

Cathodic reduction of Te(IV) on the glassy carbon electrode in hydrochloric acid media

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Astract

The process of electroreduction of Te(IV) on the glassy carbon electrode in hydrochloric acid media was considered. The effect of potential sweep rate, the concentration of Te(IV) ions and the temperature of the electrolyte were studied. It is shown that in hydrochloric acid solutions Te (IV) exhibits electrochemical activity only in the cathodic potential region. It is found that the state of tellurium ions strongly depends on the solution composition.

Key words: TELLURIUM (IV), ELECTROREDUCTION PROCESS, GLASSY CARBON ELECTRODE, TELLURIUM TETRACHLORIDE, POLARIZATION CURVE

Introduction

During electrolysis of acidic tellurium-containing solutions depending on the electrolysis conditions and the composition of the electrolyte at the cathode the coarse crystalline or close grained tellurium sediments are formed. Cathode sediments are spongy sometimes. Sponge sediments are formed mainly during electrolysis of hydrochloric acid tellurium solutions. As part of the spongy tellurium sediments TeO_2 is found, the formation of which is connected with the hydrolytic decomposition of tellurium chloride in the near-electrode layers.

From the acidic solutions for the electrolytic deposition of tellurium the best electrolytes are solutions of hydrochloric acid. The high positive value of the system potential Te/Te^{4+} in hydrochloric acid solutions and good solubility of TeO_2 and TeCl_4 in hydrochloric acid solutions are very favorable for the electroevolution of pure tellurium. Electrochemical behavior of tellurium in acid solutions was investigated in [1-4].

Experimental technique

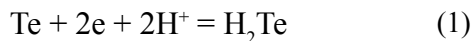
To study the electrochemical behavior of tetravalent tellurium in aqueous media registration method of potentiodynamic polarization curves on potentiostat IPC Pro MF was applied. Voltammetric measurements were performed in a thermostated three-electrode cell with separate anode and cathode spaces. As the working electrode front part of glassy carbon electrode with diameter of 2.1mm was used. The measurements were carried out with respect to silver-chloride reference electrode in saturated KCl ($E=+203$ mV). As a counter electrode a platinum wire with a large surface was used.

Results and discussion

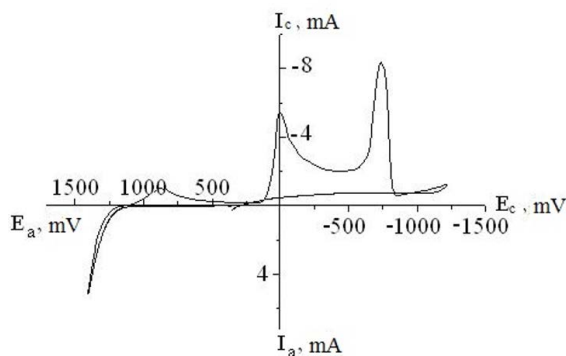
We filmed cyclic anode-cathode, cathode- anode polarization curves in the hydrochloric acid solution of tetrachloride tellurium.

In accordance with Figure 1 on the anode-cathode cyclic potentiodynamic polarization curve with the potential sweep in the anodic direction the tetravalent tellurium shows no electrochemical activity and only

the anode current of chlorine evolution is observed on this section of the curve. When the bias of potential in the cathodic direction the wave of chlorine depolarization is seen and then at the potential of 10 mV another peak of the cathode current is observed corresponding to the reduction of Te (IV) to the elemental state. At further displacement of the potential another cathode peak when the potential of -750 mV is observed, then there is a sudden drop in current. In this area of potentials there is dissolution of the elemental tellurium with formation of hydrogen telluride according to the reaction [1]:



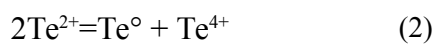
In composition of all tellurium sediments chlorine remains in the form of TeCl_2 — as a mechanical impurity [5]. Increasing the acidity of the solution, the presence in the electrolyte of alkali metal chlorides and increasing of current density lead to an increase in the content of TeCl_2 .



$V=100 \text{ mV/s}$, $t=25 \text{ }^\circ\text{C}$, $\text{HCl}=1\text{M}$, $\text{TeCl}_4=0.16\text{M}$

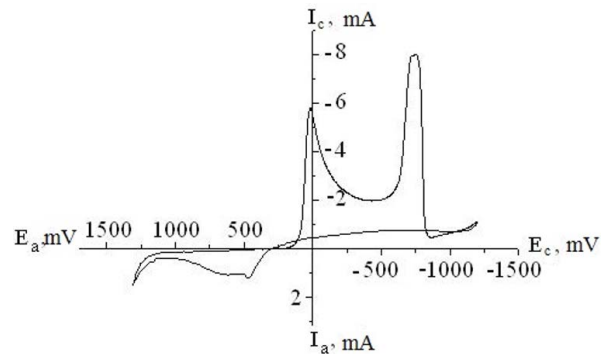
Figure 1. Anode-cathode cyclic polarization curve

Occurrence of TeCl_2 is associated with staging of ions reduction of Te^{4+} , trough Te^{2+} . Part of Te^{2+} ions in the near-electrodes layers react with ions Cl^- , forming TeCl_2 , which is precipitated on the cathode surface along with freshly precipitated layers of elemental tellurium. Another part of Te^{2+} ions undergoes further electrochemical conversion and disproportioning:



In accordance with Figure 2 on the cathode-anode cyclic potentiodynamic polarization curve with the sweep potential to negative values two cathode peaks are also observed. By offsetting the potential in the anode direction when a potential of 460 mV the anodic wave is observed apparently associated with the oxidation of elemental tellurium. According to Figure 3, if cathodic polarization is carried out only to the first peak and then potential is reversed in the opposite direction, the value of the subsequent anode peak

is much greater than in the previous case. This explanation confirms the nature of all three current peaks, since when no reaction takes place (1) and there is no demand of reduced tellurium the subsequent anode peak has a higher value.

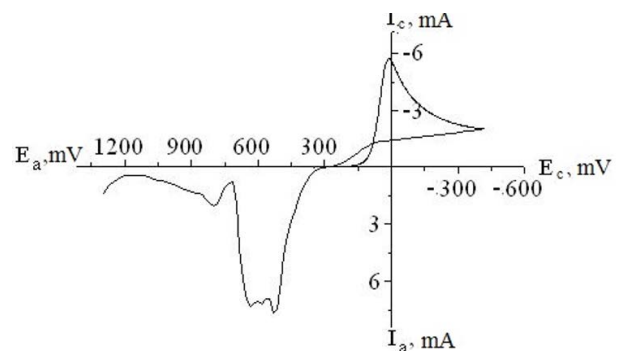


$V=100 \text{ mV/s}$, $t=25 \text{ }^\circ\text{C}$, $\text{HCl}=1\text{M}$, $\text{TeCl}_4=0.16\text{M}$

Figure 2. Cathode-anode cyclic polarization curve

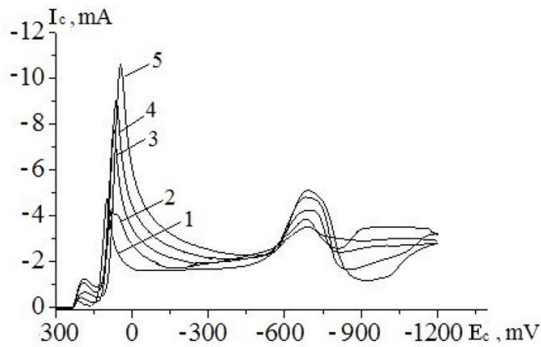
Then, the effect of potential sweep rate on the process of cathode reduction of Te(IV) was studied. The process has been conducted on the background of 7M hydrochloric acid, since its lack the tetravalent tellurium react to the form of tellurous acid which is precipitated. In accordance with Figure 4, when an excess of hydrochloric acid on the curve another cathode peak appears.

Polarograms of tetravalent tellurium were first received by authors of [6]. Depending on the acidity of the medium they observed from one to three waves which were attributed to staged reduction of Te(IV) to Te(II) , Te and Te^{2-} . However, the authors [7] have noted that the ratio of the waves-heights is of random nature and depends on the experimental conditions. The appearance of several waves, in their opinion, may be due to the presence in solution of Te(IV) particles of different composition.



$V=100 \text{ mV/s}$, $t=25 \text{ }^\circ\text{C}$, $\text{HCl}=1\text{M}$, $\text{TeCl}_4=0.16\text{M}$

Figure 3. Cathode-anode cyclic polarization curve



$t=25$ 0C, HCl=7M, TeCl₄=0,16M, V, mB/c: 1 – 25; 2 – 50; 3 – 100; 4 – 150; 5 – 200;

Figure 4. Cathode polarization curves when different rates of potential sweep

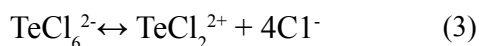
On the cathode polarization curves measured with the help of Te-electrode in hydrochloric acid solutions of tetravalent tellurium the maximum current is occurred, which increases with rising the tellurium concentration in the electrolyte, temperature and stirring rate. When HCl concentration of 2.5-5M the value of maximum current changes linearly with the concentration of tellurium in the electrolyte [8]. In this acidity range tellurium is in solution as complexion $TeCl_6^{2-}$.

With decreasing acidity of the electrolyte chlorine in the complexion is gradually replaced by H_2O or OH^- , telluride acid is precipitated and the concentration of ions Te^{4+} decreases in the solution.

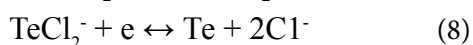
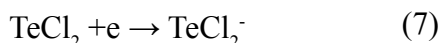
With the increase in sweep rate growth of both current peaks is occurred. The angular coefficients of the dependence lgI_p / lgV amounted to 0.65 and 0.95 for the first and second peak respectively. Overestimated values may be due to the development of the surface by reduction of tellurium, because at this acidity coarse-grained sediments should be formed.

Comparison of the results of polarization measurements with direct ion detection of Te^{2+} allows assuming the cathode deposition and anodic dissolution of tellurium from hydrochloric acid of electrolytes proceeds by stages.

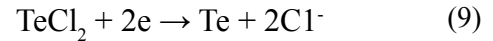
The most likely process scheme can be represented as follows [9]:



or



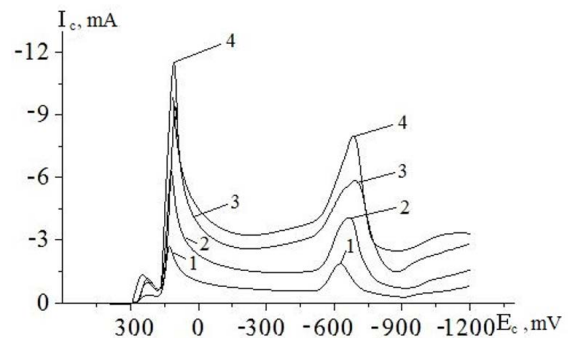
or



The effect of the Te (IV) concentration on the process of reduction has been studied. In accordance with Figure 5 with increasing the concentration of tetravalent tellurium growth of both cathode peaks takes place.

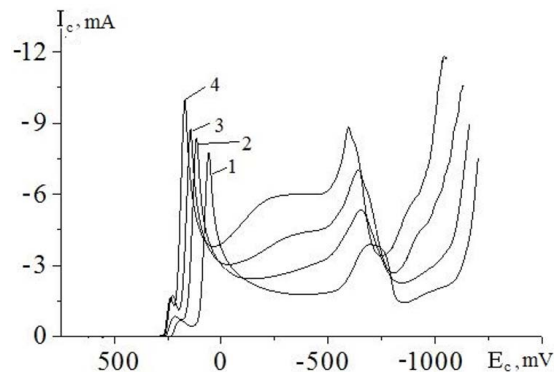
The effect of temperature on the course of the cathode curves has been studied. In accordance with Figure 6, as the temperature rises there is an increase of both peaks with simultaneous offset of the maximum potentials in the positive potentials direction indicating the cathode processes lightening.

Changing the electrolyte temperature significantly affects the mechanism of cathode deposition of tellurium and sediments nature. Fine grained gray sediment is precipitated at the cathode when 25-50°C and current densities of 10-15 mA/sm². When 75-90°C and current densities of 20 mA/sm² coarse sediments of dark gray color are precipitated, the current yield calculated using Te^{4+} is decreased from 99 when 25°C to 89% when — 90°C [5].



$t=25$ 0C, HCl=7M, V=100 mV/s, TeCl₄, M: 1 – 0.08; 2 – 0.16; 3 – 0.24; 4 – 0.32;

Figure 5. The cathode potentiodynamic polarization curves when different concentrations of tellurium



HCl=7M, V=100 mV/s, TeCl₄=0.16M, t, 0C: 1 – 20; 2 – 30; 3 – 40; 4 – 50;

Figure 6. The effect of temperature on the process of electroreduction of Te (IV)

Conclusion

Thus, in hydrochloric acid solutions Te (IV) shows electrochemical activity only in the cathodic potential region. It is found that the state of tellurium ions strongly depends on the solution composition. The hydrolysis with formation of insoluble tellurous acid is observed in weak acidic solution, and in strong hydrochloric acid solutions the tetravalent tellurium ion is stable and exists in the form of several complex compounds as evidenced by an additional cathode peak. In general, when cathode polarization tellurium is reduced by stages at the potential of 10 mV followed by formation of hydrogen telluride in the potential range of -750 mV, resulting in a further decrease of the maximum anode oxidation of elemental tellurium.

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