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CATHODE RESTORATION OF SELONIUM ANIONS WITH THE FORMATION OF ITS POWDERS

Abstract. The article shows the possibility of obtaining selenium powders by cathodic reduction of its anions in acidic and alkaline solutions. It has been established that in alkaline medium it is impossible to obtain selenium powders by reducing selenite ions. However, it is shown that selenium powders can be obtained by cathodic reduction of these ions in a sulfate medium. The main results of the conducted research are the production of selenium powders by cathodic reduction of “hardly recoverable”, and cathode “non-renewable” selenite-ions and determination of the regularities of this process.

It has been shown for the first time that in sulfate solutions in the presence of titanium (IV) ions by cathodic reduction of selenite-ions, selenium powders can be obtained. The effect of the concentration of titanium (IV) ions, selenite-ions, and cathode current density on the formation of selenium powders was studied. It has been established that in the absence of titanium (IV) ions, selenium powders are not formed, and at their concentration equal to 5.0 g/l, the current yield for selenium powder formation reaches 70%. It has been proven that titanium (IV) ions have a catalytic effect on the cathode formation of selenium powders. It is shown that the formation of selenium powders proceeds in two stages, i.e. consists of an electrochemical and chemical reaction, namely, tetravalent titanium is reduced at the cathode to the trivalent state. It has been established that the titanium (III) ions formed in this case interact in the cathode space with selenium (VI) anions, reducing them to elemental selenium as an ultrafine powder.

It is shown that an increase in the current density at the cathode leads to a decrease in the current efficiency for the formation of selenium powders. With an increase in the concentration of selenite-ions, the yield of selenium powders increases. It is established that with selenium (VI) concentration equal to 10.0 g/l, the yield of selenium powder formation is 68.1%, and at 30 g/l - 94.9%. The shapes and sizes of the obtained selenium powders were determined using an electron microscope.

Keywords: selenium powder, selenite and selenate ions, sulphuric acid, electrolysis, cathode, current output.

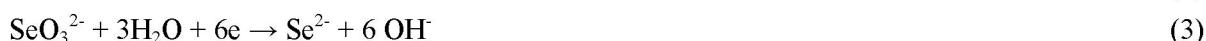
Introduction. The electrochemical properties of selenium ions in aqueous media are studied in detail [1-10].

Selenium powders can be obtained by the reduction of selenium ions with sulfur dioxide [11]:



Sulfur dioxide (SO₂) is a toxic gas so this method is not widespread.

In our first study, we considered the possibility of obtaining selenium powders by the reduction of tetravalent selenium ions in an alkaline medium. According to the literature, selenite ions can be reduced according to the following cathodic reactions in an alkaline medium [12, 13]:



From the literature, the newly formed element reacts with hydroxide ions at the moment, and a disproportionation reaction occurs [14]:



According to these data, selenite ions can be reduced at one stage simultaneously to selenide-ions or elemental selenium.

Procedure of work execution. In our initial studies, electrolysis was carried out in a solution containing 15 g/l of selenium (IV) ions and 40 g/l of NaOH. The electrolysis was carried out by a 100 ml electrolyzer and an unseparated interelectrode space. Titanium was used as a cathode, non-oxidizable iron electrodes (IX18H10T) were used as an anode.

The results of electrolysis at a current density of 50–350 A/m² on the electrodes showed that selenium powders did not form at the cathode, mainly the formation of red-brown polyselenide-ions.

The restoration of the cathode in an alkaline medium by six valence selenate ions (SeO₄²⁻) was also investigated. The electrolysis results show that this ion is not recovered. There was no formation of selenium powders in the cathode, and the color change of the electrolyte did not occur in the cathode space.

Since the main goal of our research is the production of selenium powders, we did not consider it necessary to continue research further.

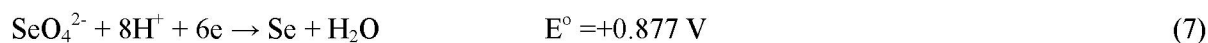
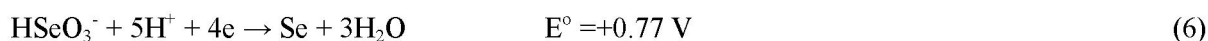
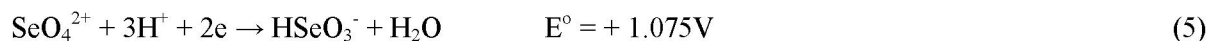
Subsequent studies of selenium powders were carried out in a solution containing sulfuric acid and tetravalent selenite-ions. Our preliminary studies have shown that selenium powders are formed on the cathode in an acidic environment.

The presented studies were carried out in the above-mentioned electrolyzer only when using a graphite electrode as an anode. Our subsequent studies showed that cathodic reduction of hexavalent selenium ions (SeO₄²⁻) does not occur in a solution with sulfuric acid, and adding titanium (IV) ions to the electrolyte, it was found that the formation of ultrafine selenium powders takes place at high speed.

Theoretical. According to the literature, hexavalent selenium ions can be reduced by strong reducing agents only in alkaline media at temperatures above 200 ° C and only at high pressures. Hydrogen, sulfides, elemental sulfur or organic reducing agents are used as reducing agents.[11-13]. In acidic environments by boiling the selenium ion to the tetravalent state in concentrated hydrochloric acid, and then gaseous sulfur dioxide restores to the elemental state. In this case, the recovery of six valence selenium ions occurs in two stages[11]. These processes significantly aggravate the working condition. Since this is a very complex process, the above steps are not available for the production of elemental selenium from six valence selenium ions.

However, the selenate ions with an octahedral shape are surrounded by oxygen atoms (shielded) that cannot penetrate into the double electrode layer on the cathode surface, which leads to kinetic difficulties. Information on the non-recoverability of selenate ions in the cathode is given in the literature.[1, 11-13].

From the point of view of thermodynamics, selenate ions should be restored at the cathode, and their standard potentials are given below:



The current output for the formation of selenium powder is determined depending on its weight. During electrolysis, the formation of red was found dispersed amorphous selenium on the surface and area of the cathode.

The effect of the concentration of sulfuric acid and titanium (IV) ions, as well as the effect of the current density of cathode electrodes in the solution on the current output for the formation of selenium powders was investigated.

Experimental. The results of the study showed that tetravalent titanium ions have a significant effect on the current efficiency of the direct reduction of selenium powder with selenate ions. For example, when the current density on the cathode electrode is 100 A/m² and the concentration of titanium in the solution is 2.5 g/l, then the current for the formation of selenium powder will be 44.1%, at 5.0 g/l - 68.5%, and at 10 g/l will be equal to 79.8%. Table 1 shows the effect of current density on the current output of selenium powder.

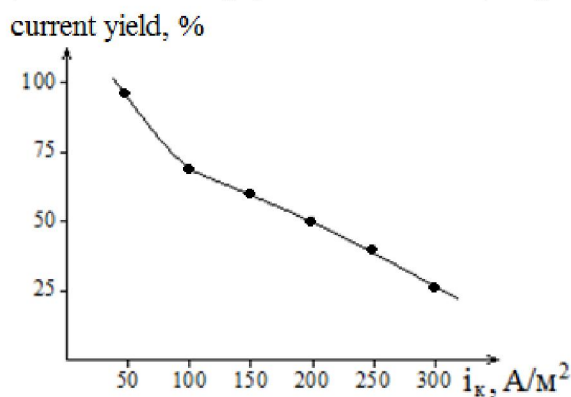
Table 1 -Influence of titanium (IV) ions present in the solution on the formation of selenium powders:
 $\text{Se (IV)} = 10 \text{ g/l}$, $\text{H}_2\text{SO}_4 = 100 \text{ g/l}$, $i_c = 100 \text{ A/m}^2$, $\tau = 1 \text{ hour}$

| | | | | | | |
|-------------------|------|------|------|------|------|------|
| Ti (IV), g/l | 0.5 | 1.0 | 2.5 | 5.0 | 7.5 | 10.0 |
| Current output, % | 20.9 | 30.5 | 44.1 | 68.5 | 72.1 | 79.8 |

If we take into account that the value of selenium ions (VI) is lower than the value of the limiting current - at 100 A/m^2 completely restores selenium powders. This phenomenon indicates that selenium (VI) ions are not restored on the cathode surface in a direct way, and their recovery occurs with the help of intermediate titanium (III) ions. Consequently, titanium (IV) ions can be reduced to three valence states at the cathode, and then the subsequent reduction of the selenite-ions to selenium powder is observed.

With an increase in the concentration of sulfuric acid in the solution (in the presence of titanium ions), a slight decrease in the current yield of selenium powder is observed.

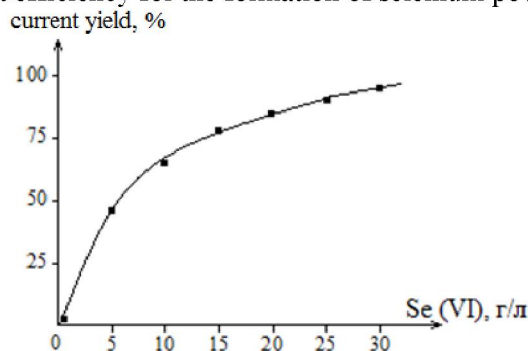
The increase in cathode current density leads to a decrease in the current for the formation of selenium powders (Fig. 1), this phenomenon can be explained by an increase in the proportion of hydrogen gas in the cathode layer, and it can be traced by the smell of hydrogen sulfide at high cathode densities. However, it was found that when the cathode current density is $50\text{-}175 \text{ A/m}^2$ and the concentration of selenium (VI) ions exceeds 10 g/l , the formation of hydrogen gas does not occur.



$\text{Se (VI)} = 10 \text{ g/l}$, $\text{H}_2\text{SO}_4 = 100 \text{ g/l}$, $\text{Ti (IV)} = 5 \text{ g/l}$

Figure 1 –The effect of cathode current density on the current output for the formation of selenium powder

Changes in the concentration of selenium ions in solution have a significant effect on the current efficiency of the formation of selenium powder at the cathode. For example, while the current density is 100 A/m^2 and the concentration of selenium ions is 5 g/l , the current efficiency will be 45.5% , and at 10 g/l it will be 68.1% , at 30 g/l it will be 94.9% . Figure 2 shows the effect of the current density on the titanium cathode on the current efficiency for the formation of selenium powder.



$\text{Ti (VI)} = 5.0 \text{ g/l}$, $i_c = 100 \text{ g/l}$, $\text{H}_2\text{SO}_4 = 100 \text{ g/l}$

Figure 2 – The effect of the concentration of selenium (VI) ions in solution on the current output for the formation of selenium powders

The aforementioned research results show that in the presence of titanium (IV) ions in solution, hexavalent selenium ions cause a direct reduction of their own powders. This phenomenon can be explained by the catalytic effect of the Ti (IV) –Ti (III) redox system.

Tetravalent titanium ions are reduced at the cathode to trivalent:



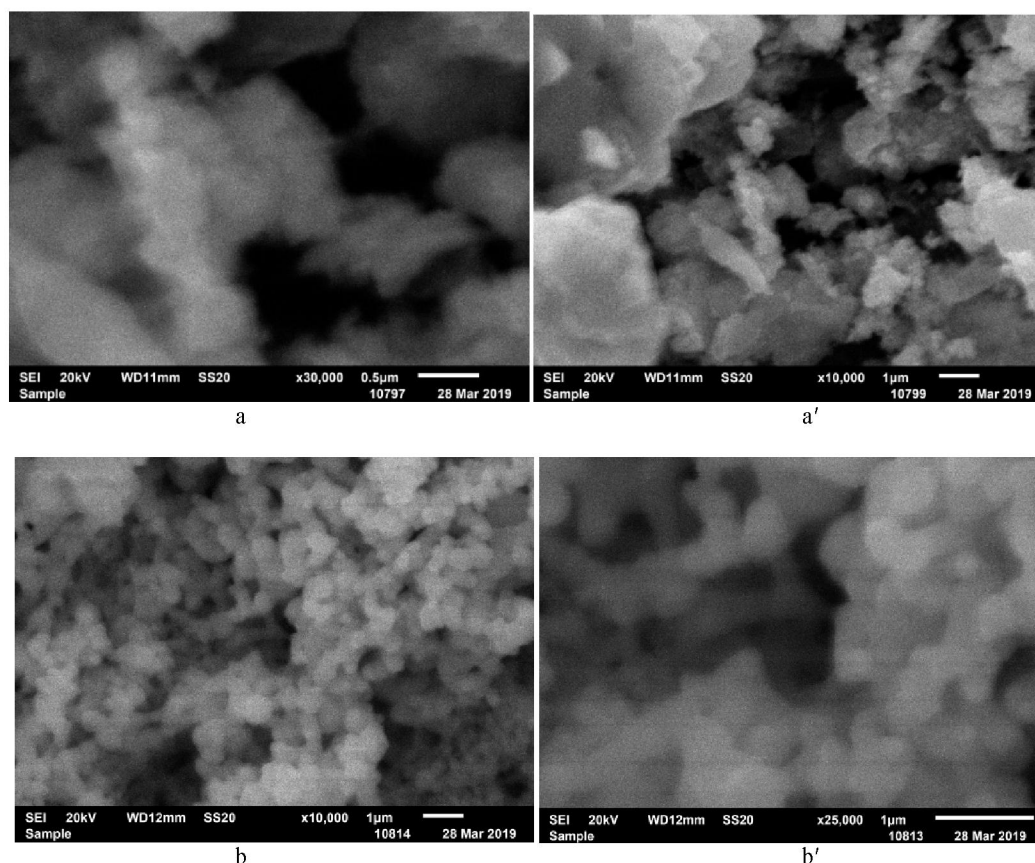
According to the literature [15], the standard potential of the Se (VI) -Se system is +0.86 V, and Ti (IV) -Ti (III) is +0.04 V.

Titanium (III) ions react with selenite-ions in the cathode region, and as a result of the redox reaction, selenium powder is formed:



As a result, tetravalent titanium ions are regenerated, then they are re-reduced at the cathode to the trivalent state and restore selenium (VI) ions in the cathode region. This process is repeated cyclically. Therefore, in this case, the reduction of selenate ions to selenium powders is a catalytic process. In our earlier works, we mentioned that titanium (IV) ions act as a catalyst in the formation of copper powders. [16-22].

The shape and size of selenium powder obtained by electrolysis were obtained using electron microscopy (JSM-6610 LV). The results of the study showed the formation of selenium powder in its mostly round shape, not exceeding 1-2 microns in size. No significant changes are observed in the shape and size of selenium powders formed on the cathode at a current density in the range of 100-150 A/m².



Se (VI) – 10g/l, H₂SO₄ – 100 g/l, Ti (IV) – 5.0 g/l, τ = 1hour

a, a' - i = 100 A/m²; b, b' - i = 150 A/m²

Figure 3 – Micrographs of selenium powder obtained by reducing selenate ions at the cathode in the presence of titanium (IV) ions

In conclusion, we showed for the first time that selenium ions “non-reducible” at the cathode are reduced in the presence of titanium (IV) ions, and we also obtained pink amorphous selenium powder. Titanium (IV) ions have been shown to have a catalytic effect. Under optimal conditions, it was found that the current for the formation of selenium powder exceeds 90%.

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СЕЛЕН АНИОНДАРЫН КАТОДТА ТОТЫҚСЫЗДАНДЫРУ АРҚЫЛЫ ОНЫҢ ҰНТАҚТАРЫН АЛУ

Аннотация. Мақалада қышқылды және сілтілі ерітінділерде селен аниондарын катодты тотықсыздандыру арқылы селен ұнтақтарын алу мүмкіншіліктері көрсетілген. Сілтілі ортада селенит-иондарын тотықсыздандыру арқылы селен ұнтақтарын алуға болмайтындығы көрсетілген. Ал бірақ бұл иондарды күкірт қышқылы ерітіндісінде катодты тотықсыздандыру арқылы селен ұнтақтарын алуға болатындығы анықталған. Жүргізілген ғылыми зерттеулердің негізгі нәтижелерінде қиын тотықсызданатын, ал катодты «тотықсызданбайтын» селенат-иондарын катодты тотықсыздандыру арқылы селен ұнтақтарын алу мүмкіншіліктері көрсетіліп, бұл процестің заңдылықтары анықталған.

Алғаш рет селенат-иондарын күкірт қышқылы ерітіндісінде титан (IV) иондары қатысында катодты тотықсыздандырып селен ұнтақтарын алуға болатындығы көрсетілген. Селен ұнтақтарының түзілу процесіне титан (IV) иондарының, селенат-иондарының концентрацияларының, катодтағы ток тығыздығының әсері зерттелді. Титан (IV) иондары қатысынсыз селен ұнтақтарының түзілмейтіндігі, ал оның мөлшері 5,0 г/л болғанда селен ұнтақтарының түзілуінің ток бойынша шығымы 70 %-ке жақындайтындығы анықталды. Селен ұнтағының катодты түзілуінде титан (IV) иондарының каталитикалық әсер көрсететіндігіне көз жеткізілді. Селен ұнтақтарының түзілуі екі стадияда, яғни электрохимиялық және химиялық реакциялардан құралатыны анықталды. Дәлірек айтатын болсақ, катодта төрт валентті титан үш валенттіге дейін тотықсызданып, катод аумағында селен (VI) иондарын элементті ультрадисперсті ұнтақ түріне дейін тотықсыздандыратындығы анықталды.

Катодтағы ток тығыздығының өсуі, селен ұнтақтарының түзілуінің ток бойынша шығымын төмендететіндігі көрсетілді. Алты валентті селенат-иондарының концентрациясының өсуімен, селен ұнтақтарының түзілуінің ток бойынша шығымының өсетіндігі анықталды. Селен ұнтақтарының түзілуінің ток бойынша шығымы селеннің (VI) концентрациясы 10,0 г/л болғанда – 68,1 % болса, ал 30 г/л-де – 94,9 % тең болатындығы көрсетілді.

Алынған селен ұнтақтарының размері мен формасы электронды микроскоп арқылы анықталды.

Түйін сөздер: селен ұнтағы, селенит-, селенат-иондары, күкірт қышқылы, электролиз, катод, ток бойынша шығым.

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КАТОДНОЕ ВОССТАНОВЛЕНИЕ АНИОНОВ СЕЛЕНА С ОБРАЗОВАНИЕМ ЕГО ПОРОШКОВ

Аннотация. В статье показана возможность получения порошков селена катодным восстановлением его анионов в кислых и щелочных растворах. Установлено, что в щелочной среде невозможно получить порошки селена восстановлением селенит-ионов. Однако показано, что путем катодного восстановления этих ионов в сернокислой среде можно получить порошки селена. Основными результатами проведенных научных исследований является получение порошков селена катодным восстановлением «трудновосстанавливаемых», а катодно «невосстанавливаемых» селенат-ионов и определение закономерностей данного процесса.

Впервые показано, что в сернокислых растворах в присутствии ионов титана (IV) катодным восстановлением селенат-ионов можно получить порошки селена. Исследовано влияние концентрации ионов титана (IV), селенат-ионов, катодной плотности тока на процесс образования порошков селена. Установлено, что в отсутствии ионов титана (IV) порошки селена не образуются, а при их концентрации, равной 5,0 г/л, выход по току образования порошков селена достигает 70%. Доказано, что на катодное формирование порошков селена ионы титана (IV) оказывают каталитическое действие. Показано, что образование порошков селена протекает в две стадии, т.е. состоит из электрохимической и химической реакции, а именно, четырехвалентный титан восстанавливается на катоде до трехвалентного состояния. Установлено, что образовавшиеся при этом ионы титана (III) взаимодействуют в катодном пространстве с анионами селена (VI), восстанавливая их до элементарного селена в виде ультрадисперсного порошка.

Показано, что увеличение плотности тока на катоде приводит к снижению выхода по току образования порошков селена. С возрастанием концентрации селенат-ионов происходит повышение выхода по току образования порошков селена. Установлено, что при концентрации селена (VI), равной 10,0 г/л выход по току образования порошков селена составляет 68,1%, а при 30 г/л – 94,9%. Формы и размеры полученных порошков селена определены с помощью электронного микроскопа.

Ключевые слова: порошок селена, селенит-, селенат-ионы, серная кислота, электролиз, катод, выход по току.

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