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FORMATION OF SELENIUM POWDER AT REDUCTION OF SELENITEIONS IN HYDROCHLORIC ACID SOLUTION ON THE SURFACE OF COPPER ANODE

Abstract. The article shows the possibility of reduction of selenite ions in the presence of copper (II) ions with the formation of dispersed selenium powders. The effect of the concentration of hydrochloric acid, copper (II) ions, the current density at the copper anode and the solution temperature on the current efficiency (CE) of the formation of selenium powder has been studied. The current efficiency of selenium powder was calculated by the weight of the powder formed. It was found that with increase in concentration of copper (II) ions and the solution temperature, the current efficiency of the formation of elemental selenium in the form of a powder increases. It was shown that at the current density below 75 A/m^2, the current efficiency of selenium powder exceeds 100%. Previous studies have shown that titanium (IV) ions cannot be used in the recovery of selenite ions. Using an electron microscope, micrographs of selenium powder were obtained. They indicate the formation of a finely dispersed selenium powder of spherical shape with an average particle size of 0.252 μm.

Key words: electrochemistry, selenium powder, selenite ion, copper (II) chloride, reduction, electrolysis, current density, hydrochloric acid.

Selenium powders have various applications, for example, 23.9% in the metallurgy of ferrous and non-ferrous metals. Thus, the presence of a small amount (0.2-0.3%) contributes to production of fine-grained structure in cast steel, freeing it from casting defects and giving good ductility. The additive of selenium to certain grades of stainless steel improves their ability to be machined. In magnesium-manganese alloys, an admixture of 0.5-3% selenium increases the corrosion resistance. Another field of application of powdered selenium is the glass and ceramic industries (25.7%). A small additive gives the glass a different beautiful color. In an elementary colloidal form, selenium stains glass (depending on the added amounts) from pink to red-orange and dark red. Glass thus painted is widely used for light signaling in the form of light filters. The composition of black glass, which has the best light absorbing properties, includes 0.6% Se and 0.1% CoC$_3$. Thus, the glass, ceramic and chemical industries, as well as electronics, have been the main consumers of selenium for a long time [1-3].

A method for producing powdered selenium, which was previously used in industry, based on the recovery of selenite ions (SeO$_3^{2-}$) is known [4]. As a reducing agent the sulfur dioxide(SO$_2$) is used, which reduces selenite ion by the reaction:

$$H_2SeO_3+2SO_2+H_2O\rightarrow Se°\downarrow+2H_2SO_4 \tag{1}$$

The disadvantage of this method is that the use of toxic sulfur dioxide in the reduction process complicates the process, since a number of problems arise during its production and storage, in addition, special sealed equipment is required that ensures maximum allowable concentration in working rooms of no more than 0.02 mg/l. In this regard, this method is not used in industry.

The most efficient are electrochemical methods for producing selenium from industrial products. In this regard, a number of scientific research is devoted to the study of the electrochemical behavior of selenium and its compounds [1, 5-15].

This paper [16] shows the possibility of producing selenium powder upon polarization by a cathodic impulse current of selenite ions (SeO_3^{2-}), in which the selenium oxidation rate is "plus four". It was shown that in a sulfuric acid solution at a cathodic current density of 100–2500 A/m^2, selenium powders with average particle sizes of 7–16 μm are formed. It was found that cathodic reduction of selenium proceeds according to the reaction:

$$SeO_3^{2+}+6H^++4e\rightarrow Se^{\circ}\downarrow+3H_2O \qquad (2)$$
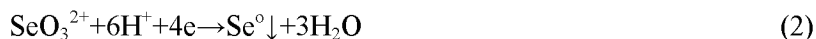
It is also shown that at high cathodic current densities, the formed selenium powders interact with atomic hydrogen and, as a consequence, there is co-formation of toxic gas - hydrogen selenide:

$$Se+2H\rightarrow\uparrow H_2Se \qquad (3)$$

We previously showed that it is possible to reduce selenate ions, in other words, anions in which selenium is in the oxidation rate of "plus six" – (SeO_4^{2-}), in the presence of Ti^{4+}ions and copper (II) [1,13,18]. The possibility of electrocatalytic reduction of selenate ions on a lead electrode was also established [17].

Our preliminary studies showed that Ti^{4+}ions cannot be used in the reduction of selenite ions, because interacting with each other, they form an insoluble compound - titanium selenite, with the approximate composition $4TiO_2SeO_3\cdot 13H_2O$ or TiO_2SeO_3, which precipitates.

The purpose of our work is to produce finely dispersed powders of selenium by reducing selenium (IV) using cuprous copper ions formed in hydrochloric acid solutions at anodic polarization.
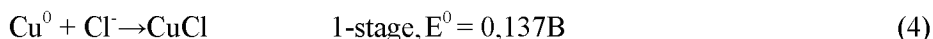
Experimental technique. The experiments were carried out in a thermostatically-controlled electrolyzer with a volume of 100 ml, the electrode spaces were separated by an MA-40 anion exchange membrane. A copper plate (99.99%) was used as the anode, and VT-1 titanium was used as the cathode. The following reagents were used: selenium (IV) oxide of chemically pure grade, copper (II) chloride – pure grade. The composition of the initial electrolyte: hydrochloric acid, copper (II) chloride and selenite ions. The effect of the concentrations of hydrochloric acid and copper (II) ions, the current density at the copper anode and the solution temperature on the current efficiency of the formation of selenium powder has been studied. The current efficiency of selenium powder was calculated by the weight of the powder formed.

Results and their discussion. We believe that if certain metals, under certain conditions (i.e., in solutions), dissolve anodically to form their lower oxidation ions, which are the reducers of selenite ions, due to the formation of a redox system with a negative potential relative to the Se(IV)-Se system, then the selenite ion should be reduced to the elemental state on the surface of this metal.
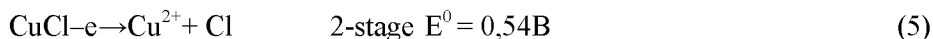
To establish the correctness of this idea, we conducted preliminary studies on the recovery of selenite ions on the surface of a copper anode in a hydrochloric acid solution. The results of the experiments clearly showed that in this case, the reduction of selenite ions on the surface of the copper anode occurs with the formation of elemental selenium in the form of a dispersed powder.

The reason for this is that the standard potential (E°) of the Cu (I) - Cu (II)redox system in the hydrochloric acid solution is -0.54 V, and the potential of the Se-Se (IV) system is 0.77 V (as is known from the reference guide [19]), i.e. the standard potential of the first system has a more negative value compared to the value of the second one. In this regard, copper ions Cu^+reduce selenite ions to form elemental selenium, while they themselves are oxidized toCu^{2+}.

In theoretical terms, the anodic oxidation of copper in a chloride solution, i.e. in a solution of sodium chloride proceeds in two stages [20]:

$$Cu^0 + Cl^-\rightarrow CuCl \qquad 1\text{-stage}, E^0 = 0,137B \qquad (4)$$

further

$$CuCl-e\rightarrow Cu^{2+}+ Cl \qquad 2\text{-stage } E^0 = 0,54B \qquad (5)$$
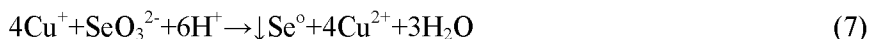
At low current densities, copper is ionized only to form copper (I) ions. Besides, in this case there is a reaction of comproportionation, i.e. a copper electrode interacts with copper (II) ions to form copper (I) chloride:

$$Cu+Cu^{2+} + 2Cl^- \rightarrow 2CuCl \tag{6}$$

Copper (I) chloride is very soluble in hydrochloric acid solution to form copper (I) ions and chlorine.

The copper (I) ions formed by the reactions (4) and (6), according to the potentials of the above redox systems Cu(I)-Cu(II) and Se-Se(IV), will instantly enter into the chemical reaction of reduction (7) on the surface of the copper anode, since the equilibrium constant (K-value) of this reaction is 10^{15} and the reaction equilibrium is strongly shifted to the right.

$$4Cu^+ + SeO_3^{2-} + 6H^+ \rightarrow \downarrow Se^o + 4Cu^{2+} + 3H_2O \tag{7}$$

It may be noted that the ions in the solution, as well as copper (II) ions formed by the reaction (7) at low cathodic current densities, are also reduced only to copper (I) by the reaction:

$$Cu^{2+} + e \rightarrow Cu^+, \tag{8}$$

The Cu^+ ions formed on the cathode surface as well may participate in the reduction of selenite ions to elemental powdered selenium by the reaction (7). But in this study, we have established the patterns of formation of selenium powder only in the anode space.

As can be seen in figure 1, an increase in the concentration of hydrochloric acid first leads to a sharp increase in the current efficiency of selenium powder formation. This effect of hydrochloric acid is due to the fact that, with an increase in its concentration, the stability of copper (I) ions - reducing agent increases, and in this regard, the ionization rate of the copper electrode in the first stage increases, as well as the process of formation of selenium powder by chemical reaction (7). On the other hand, the formed copper (I) ions bind in a complex with chlorine ions of the $CuCl_n^{n-}$ type, where the "n" number increases with increasing concentration of hydrochloric acid and, accordingly, this leads to a decrease in the reducibility of cuproions according to the reaction (7). All this in total leads to a more delayed increase in the CE of the formation of selenium powder.
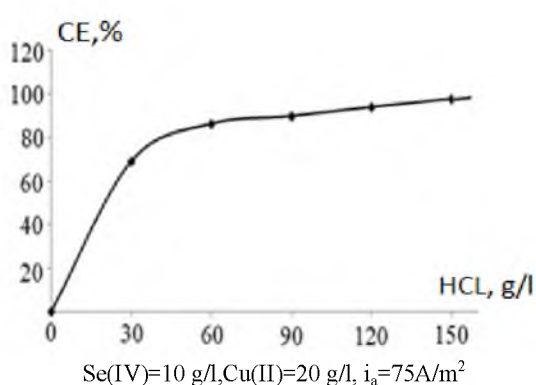

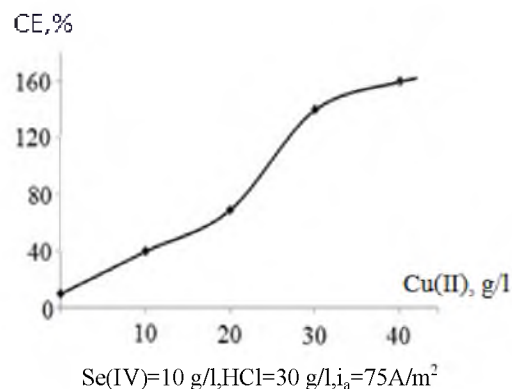| Figure 1 – Reduction of selenite ions to form selenium powder depending on the concentration of hydrochloric acid | Figure 2 – Reduction of selenite ions to form selenium powder depending on the concentration of copper (II) ions |

Se(IV)=10 g/l,Cu(II)=20 g/l, i_a=75A/m^2 Se(IV)=10 g/l,HCl=30 g/l,i_a=75A/m^2

Increase in the concentration of copper (II) ions in solution leads to a proportional increase in the current efficiency of selenium powder formation (figure 2). This is due to the formation of additional amounts of copper (I) ions due to the well-known chemical reaction (6). As can be seen in figure 2, with an increase in the concentration of copper (II) ions, the rate of formation of copper (I) ions increases.

Besides, in this case, the fraction of copper ionization reaction in the first stage increases, i.e. mainly to form copper (I) ions. Additional experiments showed that in the absence of copper (II) ions in solution, the reduction of selenite ions proceeds with a low current efficiency (CE does not exceed 10%).

As the solution temperature rises, the current efficiency of powder formation sharply increases (figure 3), which is due to an increase in the rate of formation of copper (I) ions by the chemical reaction of re-disproportionation (9).

Using the Arrhenius dependence, the apparent activation energy of 38.5 kJ/mol was calculated, which is typical for processes with a mixed diffusion-kinetic nature.

With an increase in the current density at the copper electrode, a decrease in the CE of the formation of selenium powder is observed (figure 4).
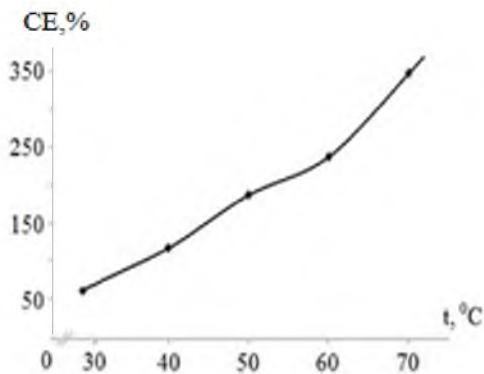
Se(IV) = 10 g/l, HCl = 30 g/l,Cu(II) = 20 g/l, i_a= 75 A/m^2

Figure 3 – Reduction of selenite ions to form selenium
powder depending on the temperature of the electrolyte
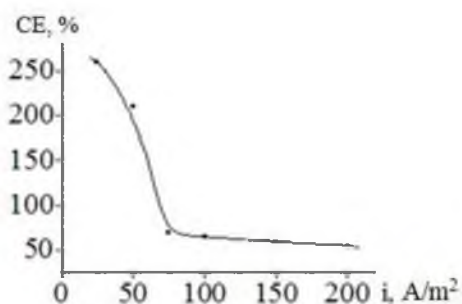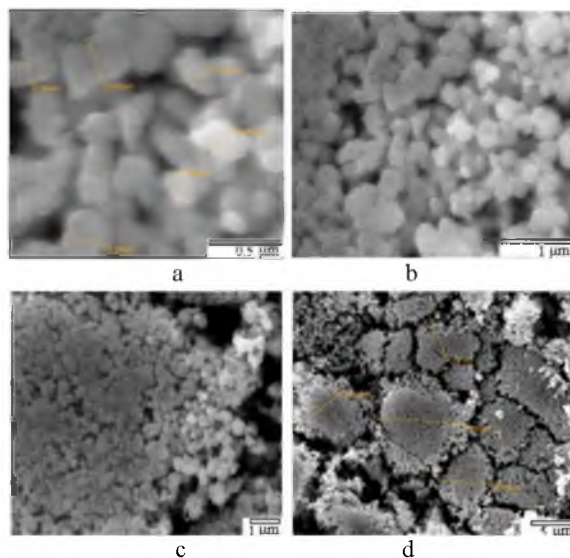

Se(IV) = 10 g/l, HCl = 30 g/l, Cu(II) = 20 g/l

Figure 4 – Reduction of selenite ions
to form selenium powder depending on the current density

This is due to the fact that, with an increase in the anode current density, according to the Tafel equation, the electrode potential shifts to the positive side, in this regard, the rate of the second stage increases, i.e. the formation of copper (II) ions, which cannot participate in the reduction reaction, i.e. in the formation of selenium powder. This leads to a decrease in CE of powder formation. It should be noted that up to a solution temperature of 60°C red amorphous selenium powders are formed, and abovethat - gray selenium.

We note that the excess of CE of selenium powder by 100% in all cases is due to the participation in the reaction of copper (I) ions formed owing to the chemical reaction of reproportionation (6). Thus, in the presence of selenium (IV) anions in solution, they are reduced on the surface of the copper anode due to cuprous copper ions formed as a result of the anodic electrochemical reaction and chemical reaction (6). But the fraction of the latter decreases with increasing current density at the copper anode to a certain value.

It should be noted that in this case, copper selenide is formed in small amounts on the surface of the copper anode.

Figure 5 shows microphotographs of the selenium powder produced on the surface of a copper anode obtained using a JSM6610Welectron microscope. As can be seen in the above microphotographs, the particles of the produced selenium powder have mainly spherical shapes, the average particle sizes of which are 0.252 μm.

Se(IV)=10 g/l; Cu(II)=10 g/l; i=75A/m^2; HCl=30 g/l

Figure 5 – Microphotographs of selenium powder produced in the anode space, magnified:
a) 50,000 times; b) 25,000 times; c) 10,000 times; d) 3000 times

Conclusions. We for the first time showed the possibility of reducing selenite ions in hydrochloric acid solutions on the surface of a copper anode. It was found that an increase in the concentration of hydrochloric acid and copper (II) ions, as well as an increase in the solution temperature leads to an increase, and an increase in the current density at the copper anode leads to a decrease in the current efficiency of selenium powder formation.

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ТҰЗ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕ СЕЛЕНИТ-ИОНДАРЫН ТОТЫҚСЫЗДАНДЫРУ КЕЗІНДЕ МЫС АНОДЫНЫҢ БЕТІНДЕ СЕЛЕН ҰНТАҚТАРЫНЫҢ ТҮЗІЛУІ

Аннотация. Зерттеулер мыс электродын тұз қышқылды ерітінділерде анодтық поляризациялау кезінде түзілетін мыстың бір валентті иондарының қатысуымен селенит иондарын тотықсыздандыруға арналған. Тәжірибелер нәтижелері осы жағдайда селенит иондарының дисперсті ұнтақ күйде түзілетін элементті селенге дейін тотықсыздануы мыс анодының бетінде және анод жанындағы кеңістікте жүретінін біржақты көрсетті.

Болған жағдай тұз қышқылындағы Cu (I) - Cu (II) тотығу-тотықсыздану жүйесінің стандарттық потенциалының ($E°$) мәні -0,54 В құрайтынымен, ал Se-Se (IV) жүйесінің потенциалы – 0,77 В құрайтынымен, демек, бірінші жүйенің стандарттық потенциалының мәні екінші жүйенің потенциалының мәніне қарағанда терістеу болуымен түсіндіріледі. Осыған байланысты Cu^+ -иондары селенит-иондарын элементті селен түзе тұра тотықсыздандырады да, өздері Cu^{2+}- ге дейін тотығады.

Теориялық тұрғыдан мыстың хлоридті ерітіндіде, демек, натрий хлориді ерітіндісінде анодтық тотығуы екі стадиямен іске асады:

$$Cu^0 + Cl^- - e \rightarrow CuCl \qquad 1\text{-стадия}, \qquad E^0 = 0,137 \text{ В},$$

ары қарай

$$CuCl - e \rightarrow Cu^{2+} + Cl \qquad 2\text{-стадия} \qquad E^0 = 0,54 \text{ В}.$$

Ток тығыздықтарының төменгі мәндерінде мыс тек мыс (I) иондарын түзе отырып тотығады. Осыдан басқа, бұл жағдайда компропорциялану реакциясы орын алады, демек, мыс электроды мыс (II) иондарымен мыс (I) хлоридін түзе отырып әрекеттеседі:

$$Cu + Cu^{2+} + 2Cl^- \rightarrow 2CuCl$$
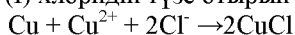
Мыс (I) хлориді тұз қышқылды ерітіндіде өте жақсы ериді, бұл кезде мыс (I) иондары және хлор түзіледі.

Жоғарыда келтірілген реакциялар бойынша түзілген мыс (I) иондары жоғарыда келтірілген Cu(I)-Cu(II) және Se-Se(IV) тотығу-тотықсыздану жүйелерінің потенциалдарының мәндеріне сәйкес тез арада мыс анодының бетінде селен (IV) иондарын химиялық жолмен тотықсыздандыру реакциясына түседі, себебі бұл реакцияның біз есептеген тепе-теңдік константасы ($K_{т-т}$) 10^{15} құрайды және тепе-теңдік оңға қарай мардымды түрде ығысқан.

$$4Cu^+ + SeO_3^{2-} + 6H^+ \rightarrow \downarrow Se^0 + 4Cu^{2+} + 3H_2O$$
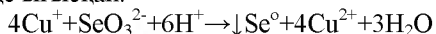
Айта кететін мәселе, ерітіндіде түзілген мыс (II) иондары да катодтық ток тығыздықтарының төменгі мәндерінде мыс (I) иондарын түзе, келесі реакция бойынша тотықсызданады:

$$Cu^{2+} + e \rightarrow Cu^+$$
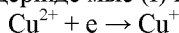
Түзілген бір валентті мыс иондары да селенит-иондарды катод бетінде және катодтық кеңістікте элементті ұнтақ түріндегі селенге дейін тотықсыздандыруға қатысады. Бірақ бұл зерттеуде біз ұнтақ түріндегі селеннің тек анодтық кеңістікте түзілу заңдылықтарын анықтадық.

Селен ұнтақтарының түзілуінің ток бойынша шығымына (ТШ) тұз қышқылы концентрациясының, мыс (II) иондарының концентрациясының, мыс анодындагы ток тығыздығының және ерітінді температура-сының әсерлері зерттелді. Селен ұнтақтарының түзілуінің ток бойынша шығымы түзілген ұнтақтың массасы бойынша есептелді. Мыс (II) иондарының концентрациясының және ерітінді температурасының өсуімен элементті селен ұнтақтарының түзілуінің ток бойынша шығымы артатындығы анықталды. 75 А/м²-ден төмен ток тығыздықтарында селен ұнтақтарының түзілуінің ток бойынша шығымы 100 %-дан асатындығы көрсе-тілді.

Электронды микроскоп көмегімен селен ұнтақтарының микросуреттері түсірілді. Бұл нәтижелер сфера пішінді бөлшектердің орта өлшемі 0,252 мкм болып келетін майда дисперсті селен ұнтақтарының түзілгенін көрсетті.

Түйін сөздер: электрохимия, селен ұнтақтары, селенит-ион, мыс (II) хлориді, тотықсыздану, электролиз, ток тығыздығы, тұз қышқылы.

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ФОРМИРОВАНИЕ ПОРОШКА СЕЛЕНА ПРИ ВОССТАНОВЛЕНИИ СЕЛЕНИТ-ИОНОВ В СОЛЯНОКИСЛОМ РАСТВОРЕ НА ПОВЕРХНОСТИ МЕДНОГО АНОДА

Аннотация. Исследования посвящены восстановлению селенит-ионов в солянокислых растворах с участием ионов одновалентной меди, образующейся при анодной поляризации медного электрода. Результаты опытов однозначно показали, что в данном случае восстановление селенит-ионов происходит с образованием элементного селена в виде дисперсного порошка на поверхности медного анода и в прианодном пространстве.

Это объясняется тем, что стандартный потенциал (Е°) окислительно-восстановительной системы Cu (I) - Cu (II) в солянокислом растворе равен -0,54 В, а потенциал системы Se-Se (IV) – 0,77В, т.е. стандартный потенциал первой системы имеет более отрицательное значение по сравнению со значением второй. В этой связи ионы меди Cu^+ восстанавливают селенит-ионы с образованием элементного селена, а сами при этом окисляются до Cu^{2+}.

Теоретически анодное окисление меди в хлоридном растворе, т.е. в растворе хлорида натрия протекает в две стадии:

$$Cu^0 + Cl^- - e \rightarrow CuCl \qquad \text{1-стадия,} \qquad E^0 = 0,137 \text{ В,}$$

далее

$$CuCl - e \rightarrow Cu^{2+} + Cl^- \qquad \text{2-стадия} \qquad E^0 = 0,54 \text{ В.}$$

При невысоких плотностях тока медь ионизируется только с образованием ионов меди (I). Кроме того, в данном случае имеет место реакция компропорционирования, т.е. медный электрод взаимодействует с ионами меди (II) с образованием хлорида меди (I):

$$Cu+Cu^{2+} + 2Cl^- \rightarrow 2CuCl$$
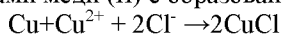
Хлорид меди (I) очень хорошо растворяется в солянокислом растворе с образованием ионов меди (I) и хлора.

Образовавшиеся по вышеуказанным реакциям ионы меди (I), согласно величинам потенциалов выше-указанных окислительно-восстановительных систем Cu(I)-Cu(II) и Se-Se(IV), будут моментально вступать в химическую реакцию восстановления селена (IV) на поверхности медного анода, так как рассчитанная нами константа равновесия (Кр) данной реакции равна 10^{15} и равновесие сильно смещено вправо.

$$4Cu^+ + SeO_3^{2-} + 6H^+ \rightarrow \downarrow Se^0 + 4Cu^{2+} + 3H_2O$$
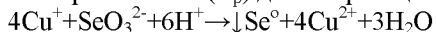
Следует отметить, что имеющиеся в растворе ионы меди (II) при невысоких катодных плотностях тока также восстанавливаются с образованием ионов меди (I) по реакции:

$$Cu^{2+} + e \rightarrow Cu^+,$$
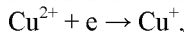
Образовавшиеся одновалентные ионы также могут участвовать в реакции восстановления селенит-ионов до элементного порошкообразного селена на поверхности катода и в прикатодном пространстве. Но в данном исследовании нами установлены закономерности формирования порошка селена только в анодном пространстве.

Исследовано влияние концентрации соляной кислоты, ионов меди (II), плотности тока на медном аноде и температуры раствора на выход по току (ВТ) образования порошка селена. Выход по току порошка селена рассчитывали по весу образовавшегося порошка. Установлено, что с увеличением концентрации ионов меди

(II) и температуры раствора повышается выход по току образования элементного селена в виде порошка. Показано, что при плотности тока ниже 75 А/м^2 кажущийся выход по току порошка селена превышает 100%.

С помощью электронного микроскопа получены микрофотографии порошка селена. Они свидетельствуют о формировании мелкодисперсного порошка селена с частицами сферической формы со средними размерами 0,252 мкм.

Ключевые слова: электрохимия, порошок селена, селенит-ион, хлорид меди (II), восстановление, электролиз, плотность тока, соляная кислота.

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