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Electroreduction of Cu (II) and Se (IV) ions on Vitreous Carbon Electrode

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Abstract

The electroreduction of copper (II) and selenium (IV) ions on vitreous carbon electrode from sulfate electrolyte has been studied. The studies have shown that during the concurrent reduction copper is first reduced within 0.15-0.05 V range of potentials. In this range of potentials the cementation reaction to form selenium compounds with copper is possible. Qualitative characteristics of Cu_2Se compound have been obtained at –0.3 V potential. The composition has been confirmed by XPA and electron-probe analysis.

Introduction

The electrochemical reactions of Cu(II) and Se (IV) ions and their co-deposition during cathode reduction are decisive in the processes of formation of thin films of CuSe, Cu_2Se, Cu_2Se_3, $CuInSe_2$, and $CuInGaSe_2$ semiconductor compounds by electrodeposition on various electrodes. The electrochemical behavior of Cu(II) ions in various electrolytes has been studied in many works [1-4]. However, such processes over vitreous carbon electrodes for Se(IV) have not been studied well enough [5].

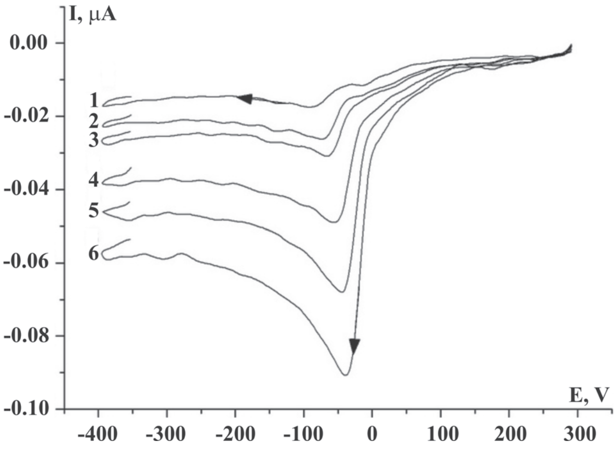
This work is aimed at determining the mechanism of Cu(II) and Se(IV) reduction in sulfate electrolytes and performing concurrent elecrodeposition.

Experimental

A vitreous carbon electrode, $S = 0.07$ cm^2 and an auxiliary platinum electrode, 1.5 cm^2 in a standard three-electrode cell were used as a working electrode. Silver-chlorine reference electrode was used. The working electrode was polished before each test with Al_2O_3 powder and rinsed with water. The studies were performed at a room temperature using a universal Volta IPC-PRO potentiostat-galvanostat with electronic data processing. The scan rate was $V = 20$ mV·s^{-1}. The electrolytes were prepared on the basis of 0.05 M H_2SO_4 + 0.45 M $CuSO_4·5H_2O$, and $NaHSeO_3$ salts of analytical grade were used.

Results

The voltammograms of Cu(II) reduction in sulfate electrolyte at +0.3 V to –0.4 V potential scan and $1·10^{-3}$ to $1·10^{-2}$M concentration of copper ions are shown in Fig. 1.



$C_{Cu(II)}$: $1 – 1·10^{-3}$, $2 – 2·10^{-3}$, $3 – 2.5·10^{-3}$, $4 - 5·10^{-3}$, $7·10^{-3}$, $1·10^{-2}$M

Fig. 1. Linear sweep voltammograms of Cu(II) (Cathode branch).

One cathode peak of Cu(II) reduction has been noted.

$$Cu(II) + 2e = Cu^0 \quad (1)$$

The relationship between the peak current maximum and Cu(II) ion concentration is straight-line (Fig. 2).

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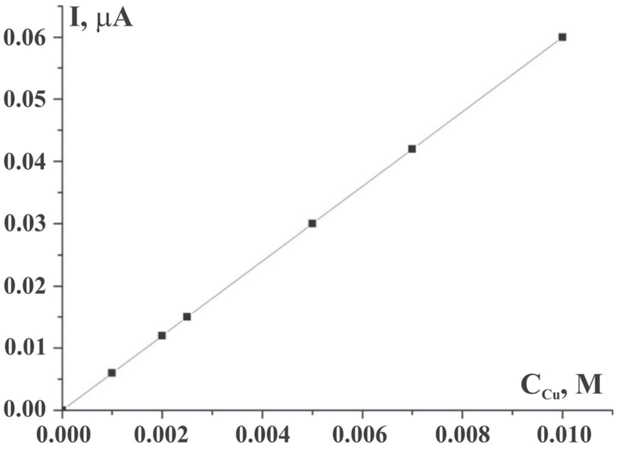

Fig. 2. Relationship between peak current maximum and Cu(II) ion concentration.

The voltammograms of Se(IV) ion reduction from sulfate electrolytes on a vitreous carbon electrode show the reduction to proceed in two stages. The first stage begins at ~ +0.2 V potential and conforms to the reduction by equation (2)

$$Se(IV) + 4e = Se^0 \quad (3)$$

$$Se^0 + 2e = Se^{-2} \quad (2)$$

The second stage at –0.42 V potential is shown as a recovery current peak related to the process of further reduction of selenium to selenide ion by reaction (3).

The anode branch of voltammogram shows the emergence of the oxidation peak of elemental selenium deposited on the electrode.

According to Fig. 3a, an increase in the concentration of Se(IV) and potential scan to –0.5 V, *i.e.* before the beginning of the second reduction stage, causes an increase in the oxidation peak indicating an increase in the amount of selenium deposited on the electrode. In case the reduction is performed to more negative potentials when a considerable amount of electrodeposited selenium is reduced to selenide ion (Fig. 3b), the selenium oxidation peak considerably decreases.

The analysis of voltammograms recorded with variation of potentials allows one to make conclusions regarding the processes occurring on the electrode during the concurrent reduction of copper and selenium ions.

In case of simultaneous presence of Se(IV) and Cu(II) ions in the sulfate electrolyte the cathode reduction causes the formation of their compounds on the electrode. To determine the range of potentials and concentration ratio in the electrolyte to obtain compounds with the specified stoichiometry is an important task.

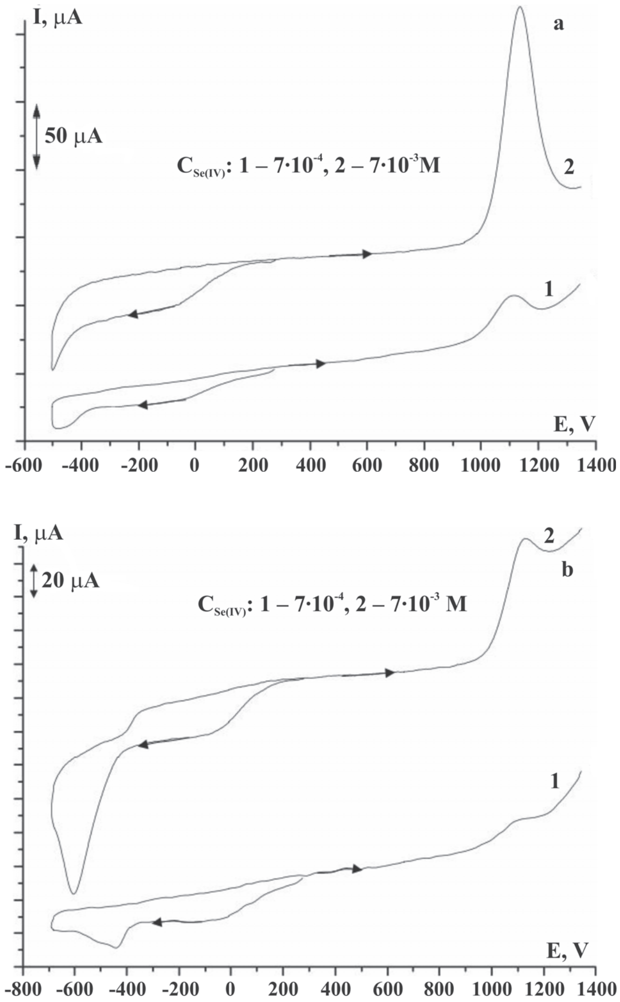

Fig. 3. Linear sweep voltammograms of Se(IV). Potential scan: *a* – from +0.3 to –0.5 V; *b* – from +0.3 to –0.7 V.

Figure 4 shows cathode and anode branches of voltammograms for the concurrent reduction of Cu (II) and Se(IV) ions from sulfate electrolyte when the concentration of Cu(II) ions remains unchanged. In the presence of excess Se(IV) ions in the electrolyte the peak of *A* potential (E_A) shifts to positive values compared to the reduction of Cu(II) ions (Fig. 1). This peak current does not virtually depend on Se(IV) concentration. On further sweep of potential a wave (*B*) of selenium (IV) ion reduction and at –0.42 potential a typical peak of Se^0 to Se^{-2} reduction appear.

Earlier [6] it was shown that the current peak is related to the selenium reduction bound in a compound with copper and to the isolation of hydrogen selenide. Two oxidation peaks appear on the anode branch of voltammogram: peak *D* relating to the cop-

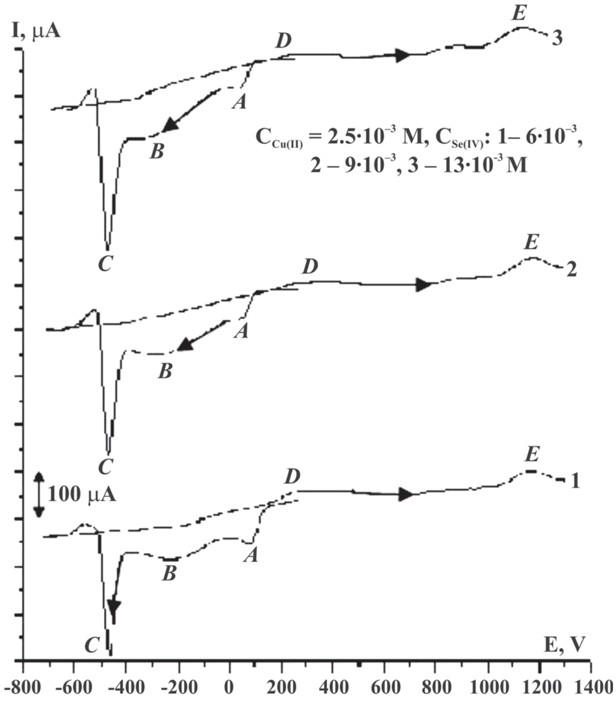

Fig. 4. Linear sweep voltammograms of Se(IV) and Cu(II) (direct and reverse).

per oxidation from the compound and peak *E* conforming to the oxidation of selenium remaining on the electrode.

To elucidate the role of each potential range in the process of compound formation, cathode branches of voltammograms in +0.3 to –0.4 V range of potentials have been studied (Fig. 5).

From Figire 5 it follows that in this range of potentials the first two reduction stages depend on the ratio of copper and selenium ion concentration. An increase in the concentration of selenium ions causes a slight shift of potential of the first reduction peak to negative values. However, the reduction current remains unchanged indicating that the selenium ions are not involved in the reduction in this range of potentials. From –0.05 V and more negative potentials the current of the next reduction stage, on the contrary, depends strongly on the selenium ion concentration. Its increase is accompanied by an increase in the current, and at five-fold excess of selenium ions compared to copper ions the peak B reduction potential shifts to more negative values.

The variation of peak *B* maximum current as a function of Se(IV) ion concentration has been analyzed (Fig. 6). The proportional growth of this current indicates the reduction of Se(IV) in this range of potentials.

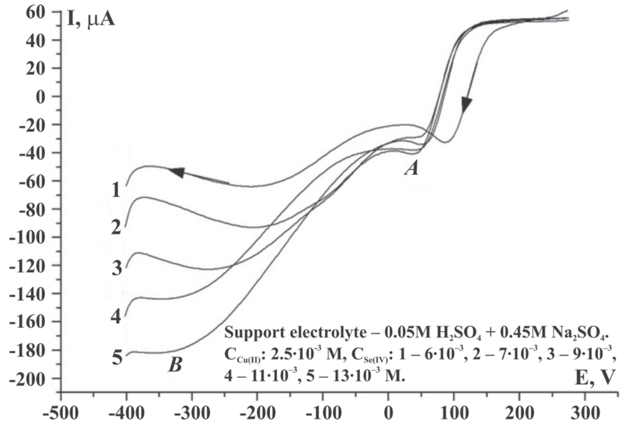

Fig. 5. Cathode branch of voltammograms of Cu(II) and Se(IV).

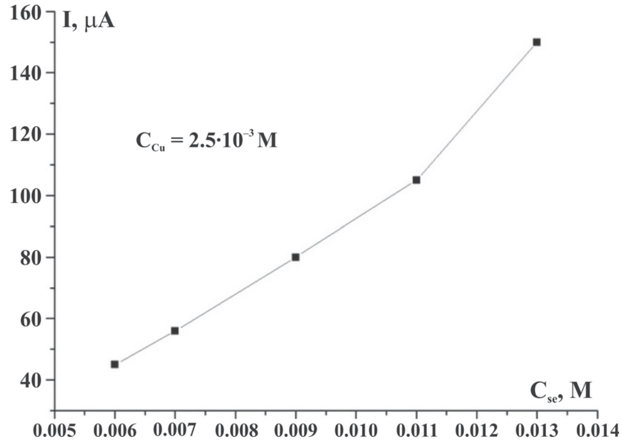

Fig 6. The relationship between peak *B* current reduction and Se(IV) concentration.

For more detailed study of the processes of electrochemical reduction of ions in the first reduction stage in the range of positive potentials, the tests on Cu(II) and Se(IV) reduction in +0.3 V to +0.05 V range have been performed. Under these conditions, the concentration of Se(IV) remains unchanged and equal to $1 \cdot 10^{-3}$M, and the concentration of Cu(II) varies from $5 \cdot 10^{-4}$ to $4 \cdot 10^{-3}$. After the potential sweep to +0.05 V, the accumulation of deposit during 5s at this potential has been carried out. The reverse potential sweep from 0.05 to +1.3 V has made it possible to determine the current oxidation products forming on the electrode (Fig. 7).

In Figure 7 it can be seen that on the anode branch of voltammogram the oxidation peak *D* in +0.2÷0.25 V range of potentials and peak *E* of oxidation current at +1050÷1100 V appear, similar to Fig. 5. The first peak (*D*) relates to the oxidation of copper from the compound with selenium, and the second (*E*) is typical for the oxidation of elementary selenium remaining on the electrode.

$$CuSe_x - 2e = xSe^0 + Cu(II) \qquad (4)$$

$$Se^0 - 4e = Se(IV) \qquad (5)$$

The emergence of Se^0 oxidation wave indicates that already at the first oxidation wave potential, at positive potential values, selenium is deposited on the electrode as a compound with copper. Since the 1-st wave current (Figs. 4,5) does not depend on Se (IV) concentration, it has been assumed that no process of electrochemical reduction of Se(IV) occurs in this range of potentials. Its presence on the electrode can be accounted for by the cementation process or inner electrolysis occurring on the electrode coated by copper. This process progresses concurrently with the basic process of copper electrodeposition.

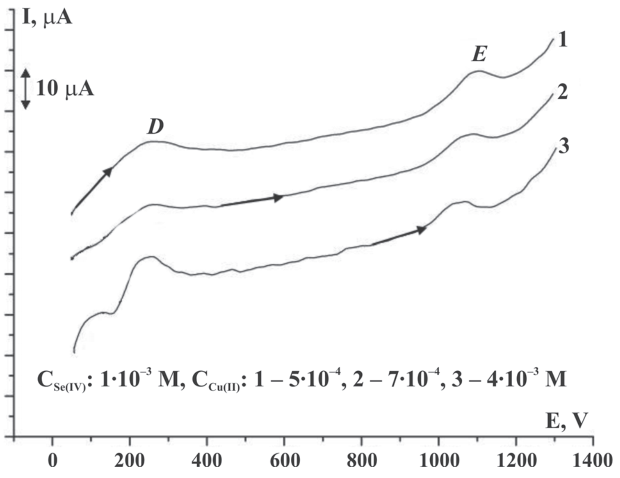

Fig. 7. Anode branch of voltammograms Cu(II) and Se(IV) after electrodeposition at +0.05 V for 5 s.

The dependence of oxidation peak currents on the concentration of components has shown the first oxidation peak (*D*) current to increase with an increase in the copper concentration. A sharp increase in the current (Fig. 8) begins after Cu(II):Se(IV) = 2:1 concentration ratio is achieved that conforms to the Cu_2Se stoichiometry. The analysis of anode oxidation peak of Se^0 allows one to note similar slow down in the current variation in the Cu(II):Se(IV) = 1:1 and 2:1 concentration ratio, and the break in the current-CCu(II) concentration relation corresponds to the stoichiometric points of CuSe and Cu_2Se compound formation.

It has been concluded that the elemental Cu deposition on the electrode is the first stage of the concurrent reduction of ions. The elemental copper enters into a cementation reaction with selenium ions in the electrolyte to form a compound by the reaction:

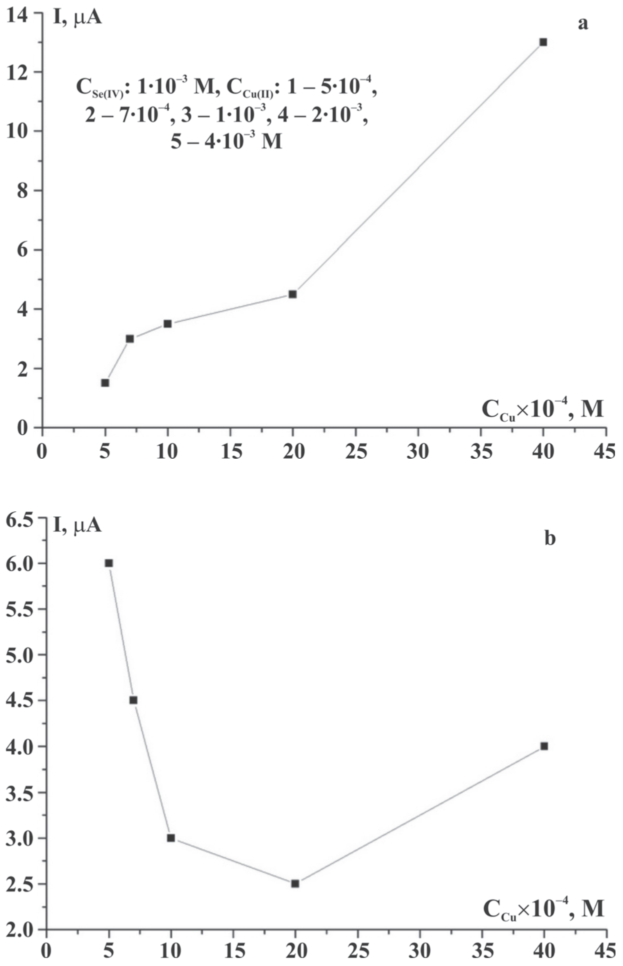

Fig. 8. Peak *D* (a) and peak *E* (b) as a function of Cu(II) concentration.

$$2Cu + SeO_3^{-2} + 6H^+ + 6e \rightarrow Cu_2Se + 3H_2O \qquad (6)$$

This process progresses at already positive potentials, +0.2÷0.05 V. The imposition of external potential and its negative shift results in the electrochemical reduction of selenium on the electrode partially coated by copper and the compound. The ratio of the rates of these two processes and ion concentrations in the electrolyte conditions the stoichiometry of the compound formed. No significant effect of possible Se(IV) and Se^{-2} reaction at the potentials more negative than –0.5 V on the anode voltammograms has been noticed.

$$Se(IV) + Se^{-2} \rightarrow Se^0 \qquad (7)$$

The electrodeposition of Cu_2Se compound on vitreous carbon substrates of 1 cm^2 surface area was performed in the controlled potential regime at two potentials: –0.3 and –0.6 V. After deposition the films were annealed for 10 minutes at 400°C in the air.

The content of components in the deposits after annealing has been determined by the electron-probe analysis to be Cu:Se = 2.6:1 in both cases. It has been noted that the films obtained by deposition at –0.30 V for 30 min have a compact structure and strong adhesion to the substrate. At –0.60 mV, in the region of Se^{-2} ion formation the deposit is very fine, and the film is thin and falls off the electrode surface.

Conclusion

The compound the phase composition of which is close to Cu_2Se has been obtained by electrodeposion on vitreous carbon electrode from sulfate electrolytes containing Cu(II) and Se(IV) ions at –0.3 V potential.

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