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ELECTROCHEMICAL SYNTHESIS OF IRON MONOSELENIDE THIN FILMS

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Abstract: In the presented research work, the kinetics and mechanism of the deposition process of thin iron, selenium and Fe-Se films have been studied by recording a cyclic and linear polarization curves by potentiodynamic method using Pt and Ni electrodes. Individual and co-deposition potential areas of the components of the electrolyte on the Pt electrode were determined. In order to determine the optimal electrolysis mode and electrolyte composition, the effect of various factors (concentration of initial components, temperature, etc.) on the co-electrodeposition process of Fe-Se was studied. In addition, Fe-Se samples deposited on the surface of Ni electrodes were thermally treated at 450°C and studied by SEM and X-ray phase analysis methods. Elemental analysis of the films shows that they contain 42.2% Fe and 57.8% Se.

Keywords: electrodeposition, iron monoselenide, polarization, electro-reduction

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Introduction

In our time, the great demand for renewable energy sources and energy storage devices with high-efficiency grows day by day [1-2]. Thin films of metal chalcogenides are widely used in these devices [3-6]. In this regard, in the last few years, iron chalcogenides attract attention due to their structure, the band gap, physicochemical, magnetic and etc. properties.

Iron monoselenide can be obtained variously. In some studies, FeSe thin films were deposited on a conductive glass electrode coated with fluorine-additive tin oxide by electron-beam evaporation of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the range of 0.18-0.03M concentration. The effect of concentration on the thickness, structure, surface morphology, composition and optical properties of deposited samples were studied [7-12]. Nanocrystalline iron monoselenide was synthesized on the surface of platinum or gold electrodes from aqueous acid solutions containing HSeO_3^- , SeO_3^{2-} and Fe^{2+} ions by potentiostatic or galvanostatic methods. The current density and potential values providing the deposition of tetragonal iron selenide were

determined by electrochemical method [13, 14].

FeSe samples consisting of polygonal crystallites were synthesized by [13-15] authors. Atomic force microscopy were used to determine the optical properties and UV-VIS spectroscopy was applied to study the surface topography of thin films. According to the results, the bandgap of the deposited films is 1.23 eV, and as the deposition time increases, the bandgap of the deposited thin films decreases. Detailed study of the samples by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and energy dispersion spectroscopy shows that they are rich in amorphous selenium. High abundance of selenium makes it possible to synthesize good crystalline, tetragonal FeSe_2 .

Selenides of transition metals are widely studied as anode materials for batteries and as an effective electro-catalyst in photo-electrochemical decomposition of water. Iron chalcogenides are widely investigated for different applications, such as hydrogen evolution reaction, light energy conversion devices, solar cells, superconductors, high-

capacity capacitors (supercapacitors) and storage devices. In terms of usefulness, these are mostly studied as photovoltaic or supercapacitors [15, 16].

Analysis of reference data shows that Fe-Se thin films were mainly synthesized from

acid solutions [13, 15, 17, 18]. Therefore, the main purpose of this study – as a continuation of our research about the synthesis of metal chalcogenides [19-22] - is to obtain thin iron selenium films from aqueous solutions using a simple and inexpensive electrochemical method.

Experimental part

Pt and Ni electrodes were used in galvanostatic synthesis and potentiodynamic research, and they were connected to an amperimeter for regulating the current. The thin films obtained by this method were thermally treated at 450⁰C in an argon medium. It was observed that the obtained thin film changed from an amorphous structure to a crystalline structure.

Potentiodynamic studies were performed using IviumSoft-programmed and computer-equipped “IVIUMSTAT Electrochemical Interface” potentiostat. In this case, a three-electrode electrochemical cell with a volume of 100 ml was used. Pt wire with an area of 0.3 cm² and Ni plate with an area of 2 cm² were used as working electrodes. Saturated silver/silver chloride (Ag/AgCl/KCl) electrode

was used as the reference electrode, and Pt plate with an area of 4 cm² applied as the auxiliary electrode.

The morphological structure and phase composition of the samples were studied by the scanning electron microscope (SEM) and “D2 Phazer” (filter CuK_α, Ni) X-ray phase analyzer of German company Bruker, respectively.

Electrolyte solutions containing 0.1 M Fe(NO₃)₃ · 9H₂O and 0.01 M H₂SeO₃ were used during the experiments. After cleaning the Pt electrode in concentrated nitric acid, it is washed with distilled water. The Ni electrode is polished chemically in nitric acid and then electrochemically in a solution consisting of concentrated sulfuric acid (H₂SO₄), orthophosphate acid (H₃PO₄) and distilled water.

Results and discussion

The deposition potential area for both iron (Fe) and selenium (Se) was determined by studying the electrochemical reduction process of the initial components separately to carry out the co-deposition process by electrochemical method. Initially, the electro-reduction potential area of iron ions in an aqueous electrolyte was specified. The experiments were performed by

the potentiodynamic method recording a polarization curve on the surface of the Pt electrode.

Fig. 1 shows the mechanism of the electrochemical reduction process of Fe ions on the Pt electrode. As is seen from the Fig., the process occurs through the following scheme in two stages within 0.6 - (-0.9) V potential range:



Here, electroreduction to divalent iron ions occurs in the potential range of 0.6 - 0.1V (1), and electro-reduction to neutral iron occurs

in the range of -0.2 - (-0.5) V according to (2) reaction [23]:



Here, after -0.5V potential, the surface of the Pt electrode is covered with iron and it becomes

passive, and thereby the current value decreases.

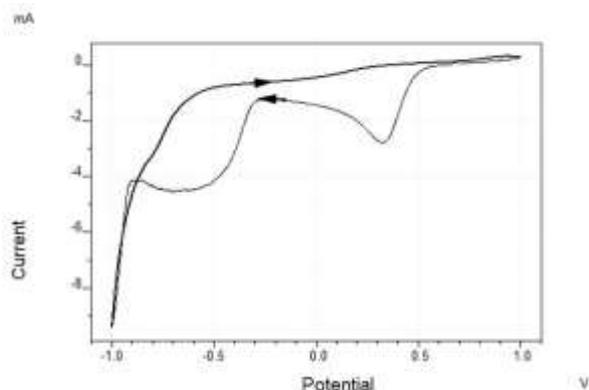


Fig. 1. Cyclic polarization curve of the electro-reduction process of iron ions in an aqueous electrolyte on the Pt electrode. Electrolyte (M): 0.1 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + H_2O , $T = 298\text{K}$, $E_V = 0.02 \text{ V/sec}$.

Then, starting from the -0.9 V potential, the free iron ions are evenly distributed on the surface of the electrode, and thus the current consumed in the process increases sharply due to the thickening of the layer deposited on the

electrode surface. After the potential of -1.0 V, the release of hydrogen gas is observed in the electro-reduction process which affects the process, so the process was studied to the potential of -1.0 V.

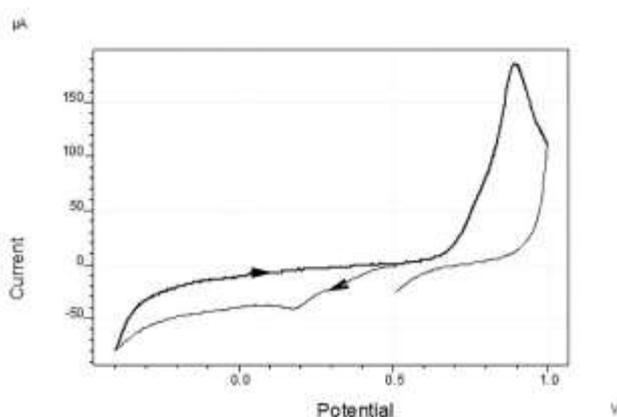
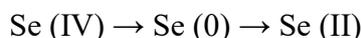


Fig. 2. Cyclic polarization curve of the electro-reduction process of selenium ions from an aqueous electrolyte on a Pt electrode. Electrolyte (M): 0.1 M H_2SeO_3 , $T = 298\text{K}$, $E_V = 0.02\text{V/sec}$

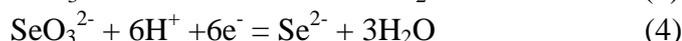
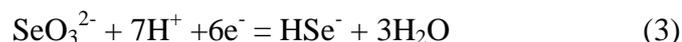
The mechanism of the electrochemical reduction process of selenite ions on the Pt electrode is shown in Fig.2. The electro-

reduction process of selenite ions proceeds in two stages in the potential range of 0.5 - 0.1 V in line with the following scheme:



Initially, the reaction (3) occurs starting from the stationary potential (0.5 V) to the 0.1 V potential, and after the 0.1 V potential, the

complete reduction of the selenide ions occurs according to the reaction (4)



After determining the deposition potential area of initial components and the mechanism of the electro-reduction process, their electrochemical co-deposition was

performed. In order to carry out this process, numerous studies were carried out and a combination of stoichiometric composition and its thin films obtained. The research work was

performed on both Pt (Fig. 3) and Ni (Fig. 4) electrodes.

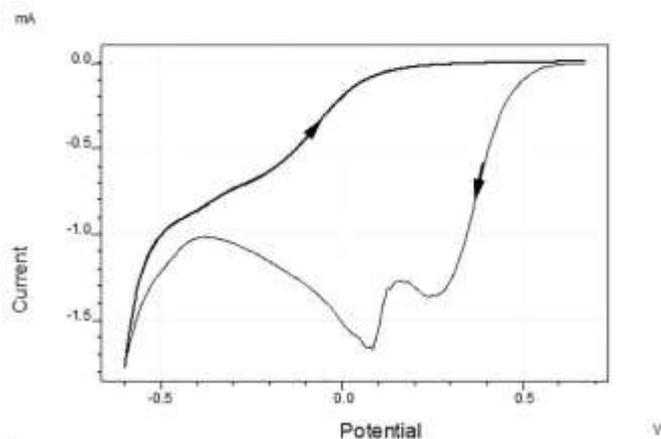


Fig. 3. Cyclic polarization curve of the electrochemical co-deposition process of Fe and Se from an aqueous electrolyte on the Pt electrode. Electrolyte (M): 0.035 Fe (NO₃)₃ + 0.0025 H₂SeO₃; T = 298 K, E_v = 0.02 V/sec.

As is seen from Fig. 3, the co-deposition process occurs at a potential of 0.65 - (-0.6) V. Here, the potential range of 0.65 - (-0.38) V indicates the electro-reduction of selenite ions. After -0.38 V potential, the Fe-Se films were deposited due to the combination of iron ions

with selenide ions formed in the electrolyte. After a potential of -0.38 V, the surface of the Pt electrode was covered with a gradually compacting layer of Fe-Se, which led to a thickening of the film. Thus, a sharp increase in current was observed (Fig. 3).

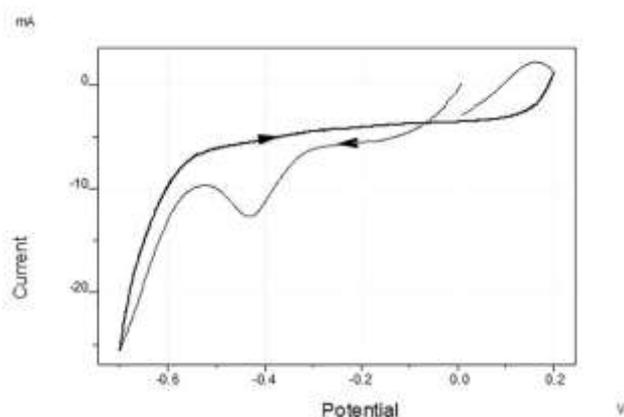


Fig. 4. Cyclic polarization curve of the electrochemical co-deposition process of Fe and Se from an aqueous electrolyte on the Ni electrode. Electrolyte (M): 0.035 Fe (NO₃)₃ + 0.0025 H₂SeO₃; T = 298 K, E_v = 0.02 V/sec.

The electrochemical co-deposition process of iron and selenium on the surface of the electrode was slightly different (Fig. 4). Thus, starting from the 0.0V potential, the -0.3 V potential range accords with the reduction of selenite ions to selenium. Starting from the -0.3V potential, selenium atoms were reduced to selenide ions and the obtained selenide ions combine with iron ions on the surface of the electrode to form a thin iron monoselenide film.

The electrochemical deposition of iron

monoselenide was also confirmed by X-ray and SEM analyzes of samples obtained on the Ni electrode.

Fig.5 shows the X-ray phase analysis of Fe-Se sample obtained from an aqueous electrolyte on the surface of Ni electrode. It is seen from the Fig. that the intensities of the diffraction peaks of this sample were very weak. The reason of this is the amorphous structure of the deposited iron monoselenide.

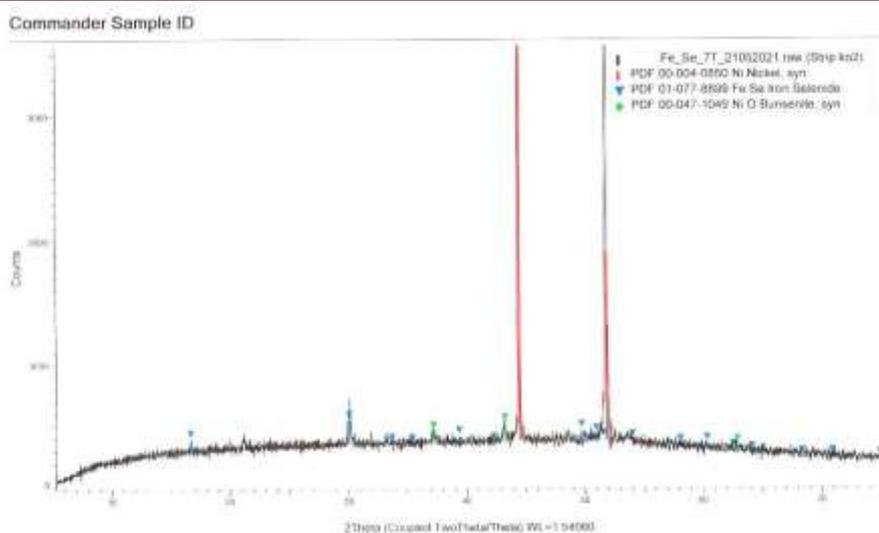


Fig. 5. X-ray phase analysis of Fe-Se sample from aqueous electrolyte on Ni electrode. Electrolyte (M): $0.035 \text{ Fe}(\text{NO}_3)_3 + 0.0025 \text{ H}_2\text{SeO}_3$; $T=298 \text{ K}$.

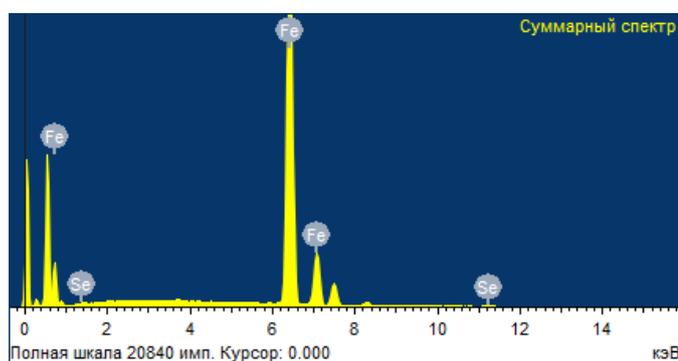
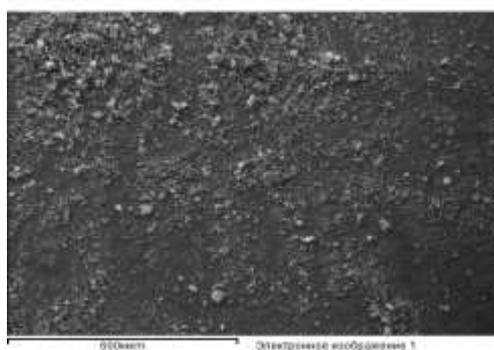
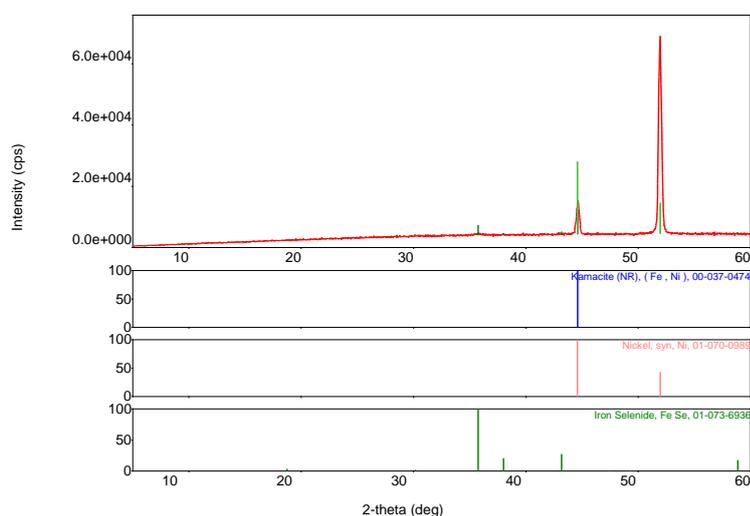


Fig. 6. X-ray phase analysis, morphology and element composition of the FeSe sample deposited on the Ni electrode. Electrolyte (M): $0.035 \text{ Fe}(\text{NO}_3)_3 + 0.0025 \text{ H}_2\text{SeO}_3$; $t=30 \text{ min}$.

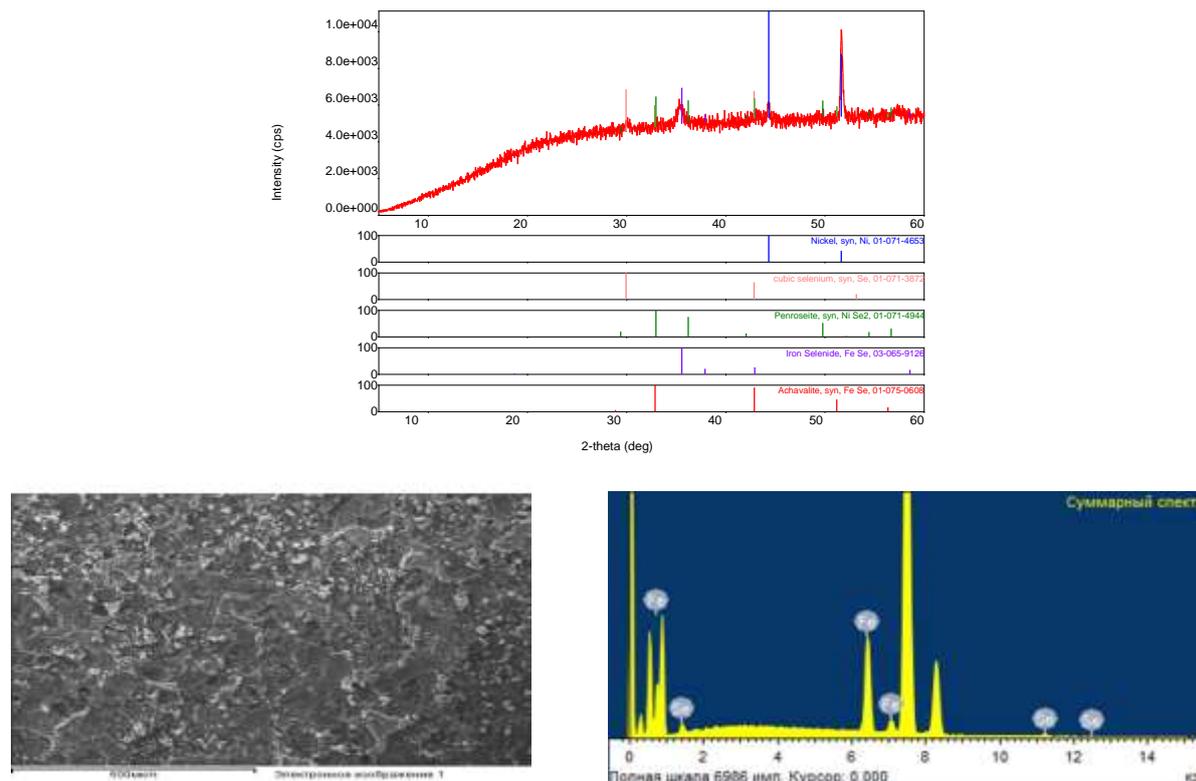


Fig. 7. X-ray phase analysis, morphology and element composition of the FeSe sample deposited on the Ni electrode; Electrolyte (M): $0.035 \text{ Fe}(\text{NO}_3)_3 + 0.0025 \text{ H}_2\text{SeO}_3$; $t=60$ min.

In order to increase the crystallinity of the samples, they were thermally processed in an Ar atmosphere at 450°C temperature for 0.5-1 hour (Figs 6, 7). The results of repeated X-ray phase analysis show that more satisfying crystals are observed in the heat-treated sample for 1 hour.

The thickness of the deposited thin films is 4-6 microns. According to the results of EDS (element composition) analysis, the composition of the films corresponds to the stoichiometry and they consist of 42.2% Fe and 57.8% Se.

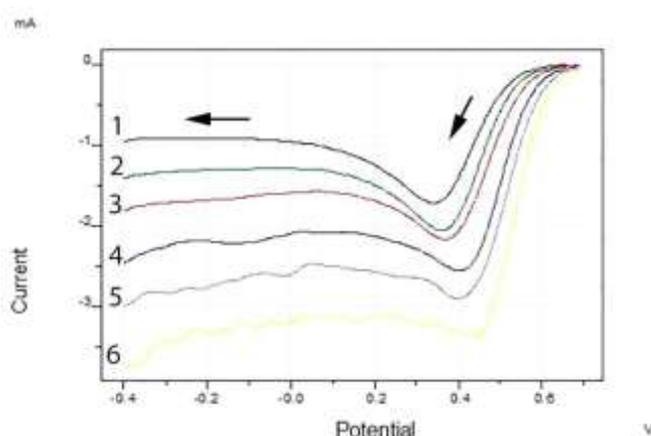


Fig. 8. The effect of temperature on the process of electrochemical co-deposition of Fe and Se from an aqueous electrolyte on the Pt electrode; Electrolyte (M): $0.035 \text{ Fe}(\text{NO}_3)_3 + 0.0025 \text{ H}_2\text{SeO}_3$; $E_V=0.02 \text{ V/s}$. T(K): 1- 298; 2 - 308; 3 - 318; 4 - 328; 5 - 338; 6 - 348

The effect of some important factors on the electrochemical deposition process was studied to determine the optimal electrolyte

composition and electrolysis condition for the deposition of iron monoselenide thin films. The effect of temperature on the co-deposition

process was studied in the range of 298-348 K (Fig. 8). As is seen from the figure, the increase in temperature has a positive effect on the electrodeposition process. Thus, at a temperature of 298 K and at 348 K, the stationary potential is 0.67V and 0.72V, respectively. That is, with the positive effect of temperature, the co-deposition potential shifts to the direction of the positive potential area of

0.05V. However, the increase in temperature has a negative effect on the quality of the deposited films. Thus, their adhesion deteriorates, they begin to break off the electrode surface, and the composition of the films deviates from the stoichiometry. Therefore, 298-308 K was chosen as the optimal temperature range.

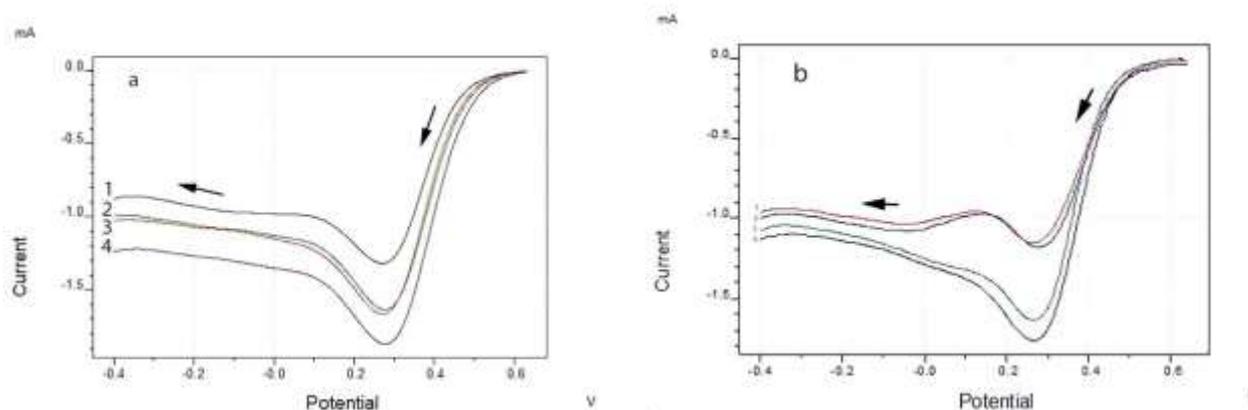


Fig. 9. The effect of concentration of ions on the electrochemical co-deposition process of Fe and Se from an aqueous electrolyte on the Pt electrode; Electrolyte (M): 1- 0.025; 2- 0.035; 3- 0.045; 4- 0.055 $\text{Fe}(\text{NO}_3)_3 + 0.0025 \text{ M H}_2\text{SeO}_3$ (Fig. 9 a); 0.035 $\text{Fe}(\text{NO}_3)_3 +$ 1- 0.0005; 2- 0.0025; 3- 0.005; 4- 0.0075 H_2SeO_3 (Fig. 9 b); $E_v = 0.02 \text{ V/s}$. $T = 298 \text{ K}$

The effect of Fe and Se on the co-deposition process of the initial ion concentration (Fig. 9 a, b) and the rate of potential change (potential gradient) (Fig. 10) were also studied by recording linear polarization curves. When studying the effect of concentration, first, the concentration of selenite ions in the solution is kept constant. The concentration of iron ions was studied in the

range of 0.025-0.055 M (Fig. 9 a). The concentration of selenite ions was examined in the range of 0.0005-0.0075M at the constant concentration of iron ions (Fig. 9 b). As is seen from the figure, in both cases there is no significant sharp potential in the electrochemical deposition process, only the current required to the process (0.5 mA) slightly increases.

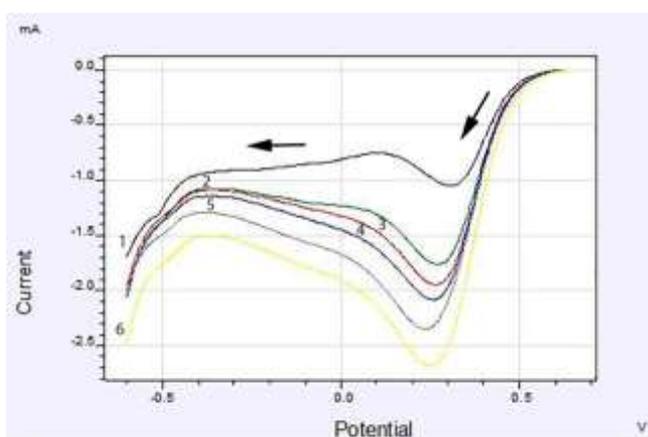


Fig. 10. Cathode polarization curves of the electrochemical deposition process of Fe and Se from an aqueous electrolyte on the Pt electrode at different rates of potential change (1- 0.005; 2- 0.02; 3- 0.04; 4- 0.06; 5- 0.08; 6- 0.1). Electrolyte (M): 0.035 M $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O} + 0.0025 \text{ M H}_2\text{SeO}_3$

The effect of rate of potential change on the co-deposition process was studied in the range of 0.005 - 0.08V/s (Fig. 10). As is seen from the figure, despite the fact that the study of the rate

of potential change does not show a positive potential shift, there is an increase in the current consumed in the electrodeposition process. This increase is approximately 0.8 mA.

Conclusion

In this work, the separate electroreduction process of iron and selenium on the surface of the Pt electrode was studied by the electrochemical method and their deposition potential areas determined. The kinetics and mechanism of the deposition process of Fe-Se thin films were studied by potentiodynamic methods and recording cyclic and linear polarization curves using Ni electrodes. The effect of various factors (concentration of initial

components, temperature, etc.) on the co-electro-deposition process was studied to determine the optimal electrolysis mode and electrolyte composition. Besides, Fe-Se samples deposited on the surface of Ni electrodes were thermally treated at 450⁰C and studied by SEM and X-ray phase analysis methods. Elemental analysis of the films shows that they contain 42.2% Fe and 57.8% Se.

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DƏMİR MONOSELENİD NAZİK TƏBƏQƏLƏRİNİN ELEKTROKİMYƏVİ SİNTEZİ

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Təqdim olunan işdə dəmir, selen və Fe-Se nazik təbəqələrinin çökmə prosesinin kinetika və mexanizmi Pt və Ni elektrodlarından istifadə etməklə potensiodinamik üsulla tsiklik və xətti polyarizasiya ayrılması çəkməklə öyrənilmişdir. Elektroliti təşkil edən komponentlərin Pt elektrodu üzərində həm ayrılıqda, həm də birgə çökmə potensial sahələri müəyyən edilmişdir. Optimal elektroliz rejimi və

elektrolit tərkibini müəyyənləşdirmək üçün Fe-Se-nin birgə elektroçökmə prosesinə müxtəlif amillərin (ilkin komponentlərin qatılığı, temperatur və s.) təsiri araşdırılmışdır. Bundan əlavə, Ni elektrodları səthinə çökdürülmüş Fe-Se nümunələri 450°C temperaturda termiki emal olunmuş, SEM və rentgen-faza analiz metodları ilə tədqiq edilmişdir. Təbəqələrin element analizi göstərir ki, onların tərkibində 42.2 % Fe və 57.8 % Se var.

Keywords: *elektroçökmə, dəmir monoselenid, polyarizasiya, elektroreduksiya*

ЭЛЕКТРОХИМИЧЕСКИЙ СИНТЕЗ ТОНКИХ ПЛЕНОК МОНОСЕЛЕНИДА ЖЕЛЕЗА

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В представленной работе исследованы кинетика и механизм процесса осаждения железа, селена и тонких пленок Fe-Se снятием циклических и линейных поляризационных кривых потенциодинамическим методом с использованием Pt и Ni электродов. Определены область потенциалов компонентов в отдельности в составе электролита и совместного их осаждения на Pt-электроде. С целью определения оптимального режима электролиза и состава электролита было изучено влияние различных факторов (концентрация исходных компонентов, температура и др.) на процесс электроосаждения Fe-Se. Кроме того, образцы Fe-Se, нанесенные на поверхность никелевых электродов, были подвергнуты термообработке при 450°C и исследованы методами СЭМ и рентгенофазового анализа. Элементный анализ пленок показывает, что они содержат 42.2 % Fe и 57.8 % Se.

Ключевые слова: *электроосаждение, моноселенид железа, поляризация, электровосстановление.*