *4* and *6*) and when alcohols with high molecular weights are employed as solvents (curves *4* and *5*).

The initial sections of the cathodic–anodic $\varphi - \lg i$ polarisation curves are described by Tafel equations with b_c = 0.055–0.060 V and b_a = 0.065–0.070 V.

In hydrochloric acid solutions in alcohols, acetic acid, and ethylene glycol both selenium and tellurium undergo vigorous anodic dissolution with formation of a mixture of chlorides. The lowest chlorides are subsequently oxidised to $SeCl_4$ or $TeCl_4$, which react with the solvent, undergoing solvolysis or solvation.

An electrolyte suitable for the electrochemical refining of tellurium can be prepared by the anodic dissolution of technical tellurium in hydrochloric acid solutions in acetic acid.

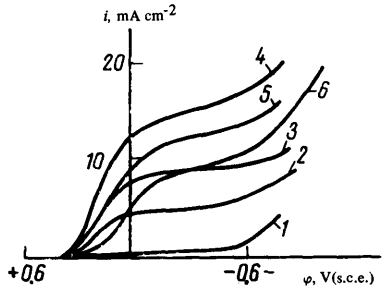


Figure 8. Polarisation curves for amine tellurium-containing solutions: 1) 0.5 M HCl + CH_3OH; 2) ditto + 0.02 M $TeCl_4$; 3) ditto + 0.03 M $TeCl_4$; 4) ditto + 0.05 M $TeCl_4$; 5) 0.05 M $TeCl_4$ + C_3H_7OH + 0.5 M HCl; 6) 0.05 M $TeCl_4$ + 5 M HCl + CH_3OH.[25]

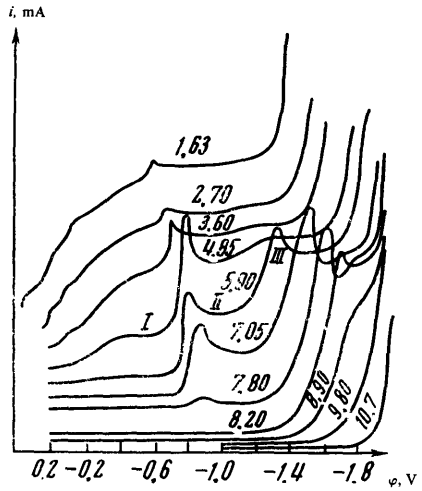


Figure 9. Polarographic curves for a 0.001 M selenium(IV) solution at different pH in the absence of surface-active substances (the pH values are indicated opposite the curves)[123].

An electrolyte with the composition 50% TeO_2 + 25% KCl + 25% LiCl was used for the electrodeposition of tellurium from fused media[118]. This composition was chosen after investigating the properties of certain TeO_2–KCl and TeO_2–LiCl binary systems and also the TeO_2–KCl–LiCl ternary system[119]. The electrolysis was carried out at 650–680°C and a current density of 0.2 A

cm^{-2}. Tellurium reduced to the elemental state accumulated in the liquid form on the bottom of the electrolyser. Impurities collected in the form of a slag on the surface of the deposited tellurium. The impurity content in the cathodic tellurium did not exceed 0.01–0.02%.

When a direct current was passed between two electrodes immersed in fused selenium, some impurities (silver, tellurium, and iron) collected in the cathodic compartment, while others (lead, arsenic, and nickel) collected in both cathodic and anodic compartments. The purest selenium remained in the central part of the cell[120].

In the cathodic–anodic polarisation of liquid selenium in the fused LiCl–KCl eutectic at 400°C, selenium is oxidised at the anode: $2Se + 2Cl^- - 2e \rightarrow Se_2Cl_2$, while the selenide is formed on the cathode: $Se + 2e \rightarrow Se^{2-}$. Under analogous conditions the oxidation of tellurium proceeds up to the formation of Te^{2+} and the cathodic process is limited to the incorporation of lithium in tellurium[121].

IV. POLAROGRAPHY OF SELENIUM AND TELLURIUM

Numerous studies have been made on the polarography of selenium and tellurium[122-178].

Selenium

Depending on the composition of the electrolyte (in the first place on the pH of the medium), the polarogram of selenous acid has up to three waves. A distinct wave, suitable for analytical purposes, appears at potentials between −1.4 and −1.5 V (s.c.e.) in the pH range 8–9. The electrode reaction then proceeds via the mechanism $HSeO_3^- + 6H^+ + 6e \rightarrow HSe^- + 3H_2O$.

There are different interpretations[122-127] of the mechanism of selenous acid reduction in acid solutions at a dropping mercury electrode.

The most likely mechanism of the formation of two waves (Fig. 9) in more acid solutions was given by Lingane and Niedrach[123]. The electrode reaction proceeds initially with participation of six electrons: $SeO_3^{2-} + 6H^+ + 6e \rightarrow Se^{2-} + 3H_2O$. The selenide ions formed at the surface of the mercury drop depolarise mercury anodically, which leads to its oxidation and the formation of a mercury selenide deposit:

$$Se^{2-} + Hg \rightarrow HgSe + 2e\ .$$

The anodic mercury oxidation wave lowers the cathodic selenite reduction wave and the overall process $SeO_3^{2-} + Hg + 6H^+ + 4e \rightarrow HgSe + 3H_2O$ corresponds to a four-electron reaction. As stated by Speranskaya[124], mercury selenide is formed as the result of the involvement of elemental selenium, formed in the reduction of the selenite, in the four-electron reaction

$$SeO_3^{2-} + 6H^+ + 4e \rightarrow Se^0 + 3H_2O,\ Se^0 + Hg = HgSe\ .$$

According to Speranskaya's data[125] the reduction of the selenite ion at dropping bismuth, lead, cadmium, zinc, and sodium amalgam electrodes entails the formation of two waves. The first wave appears at potentials between −0.2 and −0.6 V and is associated with a four-electron process which proceeds with a 100% current yield. At potentials more negative than −0.6 V the selenite is reduced to selenide ions.

According to Brdička and Wiesner[126], the polarographic waves of selenium are due to the reduction of various forms of selenous acid (SeO_3^{2-}, $HSeO_3^-$, H_2SeO_3) to elemental selenium.

In the pH range 2.7–1.6 complex waves are observed for selenium, which are a result of the occurrence of several processes, including the reduction of Se^{4+} to the elemental state and the selenide and the reduction of various forms of selenous acid.

Some information about the polarographic behaviour of selenium(IV) in acid solutions may be found in papers by Jonas[127] and Christian and Knoblock[128].

The selenide ion gives rise to an anodic wave associated with the oxidation of mercury and the formation of mercury selenide[129]. This wave can be used to determine selenides in the presence of sulphides. The electrochemical behaviour of the selenosulphide ion SeS^{2-} at a dropping mercury electrode was investigated by Tornova et al.[130]

In an ammonia buffer solution at pH 8–9.5 a single distinct wave arises on the selenium(IV) polarogram. The diffusion current is directly proportional to the concentration of selenite in solution. This wave is frequently used for a quantitative polarographic determination of selenium[131-135].

The presence of ions of heavy elements in the solutions being analysed interferes with the determination of selenium; they are either separated[136-139] or masked by the addition of suitable complex-forming reagents to the electrolyte[140-142].

The use of modern polarographic apparatus greatly extends the scope and increases the sensitivity of the selenium determination. A vector polarograph with a stationary electrode in the form of a mercury drop permits the determination of 2×10^{-7} mole of selenium or even less[143]. The alternating-current polarographic method has been used to determine selenium in semiconductor materials[144,145]. An oscilloscopic polarographic method for the determination of selenium in germanium selenide has been described[146,147].

Very small amounts of selenium (down to 5×10^{-8} M) can be determined by a pulse polarographic method[137]. Elemental selenium reacts with concentrated sulphuric acid to form $SeSO_3$. In the polarography of sulphuric acid containing selenium, a distinct wave due to the reaction

$$SeSO_3 + 6H^+ + 6e \rightarrow Se + S + 3H_2O$$

is obtained. A polarographic determination of selenium in sulphuric acid has been developed on the basis of this reaction[148].

In an alkali metal sulphite solution elemental selenium forms the selenosulphate ion $SeSO_3^{2-}$ which is reduced at a dropping mercury electrode and gives rise to a distinct wave due to the reaction $SeSO_3^{2-} + 2e \rightarrow Se^{2-} + SO_3^{2-}$.[149] The polarographic method has been used to analyse mixtures of selenothionates[150]. The polarographic determination of selenium as selenosulphate has been described[151].

In acidified solutions of sodium (or potassium) tartrate or lithium citrate at pH 1–5 in the presence of 0.01% of gelatin selenium(IV) gives rise to a distinct wave whose half-wave potential $\varphi_{1/2}$ shifts from −0.55 to −60 V when the pH is raised from 1 to 5.[152,153]

In 0.1 M ammonium acetate solution at pH 6.2 selenium(IV) gives rise to two waves with half-wave potentials of −0.81 and −0.38 V. Deshmukh and Asthana[154]

explained them by the reduction of Se^{4+} to Se^{2+} and elemental selenium. The Se^{2+} state, which was indicated at an early stage by Schwaer and Suchy[122], was not confirmed by Lingane and Niedrach[123].

The polarography of organic selenium compounds is developing successfully. The polarographic behaviour of the selenocystine–selenocysteine system, of certain five- and six-membered cyclic diselenides, and of products of the oxidation of five-membered cyclic diselenides and disulphides has been investigated in detail[155]. Certain inhibition effects of five-membered cyclic diselenides and disulphides have been studied[156]. The polarographic reduction of diphenyl diselenide and diphenyl disulphide has been described by Nygard[157].

When 3,3-diaminobenzidine or *o*-phenylenediamine is added to a solution containing selenium(IV), the product is a diazaselenole which gives rise to a distinct polarographic wave[141]. In 0.1 *N* $HClO_4$ + 0.1 *N* NH_4ClO_4 solution at pH 2.5, phenyldiazaselenole gives rise to two waves with $\varphi_{1/2} = -0.17$ and -0.64 V (s.c.e.). The height of the first wave is proportional to the concentration of selenium. The method was used to determine selenium in sulphur, sulphites, and sulphates.

Tellurium

The telluride ion gives rise to an anodic wave in acid and alkaline electrolytes. In an ammonia buffer solution Te^{2-} is oxidised reversibly to elemental tellurium[129].

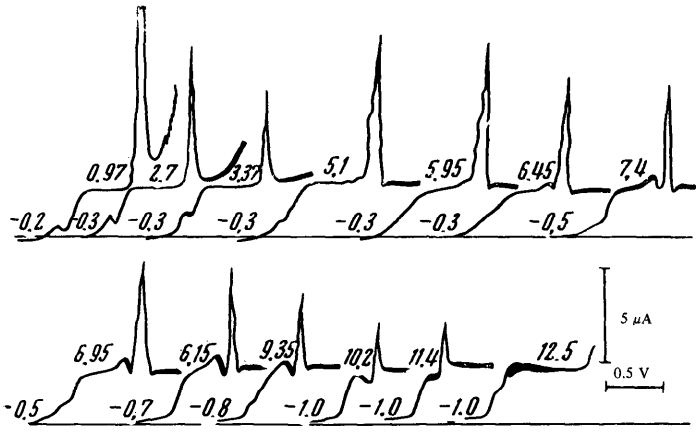


Figure 10. Polarogram for buffer solutions: CH_3COONa + $HClO_4$ + 1.46×10^{-4} M Te, pH ranging from 0.97 to 5.1, and for NaH_2PO_4 + LiOH + 1.46×10^{-4} M Te. The pH values are indicated opposite the curves (pH 5.95–12.5). The numerals at the beginning of the polarogram indicate the potentials at which the polarograms were begun[158].

Depending on the nature of the indifferent electrolyte (as in the case of selenium), there are between 1 and 3 waves on the tellurium(IV) polarogram (see Fig. 10). The mechanism of the formation of the first, main tellurium(IV) wave is similar to that of the formation of the selenium(IV) wave[123,158].

A sharp maximum, differing from the usual polarographic maxima by the fact that it occurs after the attainment of the steady diffusion current of the main wave, arises on the tellurium(IV) polarogram. Its height falls with increase of pH; at pH > 12 it does not appear at all and is readily suppressed by surface-active substances[153]. Various hypotheses have been put forward concerning the reasons for its appearance[158,159,161,162]. At the potential maximum a film of elemental tellurium is observed on the mercury drop.

It has been suggested[158] that under these conditions the anodic dissolution of mercury ceases and telluride ions [formed in the reduction of tellurium(IV)] react with tellurite ions: $2Te^{2-} + 2Te^{4+} \rightarrow 3Te$.

By titrating with hydrochloric acid 0.1 M solutions of $LiClO_4$ containing Na_2TeO_3 which had been made alkaline, it was established[158] that at pH 0.17–2.7 different tellurium species (H_2TeO_3, $HTeO_3^-$, TeO_3^{2-}) exist simultaneously in solution; the polarograms of such solutions have a complex form with several waves.

In contrast to selenium(IV), in the reduction of tellurium(IV) ions in alkaline electrolytes a distinct polarographic wave appears; it is used to determine tellurium in solutions containing selenium[160].

The nature of the reduction of tellurium(IV) and the corresponding half-wave potential depend on the concentration of H^+ ions[163,164]. In acid solutions containing tellurium(IV) catalytic evolution of hydrogen takes place. As the acidity of the electrolyte falls, the evolution of hydrogen is accompanied by partial reduction of tellurium(IV). In neutral and alkaline solutions a single wave with a maximum arises on the tellurium(IV) polarogram. The limiting current of this wave is restricted by the rate of diffusion of tellurium and is proportional to its concentration[163].

The quantitative polarographic determination of tellurium is largely based on the tellurium(IV) wave in the presence of ammonium salts as the supporting electrolyte at pH 6–9; $\varphi_{1/2}$ varies from -0.60 to -0.70 V (s.c.e.). With increase of pH, $\varphi_{1/2}$ shifts towards negative potentials, but the concentration of ammonium salts does not have an appreciable effect[136,165–170].

The polarographic determination of tellurium is interfered with by heavy metal ions (Pb, Zn, Fe, and others). Their influence is eliminated by adding Complexone III to the solution being analysed[171]. In most cases preference is given to the separation of tellurium in the elemental state by the action of reducing agents (hydrazine salts[172], $SnCl_2$,[133] hydroxylamine hydrochloride[173]).

In a tartrate–ammonia buffer solution as the supporting electrolyte, it is possible to determine down to 2×10^{-5} M of tellurium in the presence of lead, iron, and antimony[174]. The maximum arising on the tellurium wave is used for the detection and quantitative determination of microgram amounts of tellurium in selenium[161].

In the presence of large amounts of copper, KCN solutions are used as the supporting electrolyte for the determination of tellurium[175]. Tellurium in semiconductor alloys and in thin films is determined by a pulse polarographic method in the presence of 1 *N* HCl as the supporting electrolyte[176]. The polarographic determination of tellurium in the presence of antimony and gallium has been described[177]. 0.1 M NH_4CNS + Na_2SO_4 solution has been proposed as the supporting electrolyte for the determination of tellurium and selenium[178]. Distinct separate selenium and tellurium waves are obtained in this supporting electrolyte.

It should be noted that only the commonest methods for the polarographic determination of selenium and tellurium were described above. A complete description is outside the scope of this review.

REFERENCES

1. D. M. Chizhikov and V. P. Schastlivyi, "Selen i Selenidy" (Selenium and Selenides), Izd. Nauka, Moscow, 1964.
2. D. M. Chizhikov and V. P. Schastlivyi, "Tellur i Telluridy" (Tellurium and Tellurides), Izd. Nauka, Moscow, 1966.
3. A. A. Kudryavtsev, "Khimiya i Tekhnologiya Selena i Tellura" (The Chemistry and Technology of Selenium and Tellurium), Izd. Vysshaya Shkola, Moscow, 1968.
4. I. I. Nazarenko and A. I. Ermakov, "Analiticheskaya Khimiya Selena i Tellura" (Analytical Chemistry of Selenium and Tellurium), Izd. Nauka, Moscow, 1971.
5. K. W. Bagnall, "The Chemistry of Selenium, Tellurium and Polonium", Elsevier, Amsterdam, 1966.
6. D. M. Yukhtanov, "Proizvodstvo Selena i Tellura" (The Manufacture of Selenium and Tellurium), Metallurgizdat, 1955.
7. A. V. Novoselova, A. S. Pashinkin, and V. A. Pokovkin, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 557 (1960).
8. D. I. Ryabchikov and I. I. Nazarenko, Uspekhi Khim., 33, 68 (1964) [Russ. Chem. Rev., No. 1 (1964)].
9. W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions" (Translated into Russian), Inostr. Lit., Moscow, 1954.
10. H. F. Schott, E. H. Swift, and D. M. Yost, J. Amer. Chem. Soc., 50, 721 (1928).
11. Sh. D. Osman-zade and A. T. Vagramyan, Elektrokhimiya, 2, 85 (1966).
12. M. C. Day and J. Selbin, "Theoretical Inorganic Chemistry" (Translated into Russian), Izd. Khimiya, Moscow, 1969.
13. O. B. Nevskii, A. D. Gerasimov, and N. N. D'yachkova, Elektrokhimiya, 4, 624 (1968).
14. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Goskhimizdat, Moscow–Leningrad, 1951.
15. P. Z. Iofa, Wang-Hsing Wang, and M. Ridman, Radiokhimiya, 8, 14 (1966).
16. D. Reichinstein, Z. Phys. Chem., 97, 257 (1921).
17. I. A. Kasarnowski, Z. anorg. Chem., 128, 33 (1923).
18. V. S. Yakovleva and Z. A. Andreev, Uch. Zap. Leningrad. Ped. Inst. im. Gertsena, 160, 193 (1959).
19. I. M. Issa, H. Khalifa, and S. A. Awad, J. Indian Chem. Soc., 34, 275 (1957).
20. R. Schuhmann, J. Amer. Chem. Soc., 47, 356 (1925).
21. J. A. Ricketts and L. W. Tresselt, J. Amer. Chem. Soc., 81, 2305 (1959).
22. M. Pourbaix, "Atlas d'équilibres électrochimique", Paris, 1963.
23. H. Gobrecht, R. Kuhnkies, and A. Tounsend, Z. Elektrochem., 63, 541 (1959).
24. Sh. D. Osman-zade and A. T. Vagramyan, Elektrokhimiya, 3, 249 (1967).
25. A. I. Alekperov, Doctoral Thesis, Institute of Electrochemistry, USSR Academy of Sciences, 1969.
26. A. von Hippel, J. H. Schulman, and J. Rittner, Appl. Phys., 17, 215 (1946).
27. R. W. Pittman, J. Chem. Soc., 855 (1953).
28. H. Khalifa and J. M. Issa, J. Indian Chem. Soc., 34, 87 (1957).
29. J. A. Ammar and S. A. Awad, J. Electrochem. Soc., 103, 182 (1956).
30. J. O'M. Bockris and E. C. Potter, J. Electrochem. Soc., 99, 169 (1952).
31. V. A. Fishman, V. I. Lainer, and I. G. Erusalimchik, Elektrokhimiya, 5, 530 (1969).
32. B. N. Rybakov, G. V. Maslova, and L. A. Sinyagovskaya, Elektrokhimiya, 6, 1237 (1970).
33. A. N. Frumkin, O. A. Petrii, and N. V. Nikoloaeva-Fedorovich, Dokl. Akad. Nauk SSSR, 147, 878 (1962).
34. N. V. Nikolaeva-Fedorovich, B. N. Rybakov, and K. A. Radyushkina, Elektrokhimiya, 3, 1086 (1967).
35. N. V. Nikolaeva-Fedorovich, E. V. Stenina, and K. V. Rybalka, Elektrokhimiya, 3, 1052 (1967).
36. G. B. Abdullaev and N. A. Bashshaliev, Trudy Inst. Fiz. i Mat., Akad. Nauk Azerb. SSR, 8, 13 (1956).
37. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", London, New York, 1947, Vol. 10.
38. Z. W. Dennis and J. P. Koller, J. Amer. Chem. Soc., 41, 960 (1919).
39. W. Manchot and A. Wizzmuller, Z. anorg. Chem., 140, 47 (1924).
40. M. Le-Blanc, Z. Elektrochem., 11, 817 (1905).
41. E. Müller and R. Nowakowsky, Z. Elektrochem., 11, 931 (1905).
42. A. J. Panson, J. Phys. Chem., 67, 2177 (1963).
43. A. J. Panson, J. Phys. Chem., 68, 1721 (1964).
44. F. F. Faizulin and S. V. Kuzovenko, Elektrokhimiya, 4, 736 (1968).
45. S. A. Awad, J. Electrochem. Soc., 108, 468 (1961).
46. S. A. Awad, J. Electrochem. Soc., 109, 865 (1962).
47. V. M. Komandenko and A. L. Rotinyan, Elektrokhimiya, 3, 552 (1967).
48. A. I. Alekperov, F. S. Novruzova, and M. A. Babaeva, Azerb. Khim. Zhur., No. 2, 129 (1971).
49. T. Kh. Imamov and O. Abrarov, Uzbek. Khim. Zhur., No. 6, 41 (1965).
50. V. A. Fishman, V. I. Lainer, and I. G. Erusalimchik, Elektrokhimiya, 5, 304 (1969).
51. S. A. Awad, Electrochem. Acta, 13, 925 (1968).
52. S. A. Awad, Electrochem. Acta, 7, 677 (1962).
53. A. I. Alekperov and M. A. Babaeva, Azerb. Khim. Zhur., No. 1, 133 (1971).
54. E. Müller, Z. Phys. Chem., 100, 346 (1922).
55. A. Jilek and J. Lukas, Chem. Listy, 21, 546 (1927).
56. C. G. Fink and D. K. Alpern, Trans. Electrochem. Soc., 62, 369 (1932).
57. A. K. Graham, H. Z. Pinkerton and H. J. Boyd, J. Electrochem. Soc., 106, 651 (1959).
58. A. V. Krusenstiern and M. Meier, Metall., 22, 688 (1968).
59. V. V. Kuznetsov, E. N. Kon'shina, and A. S. Karasik, Uch. Zap. Perm. Univ., No. 194, 27 (1968).
60. G. Sella, Ricerca sci., 10, 1143 (1939).
61. T. Hirosawa, Nippon Kodyo Kaiyo [Nippon Kogyo Kaishi? (J. Mining Met. Inst. Japan)], 72, 815 (1956).
62. Sh. D. Osman-zade, Azerb. Khim. Zhur., No. 4, 39 (1967).

63. A. Von Hippel and M. C. Bloom, J. Chem. Phys., **18**, 1243 (1950).
64. E. A. Shugam, Zhur. Fiz. Khim., **30**, 1732 (1956).
65. A. M. de Becdelievre, J. Becdelievre, and M. J. Barbier, Mater. Res. Bull., **5**, 73 (1970).
66. Sh. D. Osman-zade and A. T. Vagramyan, Elektrokhimiya, **3**, 393 (1967).
67. E. Pacauskas, J. Janickis, and G. Buineviciene, Trudy. Akad. Nauk Lit. SSR, B, 87 (1961).
68. E. Pacauskas, J. Janickis, and E. Rinkeviciene, Trudy. Akad. Nauk Lit. SSR, **3** (46), 45 (1966).
69. B. Devis, US P. 3 585 115 (1971).
70. M. C. Bloom, US P. 2 414 438 (1947); Chem. Abs. 3383i (1947).
71. J. Janickis and A. Jokuziene, Trudy Akad. Nauk Lit. SSR, 3 (50), 57 (1967).
72. A. I. Alekperov and M. A. Babaeva, Dokl. Akad. Nauk Azerb. SSR, **24**, 16 (1968).
73. L. Müller and Schlosser, Neue Hütte, Heft 1, 17 (1964).
74. A. I. Alekperov and F. S. Novruzova, Elektrokhimiya, 5, 97 (1969).
75. A. I. Alekperov, M. A. Babaeva, F. S. Novruzova, and S. D. Dadasheva, Dokl. Akad. Nauk Azerb. SSR, 26, 26 (1970).
76. V. M. Komandenko, Zhur. Prikl. Khim., **43**, 2480 (1970).
77. G. Pellini, Atti Accad. Linc., (5), **13**, 275 (1904); A. Fisher and A. Schleicher, "Electroanalysis" (Translated into Russian), GONTI, Leningrad, 1931.
78. G. Gallo, Atti Accad. Linc., (5), **13**, 713 (1904); A. Fisher and A. Schleicher, "Electroanalysis" (Translated into Russian), GONTI, Leningrad, 1931.
79. C. Mathers and H. L. Turner, Trans. Amer. Electrochem. Soc., **50**, 293 (1928).
80. L. I. Kadaner, "Elektroosazhdenie Blagorodnykh i Redkikh Metallov (Obzor Zarubezhnoi Tekhniki) [Electrodeposition of Noble and Rare Metals (Review of Engineering Abroad)], GOSINTI, Moscow, 1962.
81. T. Kh. Imamov and O. Abrarov, Uzbek. Khim. Zhur., No. 5, 53 (1965).
82. R. K. Kadyrov and K. R. Rasulov, Elektrokhimiya, 8, 1843 (1972).
83. V. M. Komandenko, Izv. Vys. Ucheb. Zaved., Khim i Khim Tekhnol., **12**, 790 (1969).
84. F. F. Faizulin and S. V. Kuzovenko, "Sbornik Issledovanii po Elektrokhimii, Magnitokhimii i Elektroliticheskim Metodam Analiza" (Collected Studies on Electrochemistry, Magnetochemistry, and Electrolytic Analytical Methods), Kazan, 1960, No. 2, p. 79.
85. A. S. Ghosh-Mazumder and M. J. Haissinsky, Chem. Phys., **53**, 979 (1956).
86. S. A. Awad, J. Phys. Chem., **66**, 890 (1962).
87. M. A. Klochko and Z. S. Medvedeva, Izv. Sektora Fiz.-Khim. Anal., **27**, 133 (1956).
88. V. G. Trusova and D. M. Chizhikov, Trudy Inst. Metallurg. im. Baibakova, 1962, No. 2, p. 49.
89. E. Pacauskas, J. Janickis, and D. Mickevicius, Trudy Akad. Nauk Lit. SSR, 3 (62), 117 (1970).
90. M. M. Polukarov and L. M. Skryachenkov, Uch. Zap. Perm. Univ., No. 114, 74 (1966).
91. A. J. Panson, Inorg. Chem., **3**, 940 (1964).
92. J. Amosse, M. J. Barbier, and A. M. Becdelievre, Mater. Res. Bull., **5**, 376 (1970).
93. E. Pacauskas, J. Janickis, and V. Pilkauskiene, Trudy Akad. Nauk Lit. SSR, **4** (51), 11 (1967).
94. E. Pacauskas, J. Janickis, and G. Buineviciene, Trudy Akad. Nauk Lit. SSR, 1 (36), 87 (1964).
95. E. Pacauskas and J. Janickis, Trudy Akad. Nauk Lit. SSR, **3** (36), 107 (1970).
96. E. Pacauskas, J. Janickis, and I. Lasaviciene, Trudy Akad. Nauk Lit. SSR, **2** (65), 61 (1971).
97. E. Pacauskas, J. Janickis, I. Lasaviciene, and S. Riselis, "Vsesoyuznaya Nauchnaya Konferentsiya. Puti Razvitiya i Poslednie Dostizheniya v Oblasti Prikladnoi Elektrokhimii (Kratkie Tezisy Dokladov)" [All-Union Science Conference. Developments and Latest Advances in Applied Electrochemistry (Brief Abstracts of Reports)], Leningrad, 1971.
98. J. Janickis, E. Pacauskas, and A. Saudargaite, Trudy Akad. Nauk Lit. SSR, 4 (59), 75 (1969).
99. P. Fisher, Z. Elektrochem., **31**, 286 (1925).
100. E. A. Lavut and O. I. Vorob'eva, Zhur. Neorg. Khim., 5, 1813 (1960) [Russ. J. Inorg. Chem., No. 8 (1960)].
101. K. Nishimura, Mitsui Kozan Kabushiki Kaisha (Mitsui Mining Co), Japanese P. 38 085 (25/II–1921); Chem. Abs., 16, 1188 (1922).
102. A. I. Gaev, I. F. Gulikov, and V. N. Zhchur, Tsevetnye Metally, No. 5–6, 114 (1940).
103. J. Tarasake, Mining Inst., Japan, **72**, 1379 (1956); Schofield Mining Mag. (London), **100**, 141 (1959).
104. U. V. Keppel and A. K. Shillinger, "Sbornik Dokladov. Izvlechenie i Ochistka Redkikh Metallov" (Collected Reports. Extraction and Purification of Rare Metals), Atomizdat, Moscow, 1960.
105. V. S. Lovchikov and B. M. Livshits, Izv. Vys. Ucheb. Zaved., Tsvetnaya Metallurgiya, 6, 93 (1959).
106. A. M. Ovonishnikov, O. A. Khan, V. I. Aidarova, and L. K. Saltovskaya, Metallurg. Khim. Prom. Kazakhstana, 1, 49 (1960).
107. O. A. Khan and L. K. Saltovskaya, Zhur. Prikl. Khim., **33**, 2143 (1960).
108. G. A. Simonov, L. K. Smirnova, and A. L. Rotinyan, Zhur. Prikl. Khim., **36**, 1291 (1963).
109. V. M. Komandenko and A. L. Rotinyan, Zhur. Prikl. Khim., **39**, 123 (1966).
110. Yu. A. Zaitsev and T. N. Greiver, Zhur. Prikl. Khim., **40**, 1986 (1967).
111. A. I. Alekperov and A. A. Mirzoeva, Zhur. Prikl. Khim., **38**, 555 (1965).
112. P. P. Napolitano and C. L. Mantell, Trans. Metallurg. Soc. AIME, **230**, 133 (1964).
113. A. A. Solovushkova, L. A. Soshnikova, and Z. M. Matveeva, "Chistye Metally i Poluprovodniki. Trudy 1-oi Mezhvuzovoskoi Konferentsii" (Pure Metals and Semiconductors. Proceedings of the First Intercollegiate Conference, Metallurgizdat, Moscow, 1959, p. 239.
114. A. I. Alekperov, Uch. Zap. Azerb. Gos. Univ., Ser. Khim. Nauk, No. 2 (1968).
115. A. I. Alekperov and M. A. Babaeva, Symposium, "Peredovye Metody Khimicheskoi Tekhnologii i Kontrolya Proizvodstva" (Advanced Methods in Chemical Engineering and in the Control of Manufacturing Processes), Izd. Rostov. Gos. Univ., Rostov, 1964, p. 76.
116. A. I. Alekperov, Elektrokhimiya, **4**, 847 (1968).
117. A. I. Alekperov and F. S. Novruzova, Azerb. Khim. Zhur., No. 1, 114 (1969).
118. A. I. Alekperov, G. Kh. Efendiev, and P. G. Rustamov, Dokl. Akad. Nauk Azerb. SSR, **33**, 25 (1967).
119. P. G. Rustamov, A. I. Alekperov, and E. A. Geidarova, Azerb. Khim. Zhur., No. 4, 57 (1962).

120. Okada Hiroshi, Sin Dengen Kochyo Kabusiki Kaisya, Japanese P. 4307 (28.06.1957); Ref. Zhur. Khim., 53344 (1960).
121. F. J. Bodewing and J. A. Plambeck, J. Electrochem. Soc., 117, 618 (1970).
122. L. Schwaer and K. Suchy, Coll. Czech. Chem. Comm., 7, 25 (1935).
123. J. J. Lingane and L. W. Niedrach, J. Amer. Chem. Soc., 71, 196 (1949).
124. E. F. Speranskaya, Zhur. Anal. Khim., 17, 347 (1962); 18, 9 (1963).
125. E. F. Speranskaya, Elektrokhimiya, 3, 1450 (1967).
126. R. Brdička and K. Wiesner, Coll. Czech. Chem. Comm., 12, 138 (1947).
127. K. Jonas, Acta Chim. Acad. Sci. Hung., 25, 379 (1960).
128. G. D. Christian and E. C. Knoblock, Analyt. Chem., 35, 1125 (1963).
129. J. J. Lingane and L. W. Niedrach, J. Amer. Chem. Soc., 70, 4115 (1948).
130. V. F. Tornova, L. N. Medvedeva, and Yu. N. Polyakov, "Tezisy Dokladov na Vsesoyuznom Simpoziume po Analiticheskoi Khimii Selena, Tellura i Reniya" (Abstracts of Reports at the All-Union Symposium on the Analytical Chemistry of Selenium, Tellurium, and Rhenium), Izd. MITK, Erevan, 1968.
131. V. G. Sochevanov and N. V. Shmakov, Byul. VIMS, 8, 184 (1958).
132. A. Ya. Mashchukov and T. G. Maslakova, Sbornik Nauch. Trudov. VNII Gorno-Metallurg. Inst. Tsvetnykh Metallov, 5, 98 (1959).
133. G. M. Zhiteneva and Yu. V. Rumyantsev, Trudy Vostochno-Sibirskogo Fil. Akad. Nauk SSSR, 41, 155 (1962).
134. T. V. Aref'eva and L. N. Vasil'eva, Trudy Gintsvetmet, 19, 669 (1962).
135. S. A. Fer'yanchich, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 16, 106 (1968).
136. A. I. Zelyanskaya, I. E. Bykov, and L. S. Gorshkova, Trudy Inst. Metallurg. Ural'sk. Fil. Akad. Nauk SSSR, 1, 151, 155, 161 (1957); 5, 137 (1960).
137. B. Ya. Kaplan and I. A. Sorokovskaya, Zavod. Lab., 30, 783 (1964).
138. R. Ripan and G. Pop, Rev. Chim. (RPR), 14, 413 (1963).
139. M. Kotowska and I. Szczepkowska-Mamczarczyk, Techn. Poszur, 6, 59 (1957).
140. T. V. Aref'eva and A. A. Pozdnyakova, Trudy Gintsvetmet, 8, 137 (1957).
141. C. Le Peintre, Compt. rend., 252, 1968 (1961); 253, 1696 (1961).
142. R. G. Pats and T. V. Semochkina, Trudy Gintsvetmet, 28, 12 (1968).
143. R. G. Pats and T. V. Semochkina, Zavod. Lab., 33, 1491 (1967).
144. V. I. Lysenko and E. V. Lisitsina, Sbornik Nauch. Trudov. VNII Gormetallurg. Inst. Tsvetnykh Metallov, 13, 42 (1968).
145. Yu. S. Lyalikov, L. S. Kopanskaya, and Z. P. Kulieva, Zavod. Lab., 33, 1493 (1967).
146. I. A. Tserkovnitskaya and V. N. Epimakhov, Zavod. Lab., 31, 1178 (1965).
147. I. A. Tserkovnitskaya and V. N. Epimakhov, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 16, 145 (1968).
148. E. I. Patsauskas, I. V. Yanitskii, and E. P. Rankyaviciene, Trudy Akad. Nauk Lit. SSR, 3 (46), 55 (1966); 1 (36), 97 (1964).
149. V. F. Toropova, Zhur. Anal. Khim., 11, 599 (1956).
150. V. Zelionkaite and J. Janickis, Trudy Akad. Nauk Lit. SSSR, 4 (20), 71 (1959).
151. V. V. Malakhov, Zavod. Lab., 28, 408 (1962).
152. R. Bock and H. Kan, Z. Anal. Chem., 188, 28 (1962).
153. Morimoto Suzuki, J. Electrochem. Japan, 23, 544 (1955); Ref. Zhur. Khim., 19, 61864 (1956).
154. G. S. Deshmukh and O. P. Asthana, Naturwiss., 48, 477 (1961).
155. B. Nygard, Arkiv. Kemi, 27, 341, 405, 425 (1967).
156. B. Nygard, J. Olofsson, and G. Bergson, Arkiv. Kemi, 28, 41 (1968).
157. B. Nygard, Acta Chem. Scand., 20, 1710 (1966).
158. S. I. Zhdanov and R. G. Pats, Elektrokhimiya, 1, 947 (1965).
159. H. Schmidt and M. Stackelberg, J. Polarogr. Soc., 3, 49 (1962).
160. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, "Polyarograficheskii Analiz" (Polarographic Analysis), Goskhimizdat, Moscow, 1959.
161. I. A. Alekperov, Azerb. Khim. Zhur., No. 4, 133 (1961).
162. W. Hans and M. Stackelberg, Z. Elektrochem., 54, 62, 65 (1950).
163. S. I. Zhdanov and R. G. Pats, Elektrokhimiya, 1, 1092 (1965).
164. R. M. Issa and B. A. Nabey, Z. Anal. Chem., 231, 339 (1967).
165. A. I. Alekperov and S. S. Novruzova, Symposium, "Metody Analiza Veshchestv Vysokoi Chistoty" (Methods for the Analysis of Highly Pure Substances), Izd. Nauka, Moscow, 1965.
166. G. S. Deshmukh and V. S. Sancara Rao, Z. Anal. Chem., 240, 322 (1968).
167. Kuo-Huai Wu and Hsüeh-Ch'ingchieh, Ref. Zhur. Khim., 39389 (1958).
168. R. G. Pats, L. N. Vasil'eva, and T. V. Semochkina, Zhur. Anal. Khim., 23, 241 (1968).
169. L. V. Zolotareva and P. N. Kovalenko, Zhur. Anal. Khim., 19, 731 (1964).
170. T. V. Aref'eva and Z. L. Yustus, Trudy Gintsvetmet, 19, 730 (1964).
171. A. I. Zelyanskaya, I. B. Bykov, L. S. Gorshkova, and N. I. Petunina, "Metody Polyarograficheskogo Analiza Mineral'nogo Syr'ya" (Methods for the Polarographic Analysis of Minerals), Gosgeoltekhizdat, Moscow, 1960.
172. K. J. Cathro, Austral. J. Appl. Sci., 9, 255 (1958).
173. B. Ya. Kaplan, I. A. Sorokovskaya, and O. A. Shiryaeva, Zavod. Lab., 30, 659 (1964).
174. I. E. Bykov, A. I. Zelyanskaya, and L. S. Gorshkova, Trudy. Inst. Metallurg. Ural'sk Fil. Akad. Nauk SSSR, 2, 275 (1958).
175. I. E. Bykov and L. S. Gorshkova, Zavod. Lab., 25, 674 (1954).
176. Yu. S. Lyalikov and L. S. Kopanskaya, Ukrain. Khim. Zhur., 30, 91 (1964).
177. L. I. Veselago and N. S. Gertseva, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 16, 150 (1968).
178. P. N. Kovalenko and L. V. Zolotareva, "Materialy 2-go Soveshchaniya po Polyarografii" (Proceedings of the Second Conference on Polarography), Izd. Kazan. Univ., 1962.

Institute of Inorganic and Physical Chemistry, Azerbaijan SSR, Baku