NAXÇIVAN DÖVLƏT UNİVERSİTETİ/ ELMİ ƏSƏRLƏR/ 2024, № 1 (127)
NAKHCHIVAN STATE UNIVERSITY/ SCIENTIFIC WORKS/ 2024, № 1 (127)
НАХЧЫВАНСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ/ НАУЧНЫЕ ТРУДЫ/ 2024, № 1 (127)

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DOI: 10.30546/155244.2024.2.127.018

ELECTRO RECOVERY OF TELLURUM IONS FROM NON-AQUEOUS N-N DIMETHYLFORMAMIDE ELECTROLYTE

The work presents studies of the mechanism of recovery of tellurium ions from non-aqueous N-N dimethylformamide. For this, linear and cyclic current-voltage polarization curves have been recorded. The influence on the process of the concentration of tellurium ions, change of potential sweep rate and temperature has been investigated. By recording linear polarization curves, it has been established that the reducing process of tellurium ions is controlled by their diffusion to the cathode surface. The influence of the concentration of its ions in the electrolyte, the rate of change of the potential and the temperature on the tellurium deposition process was studied. By recording the cyclic polarization curve, the potential area where tellurium ions precipitate and its anodic dissolution occurs is determined. It was determined that the increase in the concentration of tellurium ions and the temperature increases the speed of the reduction process of tellurium, and the reduction process itself is controlled by the diffusion of tellurium ions on the cathode surface. To confirm the obtained data, polarization curves have been recorded on a rotating platinum disk electrode. Data received, exactly the linear dependence of i_p *on the electrode rotation speed (ω) to the power of 0.5, confirms that, that the process of reduction of tellurium electrodes in non-aqueous N-N dimethylformamide is controlled by diffusion polarization.*

Key words: *electro recovery, tellurium, diffusion, polarization, non-aqueous electrolytes, rotating disk electrode.*

Introduction

Tellurium is one of the least commonly found elements on the Earth. Its content in the Earth's crust is about 0.005 ppm and comparable to adding gold or platinum (1). Firstly, tellurium is used as an alloying additive to steel, cast iron and non-ferrous metals, forming alloys (copper, tin, lead), improving their mechanical characteristics and increasing corrosion resistance. Due to its unique crystal structure tellurium exhibits many unique properties, such as the piezoelectric effect, photoconductivity, catalytic activity and thermoelectricity (2-6).

However, particular attention is drawn to the possibility of synthesizing semiconductor compounds based on tellurium, which can be used for the production of solar cells. Tellurium-based semiconductor compounds and alloys are an important class of materials used in energy conversion

(CdTe) (7), IR detection (HgCdTe) (8), and many other devices. Elementary Te itself has interesting properties and has recently found use in devices in the form of nanostructures based on it (9,10) and in their applications (11,12). Te to form semiconductor materials such as CdTe, Bi_2Te_3 and Sb_2Te_3, most often carried out from an acidic aqueous solution using TeO_2 as a source of tellurium. Electrodeposition of tellurium from non-aqueous electrolytes has been studied by many authors. Thus, in the (13), the electrodeposition of elemental Te from $(NnBu_4)_2(TeCl_6)$ in dichloromethane has been studied, which is a weakly coordinating solvent. The reduction of the Te(IV) complex before deposition Te deposition occurs with a high over potential. It has been established that all possible Te(III) complexes, $(TeCl_5)^{2-}$, $(TeCl_4)^{-}$ and $(TeCl_3)$, are unstable and the intermediate Te(III) product is a thermodynamic barrier for the electrodeposition of Te (0) from $(TeCl_6)^{2-}$.

The authors of the work (14) proposed to carry out electrodeposition of germanium-antimony telluride (GST) alloys from a non-aqueous galvanic bath. The system provides an example of plating bath optimization for the production of complex functional materials. The GST deposits were amorphous, and the composition and morphology of the films could be easily controlled by varying the concentrations of all three alloy components and the electrodeposition potential. Adjusting the concentrations of precursors allows you to obtain both double deposits (GeSb, GeTe, Sb_2Te_3), and ternary deposits with a wide range of compositions, including the standard composition $Ge_2Sb_2Te_5$, better known as GST-225, which in its solid state is widely used in the memory industry. The process of electrochemical deposition of tellurium was studied from acid sulfate electrolytes (15). Preliminary studies of applied voltammetric and microgravimetric measurements. Electrodeposition of tellurium was carried out in potentiostatic mode and it has been found that at 25°C, tellurium deposition at a potential above -0.1 on a silver chloride electrode (Ag/AgCl) does not occur. The deposition process is observed in the potential range from -0.1 to -0.3 V. Availability of tellurium has been confirmed by X-ray diffraction (XRF) and X-ray diffraction (XRD) analyses. The deposits obtained at a potential of -0.3 V were homogeneous and compact, but the efficiency of tellurium deposition decreased due to the reduction of Te to H_2Te and the evolution of hydrogen (15). The authors of (16) studied the reduction of tellurium in solutions of $TeCl_4$ in dimethyl sulfoxide and found that cathodic deposition of tellurium occurs with noticeable polarization. Wherein, smooth and shiny coatings have been deposited on a graphite substrate in dimethyl sulfoxide, and tellurium was deposited in acetonitrile in the form of velvety deposits. In dimethyl sulfoxide solutions of $TeCl_4$ uniform electrochemical dissolution of tellurium occurs without the accumulation of dissolution products on the surface. This allows the use of soluble anodes for the deposition of tellurium films in low light conditions.

The effect of gelatin as an additive on the electrodeposition process of tellurium (Te) has been studied using linear scan voltammogram (LSV) and electrochemical impedance spectroscopy (EIS) in alkaline electrolyte (NaOH) (17). It has been found that deposition, corrosion and recrystallization occur almost simultaneously during the Te electrodeposition process, resulting in a porous structure of the deposition products. The introduction of gelatin into the electrolyte helped improve the corrosion resistance of the indicator, check the lamp current and reduce the bath potential at the same current density.

In work (18), a systematic electrochemical study of the reduction of tellurium (Te) in alkaline solutions was carried out. Tafel slopes for the two recovery reactions of Te^{4+} to Te^0 and Te^0 to Te^{-I} showed that the electrochemical recovery of Te is independent of the $TeO^{2-}{}_3$ concentration and is highly dependent on the pH of the solution. It has been established that in relatively weak alkaline solutions (pH ≤ 12.5), the $Te(OH)^+{}_3$ discharge is the stage that limits the rate of reduction of Te(IV) to Te (0). Depositions Te (0) have been found either on the electrode surface or in solution, depending on the pH of the electrolyte, which is the main parameter determining the morphology of the deposited Te^0 films in an alkaline medium.

The electroreduction of $TeCl_4$ containing eutectic molten salt LiCl-KCl at 450 °C using tungsten and glassy carbon as working electrodes was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The reduction of Te(IV) to Te (0) occurred in three stages at potentials negative than -0.4 V across the Ag/AgCl electrode, and the reduction of Te(0) to Te^{2-} occurred at potentials more negative than -2.2 V. The diffusion coefficients of Te^{4+}, Te^{2+} and Te^{2-} were determined, the value of which decreased with increasing concentration of $TeCl_4$ in the electrolyte (19).

To study the kinetics and mechanism of electro recovery of tellurium from anhydrous N-N dimethylformamide, linear and cyclic polarization curves of tellurium were recorded depending on its concentration in the electrolyte, the speed of potential sweep and temperature, as well as polarization curves on a rotating disk platinum electrode at different speeds of rotation of the electrode.

Experimental technique

During research, tellurium oxide (TeO_2) has been first dissolved in a few drops of HCl, due to its poor solubility in the main electrolyte, then it has been input into N-N dimethylformamide while heating. IVIUMSTAT Electrochemical Interface. This made it possible to determine the potential region at which tellurium ions are reduced and to study the mechanism of the deposition process itself. Polarization studies were carried out in a three-electrode electrolyzer, the working electrode was platinum, the surface was 2 mm^2, the auxiliary electrode was platinum, the surface was 4 cm^2, the reference electrode was a silver-silver chloride electrode, and all potential values given in the article are indicated in relation to this electrode. The concentration of tellurium when studying its effect on the deposition process was changed from 0.002 to 0.005 M. When studying the effect of temperature on the process of reduction of tellurium ions, the electrolyte temperature was changed in the range of 333÷373 K, the electrolyte temperature during the electrolysis process was maintained using an ultra-universal thermostat UTU-4. The choice of this temperature range is determined by the choice of electrolyte; at low temperatures in N-N dimethylformamide, which has a high viscosity, the diffusion of tellurium ions is quite low, which significantly slows down the electro recovery. Polarization curves were also recorded on a rotating platinum disk electrode with a diameter of 0.05dm and an area of $8 \cdot 10^{-3}$ dm^2.

Experimental part

The standard potential of tellurium is +0.551 V. As stated above, anhydrous N-N dimethylformamide has been chosen for co-deposition of cadmium with tellurium, since electrodeposition from non-aqueous solvents can solve the problems of both solvent viscosity and hydrogen evolution. After TeO_2 has been dissolved in HCl, it was introduced into N-N dimethylformamide; in addition, H_3BO_3 has been introduced into the electrolyte as an additive to increase the conductivity of the electrolyte and as a complexing agent. The influence of three factors on the electrodeposition of tellurium has been studied: TeO_2 concentration, potential sweep rate, and electrolyte temperature. Studying the influence of these factors contributes to a better understanding of the kinetics and mechanism of metal deposition.

After immersing a platinum electrode in an N-N dimethylformamide electrolyte, its stationary potential is established quite quickly and is approximately 0.64 V, and with increasing tellurium content in the electrolyte, its stationary potential remains almost unchanged.

The general view of the polarization curve for the recovery of tellurium ions in the potential range from +0.4 V to -0.8 V is shown in Figure 1. Three sections appear on the polarization curve of tellurium deposition. From +0.25V to +0.00V (first section), tellurium ions are reduced, the current density reaches a maximum and at these potentials smooth, shiny tellurium coatings are deposited with a current efficiency of almost 100%. In the second section (from 0.2V to -0.52V), a limiting current appears, the value of which does not change until hydrogen is released.

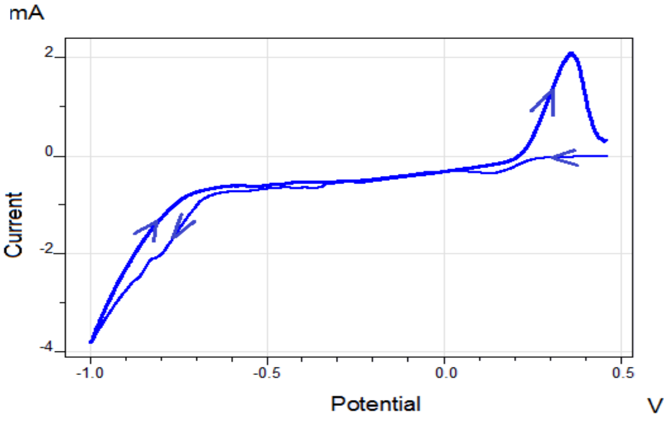

Fig.1. *Cyclic current-voltage curve of the recovery of tellurium ions in N-N dimethylformamide. Electrolyte composition (M): 0.004M* TeO_2*; 0.1* H_3BO_3*;* C_3H_7NO*; v =0.02 V/sec, pH 2; T= 363K.*

In this case, a black, powdery tellurium deposit forms on the surface of the electrode. When i_p is reached, the number of surface ions in the near-electrode space decreases, which leads to a shift in the electrode potential to the negative side, reaching a value at which hydrogen evolution occurs. Starting from a potential of -0.52 V, hydrogen ions are released on the electrode surface with the formation of H_2Te according to the reaction (20):

$$Te + H_2 = H_2Te \quad (1)$$

The formation of H_2Te on the surface of the electrode blocks its surface. At potentials -0.65V÷ -1.0V (section 3) hydrogen evolution occurs. On the anodic component of the general tellurium reduction curve, at a potential of +0.2V to +0.45V, anodic dissolution of tellurium occurs. The large difference between the potentials of cathodic reduction and anodic oxidation of tellurium ions indicates that the tellurium deposition reaction is an irreversible process.

To study the effect of the concentration of tellurium ions, solutions with TeO_2 content from 0.002 M to 0.005 M have been tested. Carrying out research at such low tellurium concentrations is due to the poor solubility of TeO_2 in C_3H_7NO.

Figure 2 shows the polarization curves of tellurium ion reduction depending on the TeO_2 concentration in the electrolyte. It is clear from the curves that with increasing TeO_2 concentration, the rate of tellurium release at the cathode increases, and the potential for its release slightly shifts towards positive values. In the range of concentrations under study, the cathodic process is characterized by the appearance of a current peak (i_p), the magnitude of which increases with increasing TeO_2 concentration in the electrolyte.

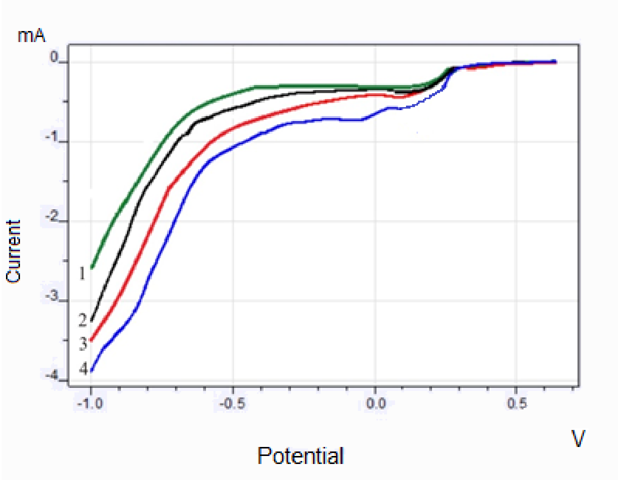

Fig.2. *Polarization curves of tellurium reduction on Pt electrode depending on the concentration of* TeO_2 *in the electrolyte 0.1* H_3BO_3*;* C_3H_7NO*;* $CTeO_2$ *(M): 1-0.002; 2-0.003; 3-0.004; 4-0.005;* v=0.02 V/sec, pH= 2; T= 363K.

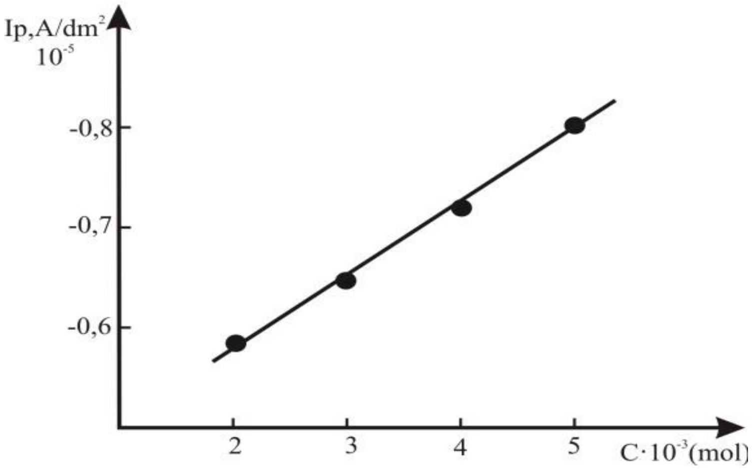

Fig.3. *Dependence of the peak current from the concentration of TeO_2 on the electrolyte*

The relationship between the current peak and tellurium concentration in the TeO_2 concentration range from 0.002M to 0.004M is linear (Fig. 3). This suggests that in this concentration range the process of reduction of tellurium ions is controlled by the diffusion of its ions, and the nature of tellurium-containing ions participating in the deposition process does not change (18).

The potential range from -0.2V to -0.5V is the region of the limiting tellurium deposition. The influence of the potential sweep rate on the process of tellurium ion reduction has been also studied. The influence of the potential sweep speed on the nature of the polarization curves is presented in Figure 4. During these studies, the sweep speed varied from 0.01 V/sec to 0.06 V/sec. It can be seen from the figure that increasing the potential sweep rate leads to an acceleration of the flow of deposited ions to the cathode and the value of the tellurium deposition current peak increases. The i_p – v dependence is linear (Fig. 5), which also indicates the diffusion kinetics of tellurium deposition in N-N dimethylformamide.

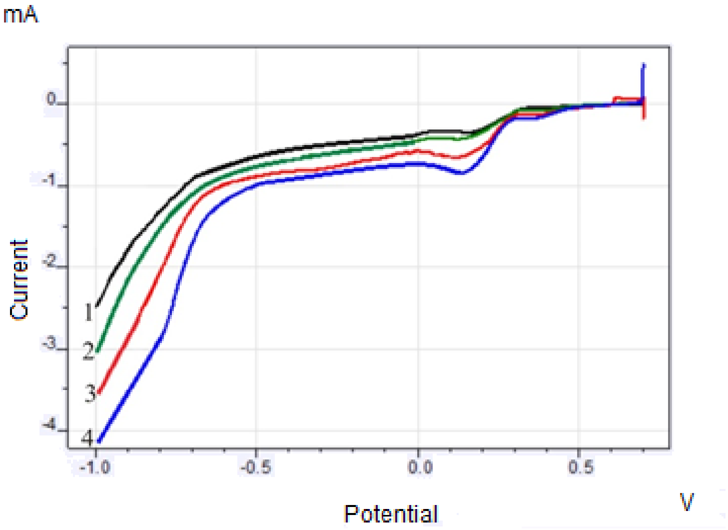

Fig.4. *Polarization curves for the recovery of tellurium ions from N, N-dimethylformamide at different potential sweep rates. Electrolyte composition (M): 0.004 TeO_2+ 0.8 H_3BO_3 +C_3H_7NO; pH=2, v (V/sec): 1-0.01, 2-0.02, 3-0.04, 4-0.06.*

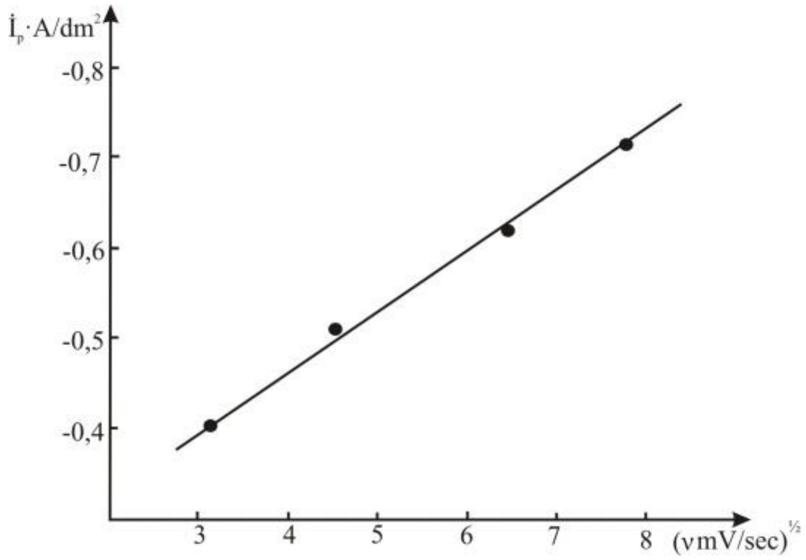

Fig.5. *Dependence of the current peak i_p on the potential sweep rate*

In addition, the effect of temperature on the process of reduction of tellurium ions in N-N dimethylformamide has been studied (Fig. 6), while the electrolyte temperature varied within 333 K÷373 K.

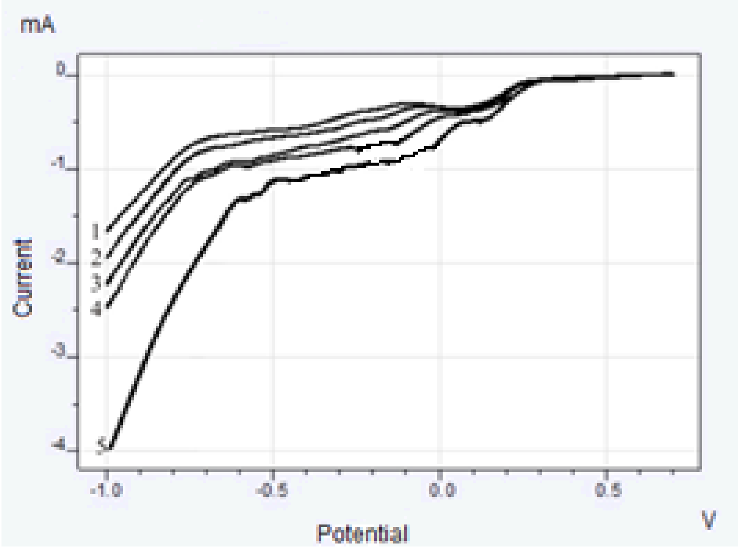

Fig.6. *Polarization curves of tellurium ion reduction as the function of temperature. Electrolyte composition (M): 0.004 TeO2, 0.8 H_3BO_3, C_3H_7NO; pH=2, v=0.02 V/sec; T (K) -1- 333; 2-343; 3-353; 4-363; 5-373;*

An increase in the temperature of the electrolyte increases the rate of tellurium deposition and the deposition potential shifts in the positive direction, which is due to the fact that the rate of deposition of tellurium ions is limited by their diffusion, and an increase in the electrolyte temperature accelerates the process of diffusion of tellurium ions to the cathode.

To verify this conclusion, the effect of forced convection on the rate of the electrode process was studied at a constant value of cathodic polarization. Figure 7 shows tellurium deposition curves taken on a rotating platinum electrode depending on its rotation speed at a tellurium concentration in the electrolyte of 0.006 M.

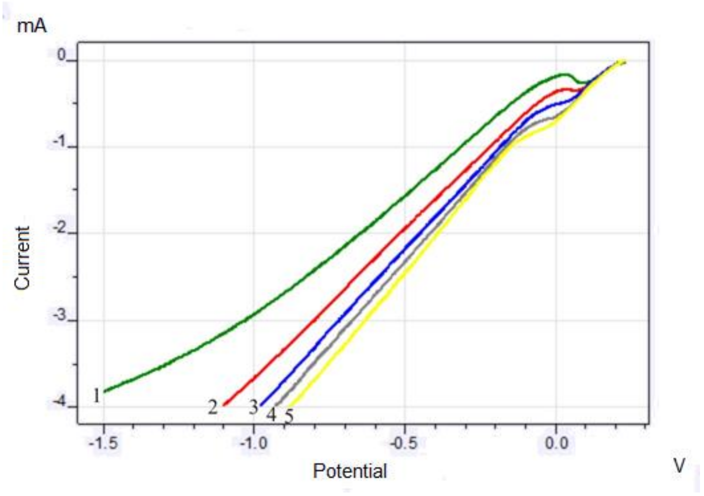

Fig.7. *Polarization curves for the reduction of tellurium ions on the rotating platinum electrode Electrolyte composition (M): 0.006 TeO_2, C_3H_7NO, 0.8 H_3BO_3; pH=2; v = 0.02V/sec, T =353 K; v (rpm): 1-500; 2-1000; 3- 2000; 4- 3000; 5-4000.*

The rotation speed of the disk electrode varied from 500 rpm to 4000 rpm. From the data shown in the figure it is clear that increasing the intensity of stirring helps to increase the rate of the cathodic process. Based on the data in Figure 7, the dependence i_p -$\sqrt{v}$ has been constructed (Figure 8), from which it can be seen that the dependence of i_p on the rotation speed of the disk electrode to the power of 0.5 is linear. This dependence of the current peak on the rotation speed of the disk electrode is characteristic of processes controlled by the diffusion of ions of the deposited element to the cathode (21).

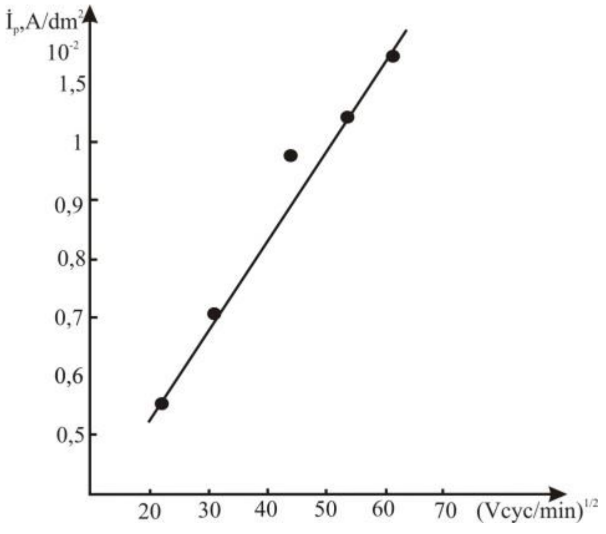

Fig.8. *Dependence of the maximum current value on the square root of the rotation speed of the disk electrode.*

Thus, the process of electrodeposition of tellurium ions from N-N dimethylformamide is characterized by the appearance of a limiting current in voltammograms and is limited by the diffusion of its ions, which has been confirmed by all studies performed.

Conclusions

By recording cyclic and linear polarization curves of tellurium in N-N dimethylformamide, the region of potentials at which deposition of tellurium coatings occurs, as well as the region of the limiting current of tellurium deposition, was established. The influence of such factors on the reduction of tellurium ions as their concentration in the electrolyte, the rate of potential sweep and the temperature of the electrolyte has been studied. Based on the data obtained, it has been concluded that the deposition process is controlled by the diffusion of tellurium ions to the electrode surface. By taking polarization curves on a rotating disk electrode, the dependence i_p -√ν, which has a rectilinear character, confirmed the conclusion about the diffusion nature of polarization during the deposition of tellurium ions from N-N dimethylformamide.

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XÜLASƏ

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SUSUZ N-N DİMETİLFORMAMİD ELEKTROLİTİNDƏN TELLUR İONLARININ ELEKTROREDUKSİYASI

Məqalədə susuz N-N dimetilformamiddən tellur ionlarının reduksiyası mexanizmi öyrənilmişdir. Bu məqsədlə xətti və tsiklik volamperometrik polyarizasiya əyriləri çəkilmişdir. Elektrolitdə tellur ionlarının qatılığının, potensialın dəyişmə sürətinin və temperaturun tellur ionlarının çökmə prosesinə təsiri tədqiq edilmişdir. Tsiklik polyarizasiya əyrisini çəkməklə, tellur ionlarının çökmə və anodda həllolma prosesinin baş verdiyi potensial sahə müəyyən edilmişdir. Müəyyən edilmişdir ki, tellur ionlarının qatılığının və temperaturun artması tellurun reduksiya prosesinin sürəti artır və reduksiya prosesinin özü tellur ionlarının katod səthinə diffuziyası ilə müşahidə olunur. Əldə edilmiş məlumatları təsdiqləmək üçün fırlanan platin disk elektrodunda polarizasiya əyriləri çəkilmişdir. Alınan məlumatlar, yəni ip-nin elektrodun fırlanma sürətindən (ω) $\nu^{2/1}$ xətti asılılığı susuz N-N dimetilformamiddə tellur elektrodlarının reduksiya prosesinin diffuziya xarakteri daşıdığını təsdiqləyir.

Açar sözlər: *Elektroreduksiya, tellur, diffuziya, polyarizasiya, susuz elektrolitlər, fırlanan disk elektrodu*