# Electrodeposition process of perrhenate ions from KNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> background electrolytes in the presence of citric acid

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Processes involved in the electrodeposition of perchanate ions were studied from two different potassium nitrate and sodium sulfate background electrolytes in the presence of citric acid on graphite electrode by cyclic voltammetry method. Anodic and cathodic potentials of deposited film were determined. After electrolysis process, morphology and content of obtained deposited layers were investigated by SEM and X-Ray methods. The coated film from sodium sulfate background electrolyte was not uniform and Re content was 60.83-65.5%, in case of potassium nitrate electrolyte, the deposited film was more densely located, and Re content was 80.94-82.52%. In the presence of nickel sulfate and citric acid, an alloy was formed with content of Re 80.94-82.52%, 14.10-11.83% of Ni, 4.96-5.66% of impurities, which were confirmed by X-Ray method. The current density decreased with addition of citric acid into sodium sulfate background electrolyte and in cathodic area, the reduction potential of perrhenate ions remained the same, but oxidation potentials changed from 0.25 to 0.35 V and from 0.5 to 0.6 V. The influence of citric acid on potentials of the processes of reduction and oxidation of perrhenate ions from potassium nitrate gave following results: reduction peaks shifted from -0.35 to -0.55 V, and multi peaks of oxidation appeared which were not noticeable without citric acid. It was shown that citric acid has inhibitory effect on reduction and oxidation of perrhenate ions. It is shown that the electrochemical reduction of perrhenate ions leads to the formation of rhenium dioxide in different forms.

Keywords: perrhenate ions; electrodeposition; rhenium; cyclic voltammetry; electrolysis.

# КNO<sub>3</sub> және Na<sub>2</sub>SO<sub>4</sub> фон электролиттерінен лимон қышқылы қатысында перренат иондарының электртұну процесі

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Циклді вольтамперометриялық әдіс арқылы графит электродындағы лимон қышқылы қатысында әртүрлі екі калий нитраты, натрий сульфаты фонды электролиттеріндегі перранат иондарының тотығу-тотықсыздану процесі зерттелінді. Тұнған қабаттың анодтық және катодтық потенциалдары анықталды. Электролиз процесінен кейін тұнған қабаттың морфологиясы мен құрамы СЭМ және РФА арқылы зерттелді. Натрий сульфаты электролитінен тұнған тұнба біркелкі тұнған жоқ, тұнбаның құрамында Re құрамы 60,83-65,5% болды, калий нитраты электролитінде тұнған тұнба тығызырақ болды, және құрамында Re 80,94-82,52% болды, никель сульфаты мен лимон қышқылы қатысында құйма түзілді, құрамы 80,94-82,52% Re, 14,10-11,83% Ni, 4,96-5,66% қоспадан тұратыны рентген әдісімен дәлелденді. Натрий сульфаты электролитінде лимон қышқылының мөлшері артуымен токтың тығыздығы төмендеді, ал катод аймағында перенат ионының тотықсыздану потенциалы өзгеріссіз қалды, бірақ тотығу потенциалы 0,25 В-тан 0,35 В-қа және 0,5 В-тан 0,6 В-қа ығысты. Лимон қышқылының калий нитраты электролитінен перренат иондарының тотықсыздану және тотығу потенциалдарына әсері келесі нәтижелер берді: тотықсыздану шыңдары -0,35 В-тен -5,5 В-қа дейін ауысты және лимон қышқылы қатысынсыз байқалмаған бірнеше мульти тотығу шыңдары пайда болды. Лимон қышқылының перренат иондарының тотықсыздануы мен тотығуына ингибиторлық әсері бар екендігі көрсетілді. Перранат иондарының электрохимиялық тотықсыздануы ренийдің әртүрлі формадағы оксидтер түзілуіне алып келеді.

Түйін сөздер: перранатиондары; электртұндыру; рений; циклдық вольтам перометрия; электролиз.

# Процесс электроосаждения перренат ионов из фоновых электролитов KNO<sub>3</sub> и Na<sub>2</sub>SO<sub>4</sub> в присутствии лимонной кислоты

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Процессы, связанные с электроосаждением перренат ионов, были изучены в двух разных фоновых электролитах: нитрат калия, сульфат натрия в присутствии лимонной кислоты на графитовом электроде методом циклической вольтамперометрии. Были определены анодные и катодные потенциалы осажденной пленки. После процесса электролиза морфология и состав полученного осажденного слоя были исследованы методами СЭМ и РФА. Полученная пленка из фонового электролита сульфата натрия была неоднородной, и содержание рения составило 60,83-65,50%, в случае электролита нитрата калия осажденная пленка была более плотной, и содержание Re составляло 80,94-82,52%, в присутствии сульфата никеля и лимонной кислоты образовавшийся сплав имел следующий состав: Re – 80,94-82,52%, Ni – 14,10-11,83% и 4,96-5,66% примесей, что было подтверждено методом РФА. С добавлением лимонной кислоты в фоновый электролит сульфата натрия плотность тока уменьшалась, и в катодной области потенциал восстановления ионов перрената оставался тем же, но потенциалы окисления были смещены с 0,25 В до 0,35 В и с 0,5 В до 0,6 В. Наличие лимонной кислоты в электролите (нитрат калия) повлияло на потенциалы процессов восстановления и окисления перренатных ионов: пики восстановления сместились с -0,35 В до -0,55 В, и появились мульти пики окисления, которые не были заметны без лимонной кислоты. Было показано, что лимонная кислота оказывает ингибирующее действие на восстановление и окисление перренат ионов. Показано, что электрохимическое восстановление перренат ионов приводит к образованию оксида рения в различных формах.

Ключевые слова: перренат ионы; электроосаждение; рений; циклическая вольтамперометрия; электролиз.

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# Electrodeposition process of perrhenate ions from KNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> background electrolytes in the presence of citric acid

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#### 1. Introduction

Rhenium is one of the rare metals in our Earth crust. This metal is in high demand because of its unique properties. World rhenium reserves are contained mostly in molybdenum copper deposits [1]. This rare metal is found as the alluvial deposits of copper in our country. The Zhezkazganredmet is the state owned producers of rhenium in our homeland [2]. Kazakhstan is an exporter of ammonium perrhenate to other countries. Price of pure rhenium is much higher in comparison with its compounds [3]. Hence, our country needs to develop the methods of producing pure metallic rhenium, which would be more advantageous to the economy of our country.

Application areas of rhenium and its compounds are developing in recent decades. They are used in different fields as contact points, metallic coatings, heating elements, x-ray tubes, and catalysts etc., [4]. Rhenium alloys are mostly used in rocket industry for parts of missiles as such alloys have high melting point, resistant to corrosion and light [5]. Rhenium catalyst replaced many other previously used catalysts in refinery plants. In order to obtain gasoline which free from lead a catalyst made from rhenium compounds are used [3]. During last decades researchers have high interest in investigating of biosensors made from different electrodes. The choice of electrode material and its modification is becoming popular topic because it can be used as sensors. Modification of electrode surface with different polymers to get precise signal from analyte is under the investigation. Therefore, rhenium also is a good candidate to be used as transducers in making sensors as it has catalytic properties [6].

Rhenium based films can be deposited using chemical or physical gas phase condensation method known as CVD (chemical vapor deposition) and PVD (physical vapor deposition) or by other methods like electron beam physical vapor deposition (EB-PVD), powder metallurgy (PM). The drawbacks of using the above-mentioned methods are the difficulties of obtaining uniform coatings and not usual possible to deposit multilayer films and composites. Additionally, they are technically complicated and consume a lot energy to maintain high condensing temperature [7]. Not to mention that these methods need to maintain vacuum and high temperature inside device. Hence, it is not effective economically to use expensive devices to obtain metallic coatings.

It is very important to choose the optimal condition for electrolysis including the electrolyte composition. Nowadays the different type of background electrolyte exist. One of them is the using of citrate electrolyte at deposition of metals and metal alloys. Citrate based electrolytes have been used at electrodeposition of copper [8], nickel [9], gold [10], zinc [11] and Fe-W [12], Fe-Mo [13], Ni-W [14] other alloys. The citrate electrolyte has properties as buffering, brightening, complexing agent and as facilitator of codeposition. The reduction process of alloy takes place at more negative potentials as a result of the formation of metal complexes with citrate [14]. It was revealed that the addition of citric acid into the bath led to the deposited nickel grain size decrease [15]. Codeposited Re-Ni alloy from the KReO, in a citrate electrolyte bath had a monocrystalline structure [16]. Investigation of plating gold from citrate and phosphate electrolytes showed that the microhardness of gold film coated from citrate electrolyte was higher than from phosphate electrolyte [10]. Aqueous citrate based electrolyte as it is nontoxic, provides stable pH (4-6) and forms strong complexes with Zn ions which are widely used at deposition of this metal and its alloys [11]. Co-Mo-Re ternary alloy was codeposited from citrate electrolyte with good quality at pH=6.3 and 3.5 with current efficiency 20.3-84.5% and 47% with alloy content  $Co_{35,5}Mo_{4.1} Re_{60.4}$  ÷  $Co_{10.8}Mo_{36.3}Re_{36.3}$  and  $Co_{41.0}$ Mo<sub>29.5</sub> Re<sub>29.5</sub> [17].

The electrochemical deposition of rhenium and alloys from an aqueous solution is convenient and promising alternative method. Electrochemical method of metal deposition has comparatively more advantages than CVD and PVD. Nevertheless, here in this method there are its own drawbacks that need to be studied in order to eliminate them. Hindering factor in electrodeposition process off perrhenate ions is hydrogen over potential in case of aqueous solvent. Electroreduction potential of rhenium near to the electroreduction potential of hydrogen atoms [18]. Reduction of rhenium from aqueous electrolytes has its drawbacks. It goes with presence of hydrogen overvoltage process [19]. Consequently, it decreases efficiency of deposition by interfering into uniformity of deposited film on electrode surface. Therefore, it is important to optimize the electrodeposition process of perrhenate ions.

The purpose of [20] has been to study the influence of electrolyte pH and it has been reported that the electrodeposition of rhenium occurs better in an acidic environment than an alkali solution. Electrodeposition process of rhenium reduction from acidic and alkali environment has also been extensively investigated by Mendez.E [19] research group. Rhenium oxides activates hydrogen evolution reaction. Alejandro Vargas Uscategui research group investigated reduction of rhenium oxide from alkaline aqueous electrolyte into indium tin doped oxide by pulsed current deposition and rhenium oxide catalytic effect towards hydrogen evolution reaction [21]. It was reported that high acidic environment and low concentration of perrhenate ions leads to the formation of metallic Re with probable reduction process:  $ReO_{A} \rightarrow ReO_{A}$  $\rightarrow Re^{3+} \rightarrow Re^{0}$ . Reversely, if concentration of  $ReO_{4}^{-}$  is high it is inclined into the formation of ReO<sub>2</sub>, with following process:  $ReO_{A} \rightarrow ReO_{A} \rightarrow ReO_{A}$ ,  $ReO_{A}$ , which enhance HER reaction [22]. Q. Huang research group tested the water in salt electrolyte at depositing of rhenium. Here a high concentration of lithium chloride was used that significantly improved the morphology of Re deposit and the HER was suppressed [23].

In summary the various sediment are formed at elctrodeposition of perrhenate ions in diverse solutions but optimum condition and theory of analysis of reduction and oxidation process have not reached an agreement yet. A survey of literature indicates that electrodeposition of rhenium from perrhenate ions in citrate bath have not been done. The electrodeposition of rhenium alloys from citrate bath is not enough studied. Thus, the aim of this research work is to investigate the electrodeposition process of perrhenate ions from the KNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> background electrolytes in the presence of citric acid.

#### 2. Methods of investigation

The investigation was done using cyclic voltammetry method, electrolysis, X-ray method, scanning electron microscopy method. CV measurement was done on 797 VA Computrace voltammetry techniques. Electrochemical cell of voltammetry consists of three electrodes: working electrode, reference electrode, and auxiliary electrode. The graphite electrode was used as working electrode; the saturated silver chloride was used as reference electrode; platinum electrode material was as auxiliary electrode. Before each experiment, glassy carbon electrode surface was polished with figure eight motion on a polishing pad [24]. After mechanical cleaning on polishing pad the surface of electrode was treated with 0.1M HNO, solution, afterwards with 0.1M NaOH solution and then was rinsed with distilled water in order to avoid any surface contamination. CV measurement parameters were kept constant in all experiments. Conditions of cycles: start potential was -0.050 (V), end potential was 2.000 (V); Hydrodynamic (measurement): cleaning potential was 0.800 (V), cleaning time was 60 (s), deposition potential was -0.600 (V), deposition time was 60 (s), equilibration time was 5.000 (s). Sweep: start potential was -0.050 (V), first vertex potential was -0.900 (V), second vertex potential was 0.900 (V), voltage step 0.009 (V), sweep rate 0.1 V/s.

The x-ray spectrum identification of elemental composition on surface of electrode and SEM analysis were done on The Energy-dispersed INCA Energy spectrometer from Oxford Instruments (England), located in the electro-probe micro analyzer with the brand "Superprobe 733". (U=25  $\kappa$ V, I=25 mA). During the electrolysis process, the electrolyte solution was stirred with magnetic stirrer whose basic brand is IKA RET to ensure liquid samples are homogeneous in consistency and temperature. Electrolysis process was carried out during 30 min. The potential of electrolysis was 30 mV.

In electrolysis, the graphite was used as cathode material, while platinum was used as anode. Before every electrolysis process the electrode surface was degreased, cleaned, and rinsed with distilled water, then after dried electrodes was weighed on analytical balances. Electrolysis cell, voltammetry, ammeter, rheostats are main parts of the electrolytic device. The voltage maintained during electrolysis was 0.26 V.

The reagents used at investigating: Na<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub> were used with the constant concentration of 0.1M. The concentration of depolarizer NH<sub>4</sub>ReO<sub>4</sub> under study was constant 0.001 M. The concentration of nickel sulfate NiSO<sub>4</sub> was 0.001 M. The citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> used with concentrations between 0.1-0.001 M. All reagents were of analytical grade. All solutions were prepared in accordance to the standard and was stored according to the standard.

## 2.1 Electrolysis of ammonium perrhenate

Electrolysis process was conducted with graphite electrode as cathode and platinum electrode as anode. The electrolysis time was 30 min. After CV results electrolysis of above described 3 experiments were investigated.

Experiment 1: Background electrolyte  $Na_2SO_4$  (0.1 M) 20 ml,  $NH_4ReO_4$  (0.001 M) 10 ml, citric acid (0.01 M) 10 ml.

Experiment 2: Background electrolyte  $KNO_3$  (0.1 M) 20 ml, NH<sub>4</sub>ReO<sub>4</sub> (0.001 M) 10 ml, citric acid (0.01 M) 10 ml.

Experiment 3: Background electrolyte  $Na_2SO_4$  (0.1 M) 20 ml,  $NH_4ReO_4$  (0.01 M) 10 ml, nickel and citric ions (0.01 M) 10ml.

Reduction process of perrhenate ions were conducted in presence of complexing agent citric acid at 3 different background electrolytes. The electrolysis time was about 30 minute. After electrolysis the different types of films were obtained depending on background electrolyte. Before electrolysis each electrode mass were weighed and values were written. After electrolysis they were weighed again in order to find mass difference.

#### 3. Results and Discussion

3.1 Reduction and oxidation of perrhenate ions in the presence of citric acid in background sodium sulfate electrolyte

Sodium sulfate electrolyte was taken as background electrolyte, whereas citric acid was added as complexing agent in the redox process of perrhenate ions from aqueous solution. In order to investigate the influence of citric acid at first experiment, the volume of citric acid was varied and concentration of perrhenate ions and background sulfate electrolyte were kept constant.

As it can be seen from the voltammograms (Figures 1,2), the reduction potential of perrhenate ions corresponds to -0.5 V, notably this peak appeared when volume of citric acid was 8 ml and perrhenate ions volume was 10 ml. In presence of citric acid perrhenate ions oxidized between 0.35-0.6 V potentials. In oxidation curve of perrhenate ions multi peaks in potentials about 0.25-0.3V and 0.55-0.6V were observed. They give the indication according literature reviews the different oxidation state of rhenium, or correspond to the different oxides of rhenium. Relying on information from literature review the rhenium oxidizes in the form of different oxides in following potentials [20]:

ReO <sub>4</sub> <sup>-</sup> +2H <sup>+</sup> +e-=ReO <sub>3</sub> +H <sub>2</sub> O; E=+0.77B	(1.1)	
$ReO_{3}+2H^{+}+2e^{-}=ReO_{2}+H_{2}O; E=+0.4B$	(1.2)	
ReO_+4H <sup>+</sup> +4e <sup>-</sup> =Re+2H_O; E=+0.26B	(1.3)	

According to works of Noar and Eliaz it was found that citric acid and perrhenate form complex  $[ReO4H2Cit]^{2-}$  [25]. Perrhenate ion is an anion, so it has a negative charge, and cathode also has a negative charge. In order to reduce perrhenate ions into rhenium some energy requires to overcome repulsion force between cathode and perrhenate ions. It is an additional hindering factor to reduce rhenium. It can be predicted that in anodic potential formed complex ions due to strong electrostatic forces can be adsorbed on surface of electrode and oxidize easily. 0.35 V potential matches with oxidation potential of  $ReO_4^{-}/Re^0$ . By analyzing the graphs, it can be observed that with increasing of citric acid concentration the anodic peaks decreased, accordingly the value of current is decreased.

In the second experiment, potassium nitrate was chosen as second background electrolyte. Concentration of potassium nitrate and perrhenate ions concentration were constant as in previous first experiment.



**Figure 1** – The reduction polarization curve of 0,001 M ammonium perrhenate ( $NH_4ReO_4$ ) in the presence of 0.001 M citric acid on the graphite electrode in background solution of 0.1M Na<sub>2</sub>SO<sub>4</sub>



Figure 2 – The oxidation polarization curve of 0,001M ammonium perrhenate ( $NH_4ReO_4$ ) in the presence of 0.001 M citric acid on the graphite electrode in background solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub>

The reduction potential of perrhenate ions was moved towards cathodic area when increasing concentration of citric acid in electrolyte from -0,35 V to -0,55 V (Figure 3). One weak peak in potential around 0.35 V was observed in anodic area in  $KNO_3$  electrolyte without presence of citric acid. As it is seen from Figure 4 the multi anodic peaks at 0.35 V, 0.6 V, 0.7 V appeared at adding of citrate ions into electrolyte. The first peak might be the peak of phase sedimentation on surface of graphite electrode. The next peaks might be the peaks of adsorptions and oxidations. The initial peak of oxidation was shifted from 0.3 V to 0.35 V of anodic area. In the next oxidation, the peaks were not noticeable in oxidation potential. It was



**Figure 3** – Polarization reduction curves of 10 ml 0.001 M of perrhenate ions in the presence of 0.001 M citric acid in 0.1 M KNO<sub>3</sub> background solution



**Figure 4** – Polarization oxidation curves of 10 ml of 0.001M perrhenate ions in the presence of 0.001 M citric acid in 0.1M KNO<sub>3</sub> background solution

predicted that they might indicate the oxidation potentials of following compounds  $\text{ReO}_4^-/\text{Re}^0$ , +36 V,  $\text{ReO}_4^-/\text{ReO}_2$ +0.594 V,  $\text{ReO}_4^-/\text{ReO}+0.77$  V.

The following solutions were taken for further investigation:  $Na_2SO_4$  (0.1 M) 10 ml,  $H_2SO_4$  (0.1 M) 10 ml,  $NH_4ReO_4$  (0.001 M) 10 ml, nickel and citrate ions' volume ratio at 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 1:9. As it is observed (Figure 5), the reduction process was around at -0.45V potential.

The alloy of nickel and rhenium is reduced on the surface of electrode. From Figure 6 two anodic dissolution processes were noticed, first one corresponds to 0.45 V potential, second – to 0.65 V potential. They confirm that the first peak is the peak of nickel oxidation; the second one corresponds to the rhenium oxidation process.



**Figure 5** – Polarization reduction curves of 0.001 perrhanate ions in the presence of 0,001M nickel sulfate and citric acid in different ratio of NiSO<sub>4</sub>: $C_6H_7O_8$ 



Figure 6 – Polarization oxidation curves of 0.001 M perrhenate ions in the presence of 0.001 M nickel sulfate and citric acid in the different ratio of NiSO<sub>4</sub>:C<sub>2</sub>H<sub>2</sub>O<sub>8</sub>

The reaction of these processes explained in following way as given below. According to investigation of Noar [25] during adsorption process of nickel on surface of electrode occur intermediate space, which create proper condition to reduction process of perrhenate ions until metallic form.

$$[Ni(Cit)2]^{4-} = Ni^{2+} + 2Cit^{3-}$$
(1.4)

$$Ni^{2+} + 2e = Ni^0$$
 (1.5)

$$7Ni^{0} + 2(ReO_{4}H,Cit)^{2^{2}} + 16H + = 7Ni^{2^{+}} + 2Re^{0} + 8H_{2}O + 6H^{2^{-}}$$

### 3.2 Results obtained from X-ray analysis

X-ray analysis spectra of deposited film was carried out. Rhenium deposition from  $Na_2SO_4$  and  $KNO_3$  in the presence of citric acid were about 60.83-65.5 and 92.92-93.65 % respectively (Table 1). According to X-ray analysis, codeposited nickel and rhenium alloy content found to be about 80.94-82.52 % rhenium and about 14.10-11.83 % of nickel with impurities of 4.96-5.66 %.

Appearance of obtained films after electrolysis was different. In the first experiment, the color of coated film was between grey and black. In the second experiment, the film color was black, in the third – it was shiny yellow. The film obtained in the third experiment proved the reduction of the

alloy, as the color of the film became shiny. The further investigation of the obtained film by SEM and EDS methods has been shown in Table 2. It should be noticed, in the first experiment in sodium sulfate background electrolyte deposited film was not uniform. In case of the second experiment, the deposited film in potassium electrolyte was more densely located comparing with the first experiment. Nevertheless, there are still empty places between deposited particles. According to the third experiment, it can be concluded that the alloy has very high density, therefore, in Table 3 it cannot be seen as porous film.

#### Table 1 - X-ray data and deposited film mass after electrolysis

Content Experiment	Re, %	Ni, %	Other impurities, %	Deposited $\text{Re}_{x}O_{y}$ and ReNi after electrolysis, ( $\Delta m$ ), g
Na <sub>2</sub> SO <sub>4</sub> C <sub>5</sub> H <sub>2</sub> O <sub>8</sub>	60.83-65.5		37.51-25.54	0.0008
KNO <sub>3</sub> C <sub>6</sub> H <sub>7</sub> O <sub>8</sub>	92.92-93.65		7.08-6.35	0.0009
Na <sub>2</sub> SO <sub>4</sub> , NISO <sub>4</sub> , C <sub>6</sub> H <sub>7</sub> O <sub>8</sub>	80.94-82.52	14.10-11.83	4.96-5.66	0.0018

**Table 2** – The appearance of graphite electrodes after electrolysis in the presence of depolarizer  $NH_4ReO_4$  in following supporting electrolytes

Na<sub>2</sub>SO<sub>4</sub> and citrate bath

KNO<sub>3</sub> and citrate bath

Na<sub>2</sub>SO<sub>4</sub>, citrate and NiSO<sub>4</sub>





**Table 3** – SEM and EDS pictures of obtained films after electrolysis in the presence of depolarizer  $NH_4ReO_4$  in following supporting electrolytes:



#### 4. Conclusion

The deposition of rhenium in the presence of citric acid using KNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> background electrolytes on graphite electrode was studied. The recovery and oxidation potentials of rhenium in these electrolytes were determined using cyclic voltammetry. The content and morphology of deposited film on electrode was identified by using X-ray method and SEM method. Deposited film in the background electrolyte of sodium sulfate was non-uniform. It was observed that the reduction potential of perrhenate ions from Na2SO4 in the presence of citric acid was not experienced potential shift, but current density decrease was observed. In oxidation area with addition of citric acid into the cell shift of the initial fist peak from 0.25V to 0.35V potential and from 0.5V to 0.6V potential was detected by indicating inhibitor effect of citric acid. In case of KNO, background electrolyte the addition of citric acid into the system shifted reduction potential of perrhenate ions from

-0.35V to -0.55V showing also inhibitory effect of citric acid into reduction potential. In the oxidation potentials multi peaks appeared by addition of citric acid which was not detected from  $KNO_3$  without citric acid. The film was deposited more dense with more rhenium content from the potassium nitrate than from sodium sulfate electrolyte in the range 92.92-93.65 and 60.83-65.5 respectively. In presence of nickel sulfate and citric acid the yield of deposited alloy contained 80.94-82.52 % rhenium and about 14.10-11.83 % of nickel with impurities 4.96-5.66% which was confirmed by X-Ray analysis. Reduction potential corresponded to -0.5V. Two oxidation peaks was detected at 0.45V and 0.65V.

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## **References (GOST)**

1 Uscategui A.V., Mosquera E., Cifuentes L. Transmission electron microscopy study of electrodeposited rhenium and rhenium oxides // Materials Letters. – 2013. – Vol.94. – P.44-46.

2 Naumov A.V. Rhythms of rhenium // Russian Journal of Non–Ferrous Metals. – 2008. – Vol.48, Is.6. – P.418-423.

3 Polyak D.E. Rhenium [Advance release]. – 2011.

4 Casas J.M., Sepúlveda E., Bravo L., Cifuentes L. Crystallization of sodium perrhenate from NaReO4–H2O–C2H5OH solutions at 298 K // Hydrometallurgy. – 2011. – Vol.113-114. – P.192-194.

5 Cao H., Chai D., Wu L., Zheng G. Communication—A Mechanistic Study on Electrodeposition of Rhenium from Acidic Solution of Ammonium Perrhenate // Journal of The Electrochemical Society. – 2017. – Vol.164, Is.13. – P.D825-D827.

6 Veerakumar P., Rajkumar C., Chen S.M., Thirumalraj B., Lin K.C. Activated porous carbon supported rhenium composites as electrode materials for electrocatalytic and supercapacitor applications // Electrochimica Acta. – 2018. – Vol.271. – P.433-447.

7 Zhulikov V.V., Gamburg Y.D. Electrodeposition of rhenium and its alloys // Russian Journal of Electrochemistry. – 2016. – Vol.52, Is.9. – P.847-857.

8 Ni J.Q., Han K.Q., Yu M.H., Zhang C.Y. Effect of sodium citrate on electrochemical behaviour of copper in acid bath // Materials Science Forum. – 2018. – Vol.913. – P.445-450.

9 Li C., Li X., Wang Z., Guo H. Mechanism of nanocrystalline nickel electrodeposition from novel citrate bath // Rare Metal Materials and Engineering. – 2015. – Vol.44, Is.7. – P.1561-1567.

10 Dolmatov V.Y., Rudenko D. V., Burkat G.K., Aleksandrova A.S., Vul' A.Y., Aleksenskii A.E., Kozlov A.S., Myllymäki V., Vehanen A., D'yakov I.A., Dorokhov A.O., Kiselev M.N. A Study of the process of gold plating from citrate and phosphate electrolytes in the presence of modified detonation nanodiamonds // Journal of Superhard Materials. – 2019. – Vol.41, Is.3. – P.169-177.

11 Kazimierczak H., Szymkiewicz K., Rogal Ł., Gileadi E., Eliaz N. Direct current electrodeposition of Zn–SiC nanocomposite coatings from citrate bath // Journal of the Electrochemical Society. – 2018. – Vol.165, Is.11. – P.D526-D535.

12 Belevskii S.S., Gotelyak A.V., Yushchenko S.P., Dikusar A.I. Electrodeposition of nanocrystalline Fe—W coatings from a citrate bath // Surface Engineering and Applied Electrochemistry. – 2019. – Vol.55, Is.2. – P.119-129.

13 Kuznetsov V.V., Golyanin K.E., Ladygina Y.S., Pshenichkina T.V., Lyakhov B.F., Pokholok K.V. Electrodeposition of ironmolybdenum alloy from ammonium-citrate solutions and properties of produced materials // Russian Journal of Electrochemistry. - 2015. - Vol.51, Is.8. - P.748-757.

14 Benaicha M., Allam M., Dakhouche A., Hamla M. Electrodeposition and characterization of W–rich NiW alloys from citrate electrolyte // International Journal of Electrochemical Science. – 2016. – Vol.11, Is.9. – P.7605-7620.

15 Ye T., Institute of Microelectronics of Chinese Academy of Sciences, IEEE Electronics Packaging Society, Zhongguo dian zi xue hui. Electronics Manufacturing & Packaging Technology Society, Fu dan da xue (Shanghai C., Institute of Electrical and Electronics Engineers Di shi ba jie dian zi feng zhuang ji shu guo ji hui yi) // The 19<sup>th</sup> International Conference on Electronic Packaging Technology. – 2018. – August 8-11, Shanghai, China.

16 Bersirova O.L., Kublanovsky V.S. Nickel–Rhenium electrolytic alloys: Synthesis, structure, and corrosion properties // Materials Science. – 2019. – Vol.54, Is.4. – P.506-511.

17 Yapontseva Y.S., Kublanovsky V.S., Vyshnevskyi O.A. Electrodeposition of CoMoRe alloys from a citrate electrolyte // Journal of Alloys and Compounds. – 2018. – Vol.766. – P.894-901.

18 Hahn B.P., May R.A., Stevenson K.J. Electrochemical deposition and characterization of mixed–valent rhenium oxide films prepared from a perrhenate solution // Langmuir. – 2007. – Vol.23, Is.21. – P.10837-10845.

19 Méndez E., Cerdá M.F., Castro Luna A.M., Zinola C.F., Kremer C., Martins M.E. Electrochemical behavior of aqueous acid perrhenate–containing solutions on noble metals: critical review and new experimental evidence // Journal of Colloid and Interface Science. – 2003. – Vol.263, Is.1. – P.119-132.

20 Salakhova E., Majidzade V., Novruzova F., Kalantarova P., Huseynova R. The electrodeposition of rhenium in alkaline and acidic elektrolytes // Journal of Chemistry and Chemical Engineering. – 2012. – Vol.6. – P.489-494.

21 Vargas–Uscategui A., Mosquera E., Chornik B., Cifuentes L. Electrocatalysis of the hydrogen evolution reaction by rhenium oxides electrodeposited by pulsed–current // Electrochimica Acta. – 2015. – Vol.178. – P.739-747.

22 Cao H., Chai D., Wu L., Zheng G. Communication — A mechanistic study on electrodeposition of rhenium from acidic solution of ammonium perrhenate // Journal of the Electrochemical Society. – 2017. – Vol.164, Is.13. – P.D825-D827.

23 Huang Q., Hu Y. Electrodeposition of superconducting rhenium with water-in-salt electrolyte // Journal of the Electrochemical

Society. - 2018. - Vol.165, Is.16. - P.D796-D801.

24 Elgrishi N., Rountree K.J., McCarthy B.D., Rountree E.S., Eisenhart T.T., Dempsey J.L. A practical beginner's guide to cyclic voltammetry // Journal of Chemical Education. – 2018. – Vol.95, Is.2. – P.197-206.

25 Naor A., Eliaz N., Gileadi E. Electrodeposition of rhenium–nickel alloys from aqueous solutions // Electrochimica Acta. – 2009. – Vol.54, Is.25. – P.6028-6035.

#### References

1 Uscategui AV, Mosquera E, Cifuentes L (2013) Mater Lett 94:44-46. http://doi.org/10.1016/j.matlet.2012.12.005

2 Naumov AV (2008) Russ J Non-Ferrous Met 48:418-423. http://doi.org/10.3103/s1067821207060089

3 Polyak DE (2011) Rhenium [Advance Release].

4 Casas JM, Sepúlveda E, Bravo L, Cifuentes L (2011) Hydrometallurgy 113-114:192-194. http://doi.org/10.1016/j. hydromet.2011.12.022

5 Cao H, Chai D, Wu L, Zheng G (2017) J Electrochem Soc 164:D825-D827. http://doi.org/10.1149/2.0871713jes

6 Veerakumar P, Rajkumar C, Chen SM, Thirumalraj B, Lin KC (2018) Electrochim Acta 271:433-447. http://doi.org/10.1016/j. electacta.2018.03.165

7 Zhulikov V V., Gamburg YD (2016) Russ J Electrochem 52:847-857. http://doi.org/10.1134/s102319351609010x

8 Ni JQ, Han KQ, Yu MH, Zhang CY (2018) Mater Sci Forum 913:445-450. http://doi.org/10.4028/www.scientific.net/MSF.913.445

9 Li C, Li X, Wang Z, Guo H (2015) Rare Met Mater Eng 44:1561-1567. http://doi.org/10.1016/s1875-5372(15)30093-x

10 Dolmatov VY, Rudenko D V., Burkat GK, Aleksandrova AS, Vul' AY, Aleksenskii AE, et al. (2019) J Superhard Mater 41:169-177. http://doi.org/10.3103/S1063457619030043

11 Kazimierczak H, Szymkiewicz K, Rogal Ł, Gileadi E, Eliaz N (2018) J Electrochem Soc 165:D526-D535. http://doi. org/10.1149/2.0421811jes

12 Belevskii SS, Gotelyak A V., Yushchenko SP, Dikusar AI (2019) Surf Eng Appl Electrochem 55:119-129. http://doi.org/10.3103/ S1068375519020054

13 Kuznetsov VV, Golyanin KE, Ladygina YS, Pshenichkina TV, Lyakhov BF, Pokholok KV (2015) Russ J Electrochem 51:748-757. http://doi.org/10.1134/S1023193515080066

14 Benaicha M, Allam M, Dakhouche A, Hamla M (2016) Int J Electrochem Sci 11:7605-7620. http://doi.org/10.20964/2016.09.17

15 Ye T, Institute of Microelectronics of Chinese Academy of Sciences, IEEE Electronics Packaging Society, Zhongguo dian zi xue hui. Electronics Manufacturing & Packaging Technology Society, Fu dan da xue (Shanghai C, Institute of Electrical and Electronics Engineers Di shi ba jie dian zi feng zhuang ji shu guo ji hui yi = the 19th International Conference on Electronic Packaging Technology : August 8-11, Shanghai, China. ISBN 9781538663868

16 Bersirova OL, Kublanovsky VS (2019) Mater Sci 54:506-511. http://doi.org/10.1007/s11003-019-00211-4

17 apontseva YS, Kublanovsky VS, Vyshnevskyi OA (2018) J Alloy Comp 766:894-901. http://doi.org/10.1016/j.jallcom.2018.07.018

18 Hahn BP, May RA, Stevenson KJ (2007) Langmuir 23:10837-10845. https://doi.org/10.1021/la701504z

19 Méndez E, Cerdá MF, Castro Luna AM, Zinola CF, Kremer C, Martins ME (2003) J Colloid Interface Sci 263:119-132. http://doi. org/10.1016/S0021-9797(03)00165-6

20 Salakhova E, Majidzade V, Novruzova F, Kalantarova P, Huseynova R (2012) J Chem Chem Eng 6:489-494.

21 Vargas-Uscategui A, Mosquera E, Chornik B, Cifuentes L (2015) Electrochim Acta 178:739-747. http://doi.org/10.1016/j. electacta.2015.08.065

22 Cao H, Chai D, Wu L, Zheng G (2017) J Electrochem Soc 164:D825-D827. http://doi.org/10.1149/2.0871713jes

23 Huang Q, Hu Y (2018) J Electrochem Soc 165:D796-D801. http://doi.org/10.1149/2.0261816jes

24 Elgrishi N, Rountree KJ, McCarthy BD, Rountree ES, Eisenhart TT, Dempsey JL (2018) J Chem Educ 95:197-206. http://doi. org/10.1021/acs.jchemed.7b00361

25 Naor A, Eliaz N, Gileadi E (2009) Electrochim Acta 54:6028-6035. http://doi.org/10.1016/j.electacta.2009.03.003