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Selection of sorption materials for the extraction of nickel and cobalt from the ore of the Gornostaevskoye deposit

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Oxidized nickel ores account for the majority of industrial ores suitable for nickel production. The processing of such ores using traditional pyrometallurgical technology is not economically viable due to the low nickel content. One of the most cost-effective methods of processing oxidized nickel ores is sulfuric acid leaching technology followed by sorption extraction. The aim of this work is to establish the kinetic and thermodynamic parameters of the sorption extraction of nickel and cobalt using iminodiacetate chelating ion-exchange sorbents from various manufacturers, to select a desorbing solution and to determine the degree of desorption. The sorption of nickel and cobalt was carried out in a weakly acidic medium from a model solution containing impurities of other metals in static and dynamic modes. The limiting sorption capacity for the studied sorbents is 18-26 mg/g for nickel and 1-2 mg/g for cobalt in the static mode. The sorption capacity in the dynamic mode for nickel is equal to 25.5 g/L for Purolite S 930, 29.2 g/L for Lewatit TP 207, 1.4 g/L, and 1.8 g/L for cobalt, respectively. The best desorption parameters are achieved when using a 2 M sulfuric acid solution. The degree of desorption for sorbents Purolite S 930 and Lewatit TP 207 exceeds 90%. The use of the Lewatit TP 207 sorbent for the extraction of nickel from the leaching solution of nickel ore of the Gornostaevskoye deposit in 5 cycles made it possible to obtain a commercial desorbate with a nickel content of 18 g/L. The use of a part of the commercial desorbate obtained in the previous cycle, further strengthened to the initial concentration of sulfuric acid, for re-extracting nickel from the saturated sorbent during a cyclic process leads to a deterioration in desorption characteristics. It is recommended to remove the commercial desorbate from the process after several cycles of desorption and supply new solution of sulfuric acid for desorption to restore the sorption parameters.

Keywords: nickel; sorption; desorption; iminodiacetate sorbents; kinetics; sorption capacity; output curves; commodity desorbate.

Горностаев кен орнының кендерінен никель мен кобальтті бөлу үшін сорбциялық материалдарды таңдау

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Тотыққан никель кендері никель өндіруге жарамды өнеркәсіптік кендердің көп бөлігін құрайды. Мұндай кендерді дәстүрлі пирометаллургиялық технология бойынша өңдеу никельдің төмен болуына байланысты экономикалық тұрғыдан тиімді емес. Тотыққан никель кендерін өңдеудің ең тиімді әдістерінің бірі күкіртқышқылды шаймалау технологиясы, содан кейін сорбциялық экстракция. Бұл жұмыстың мақсаты әртүрлі өндірушілердің иминодиацетатты хелатирлейтін ион алмастырғыш сорбенттерінің көмегімен никель мен кобальтты сорбциялық алудың кинетикалық және термодинамикалық параметрлерін белгілеу болып табылады. Никель мен кобальттың сорбциясы басқа металдардың қоспалары бар модельдік ерітіндіден сәл қышқыл ортада жүргізілді. Зерттелген сорбенттер үшін шекті сорбциялық сыйымдылық никель бойынша 18-26 мг/г және кобальт бойынша 1-2 мг/г құрайды. Десорбцияның ең жақсы параметрлеріне 2 М күкірт қышқылы ерітіндісін қолдану арқылы қол жеткізіледі. Purolite S 930 және Lewatit TP 207 сорбенттеріне арналған десорбция дәрежесі 90% – дан асады. Горностаев кен орнының никель кендерін 5 циклде сілтісіздендіру ерітіндісінен никельді алу үшін пайдалану құрамында 18 г/л никель бар тауарлық десорбат алуға мүмкіндік берді, алдыңғы циклде алынған күкірт қышқылының бастапқы концентрациясына дейін нығайтылған тауарлық десорбаттың бір бөлігін пайдалану, циклдік процесс кезінде қаныққан сорбенттен никельді қайта алу үшін десорбциялық сипаттамалардың нашарлауына әкеледі. Десорбцияның бірнеше циклын өткізгеннен кейін тауарлық десорбатты процестен шығару және десорбцияға күкірт қышқылының жаңа ерітіндісін беру ұсынылады, бұл сорбциялық көрсеткіштерді қалпына келтіруге мүмкіндік береді.

Түйін сөздер: никель; сорбция; десорбция; иминодиацетатты сорбенттер; кинетика; сорбциялық сыйымдылық; шығу қисықтары; тауарлық десорбат.

Подбор сорбционных материалов для извлечения никеля и кобальта из руды Горностаевского месторождения

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Окисленные никелевые руды составляют большую часть промышленных руд, пригодных для производства никеля. Переработка таких руд по традиционной пирометаллургической технологии экономически не выгодна ввиду низкого содержания никеля. Одним из наиболее рентабельных способов переработки окисленных никелевых руд является сернокислотная технология выщелачивания с последующим сорбционным извлечением. Целью данной работы является установление кинетических и термодинамических параметров сорбционного извлечения никеля и кобальта с помощью иминодиацетатных хелатирующих ионообменных сорбентов различных производителей. Сорбцию никеля и кобальта проводили в слабокислой среде из модельного раствора, содержащего примеси других металлов. Предельная сорбционная емкость для изученных сорбентов составляет 18-26 мг/г по никелю и 1-2 мг/г по кобальту. Наилучшие параметры десорбции достигаются при использовании 2 М раствора серной кислоты. Степень десорбции для сорбентов Purolite S 930 и Lewatit TP 207 превышает 90%. Использование сорбента Lewatit TP 207 для извлечения никеля из раствора выщелачивания никелевой руды Горностаевского месторождения в 5 циклах позволило получить товарный десорбат с содержанием никеля 18 г/л. Использование части полученного в предыдущем цикле товарного десорбата, доукрепленного до исходной концентрации серной кислоты, для повторного извлечения никеля из насыщенного сорбента при циклическом ведении процесса приводит к ухудшению десорбционных характеристик. Рекомендуется после проведения нескольких циклов десорбции выводить товарный десорбат из процесса и подавать на десорбцию новый раствор серной кислоты, что позволяет восстановить сорбционные показатели.

Ключевые слова: никель; сорбция; десорбция; иминодиацетатные сорбенты; кинетика; сорбционная емкость; выходные кривые; товарный десорбат.

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Selection of sorption materials for the extraction of nickel and cobalt from the ore of the Gornostaevskoye deposit

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1. Introduction

Nickel is a strategic metal due to the use of a large number of different alloys. The main consumers of nickel in the world market are China, the USA and Japan. Nickel is produced for large-scale commercial use in 23 countries around the world, including Russia, Canada, Indonesia and South Africa.

There are over 30 nickel and cobalt deposits on the territory of the Republic of Kazakhstan. "Kaznickel" LLP, a subsidiary of Fincraft Resources, is currently investing in the launch of mines at Gornostaevskoye, one of the largest cobalt and nickel deposits in Kazakhstan. The field is located in the East Kazakhstan region, 110 km west of Semipalatinsk. The reserves of the field are estimated at more than 1 million tons of nickel and more than 65 thousand tons of cobalt. In 2018, it was decided to choose a new strategy for the development of the field by applying the method of underground borehole sulfuric acid leaching.

Productive solutions obtained in the process of sulfuric acid leaching of oxidized nickel ores are characterized by a rather low content of the base metal (1.0-2.0 g/dm^3) and an increased content of impurities (depending on the composition of the original ore: iron, aluminum, magnesium, etc.) [1-3], which significantly complicates their further processing. The most economical method for extracting nickel from such solutions can be sorption concentration using selective ion-exchange materials.

For the sorption of nickel, cation-exchange sorbents with carboxyl, iminodiacetate, phosphonic groups, as well as polyampholytes with complexing properties are used. A number of works [4-8] describe the results of studying the sorption of nickel from solutions of various compositions on weakly acidic macroporous cation exchangers with chelate groups of iminodiacetic acid. The authors of [9] synthesized a number of new polymeric organic sorbents with functional groups of iminodipropionic acid and showed the possibility of their use for group extraction of copper, nickel, zinc, and cobalt ions.

In [10], for the concentration of copper and nickel, nitrogen and sulfur-containing polyampholyte based on granular polyvinyl chloride was used. The established regularities of sorption suggest the possibility of selective extraction of non-ferrous metal ions from technological solutions of metallurgical enterprises.

The work [11] shows the advantages (selectivity, extraction efficiency, simplicity of the sorption and desorption process) of the use of polymer complexing sorbents containing in their structure hydroxyazofunctional-analytical groups and n-substituents of various electronic nature for the concentration of trace amounts of nickel ions from various objects of complex chemical composition.

The technological scheme of processing real technological solutions developed by the authors [12] after leaching ores from a number of Ural deposits provides for sorption concentration of nickel on aminocarbon ion exchangers with subsequent desorption and precipitation of nickel hydroxide concentrate. This scheme ensures the recovery of nickel from solution into concentrate at the level of 96-98%.

Due to the wide range of sorption materials used and the complex salt composition of real technological solutions, the problem of developing effective hydrometallurgical technologies for extracting nickel and cobalt at low costs is an urgent ecological and economic problem.The aim of the work is to determine the parameters of sorption of nickel (II) and cobalt (II) ions on iminodiacetate chelating ion-exchange sorbents from a model solution and a solution of sulfuric acid leaching of ore from the Gornostaevsky cobalt-nickel ore deposit (East Kazakhstan).

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2. Experiment

2.1 Preparation of a model solution

Solutions of nickel (II) chloride ("Ukrainalitika" LLC, Ukraine, pure for analysis), calcium (II) chloride (JSC "Bashkir Soda Company", Russia, pure for analysis), cobalt (II), magnesium (II), iron (II), aluminum (III) sulfates (CJSC "Khimreaktivsnab", Russia, pure for analysis) with the desired concentration were prepared by dissolving the appropriate salt samples in distilled water. The pH value was determined by adding the required amount of 1 M of sulfuric acid solution.

2.2 Sorbent preparation for research

The sorbent was placed in a glass filled with distilled water. Water was added in such an amount that its level was 10 cm above the level of the sorbent. The sorbent was left to swell for 8 h, stirred, and then the water was decanted off. This operation was repeated until a clear and colorless wash water was obtained. To convert the sorbent into the Na^+-form, treatment was performed with a sodium hydroxide solution (1-2 mol/L) for 1-2 h with periodic stirring. The solution was decanted, the sorbent was washed with distilled water until the wash water was neutral.

2.3 Method for studying the kinetics of sorption

The study of the kinetics of sorption was carried out in a static mode. 1 g of a saturated sorbent and 100 mL of a model solution were placed in a glass. The solution with the sorbent was stirred using a mechanical stirrer at room temperature for different time intervals for each beaker (45-300 min). At the end of the sorption, the sorbent was separated from the solution by filtration through a paper filter "red ribbon" ("Chemical technologies" LLC, Russia). The filtrate was analyzed for nickel and cobalt content. Based on the data obtained, kinetic curves were plotted for the dependence of the element content in the solution on the stirring time.

The sorption capacity of ion exchanger A (mg/g) was calculated by the formula:

$$A = (C_{init} - C_{equil}) \cdot V/m,$$

where, C_{init} – initial concentration of metal in solution, mg/L;

C_{equil} – equilibrium concentration of metal in solution, mg/L;

V – volume of test solution, L;

m – mass of sorbent, g.

2.4 Selection of an eluent for desorption of the sum of elements

Desorption of nickel and cobalt was carried out by washing the saturated sorbent with different specific volumes (1-4 volumes of solution/volume of sorbent) aqueous solutions of mineral acids of various concentrations (0.25-4.0 M). The sorbent was analyzed for the content ofmetal.

2.5 Method for studying the kinetics of desorption

The study of the kinetics of desorption was carried out in a static mode. The glass was filled with 1 g of saturated sorbent and 100 mL of desorbing solution. The solution with the sorbent was stirred with a mechanical stirrer at room temperature for different time intervals for each beaker (1-10 h). At the end of desorption, the sorbent was separated from the solution by filtration through a paper filter. The sorbent was analyzedfor the content of metal.

2.6 Method for studying sorption in a dynamic mode

The adsorption of elements in a dynamic mode was carried out in a sorption column equipped with a container for feeding the leach solution. A model solution was passed through a column loaded with a sorbent from bottom to top at a specific load of 5 h^{-1}. The volume of the loaded sorbent is 30 mL. Sorption was carried out in a clamped layer. At the outlet of the column, at certain time intervals, samples of the solution were taken, which were analyzed for the content of sorbed elements. Sorption was continued until the concentration of the element in the solution at the exit from the column approaches or becomes equal to its concentration in the initial solution. At the end of the sorption, the sorbent was removed from the columns, washed with distilled water, and analyzed for the content of sorbed elements. The obtained experimental data were used to plot the output sorption curves.

2.7 Method for studying desorption in dynamic mode

The saturated sorbent was sent for desorption when it reached an equilibrium state with the initial solution. Desorption in a dynamic mode was carried out in a laboratory column. A desorbing solution is passed through a column loaded with a sorbent from bottom to top at a specific load of 1 h^{-1}. At the outlet of the column, at regular intervals, samples of the solution were taken, which were analyzed for the content of extracted components. After the end of desorption, the column was unloaded, and the sorbent was washed with distilled water. Then the content of the recoverable components in the sorbent was determined. The output desorption curves were plotted from the experimental data.

2.8 Method for ore leaching

Ore samples were pre-crushed to – 150 meshes on the ID 175M disc eraser ("Vibrotechnik" LLC, Russia) and sifted using a set of soil sieves according to State standard 12536-2014 ("Vibrotechnik" LLC, Russia). Leaching was carried out in a laboratory reactor IKA LR-2.ST (Germany) with heating and constant stirring. Leaching conditions: temperature – 60-75°C; duration – 6 h; the ratio L/S= 5/1; the initial concentration of sulfuric acid is 150 g/L. At the end of leaching, the pulp was filtered and the solution was analyzed for the content of the main components.

2.9 Method for analytical measurement

The metal content in the solution and sorbents was

determined using an inductively coupled plasma emission spectrometer ICAP 7400 Duo manufactured by Thermo Fisher Scientific (USA). The relative standard deviation of the output signal is 1.0%. The accuracy of determining the elements at the level of 0.01-0.05% rel., complete analysis of the sample in 20 sec.

For the analysis of the sorbents, decomposition was performed. The suspension of the sorbent 0.5 g is taken in a polypropylene container, determining the weight of the suspension on the analytical balance MS-4002S (Mettler Toledo) by the difference in the mass of the container. The container is filled with ~2.5 mL of concentrated nitric acid ("Technochemistry" LLP, Russia, chemical pure), the lid is screwed on and placed in a heat block heated to 80°C. They are kept in a thermoblock until the sample is homogenized. After that, take an aliquot of 0.25 mL of concentrated hydrofluoric acid (Sigma-Aldrich, Canada, pure for analysis), pour it into the solution, place it in a thermoblock heated to 80°C. Stand with the lid open for no more than 5 min. After that, the sample is cooled and brought to the mark with deionized water.

Working standard solutions were prepared from the multi-element standard High Purity Standards (USA) 48 element standards ICP-MS-68A-100 Solution A in 2% HNO_3. The metal content was determined according to ST RK ISO 8288-2005 (ISO 8288-1986) "Water quality. Determination of cobalt, nickel, copper, zinc, cadmium and lead. Flame atomic absorption spectrometric methods".

3. Results and Discussion

For testing the sorption extraction of nickel and cobalt from solutions, the following commercially available iminodiacetate chelating ion-exchange sorbents were selected:

1. Amberlite IRC 748 (Dow Chemical Company, USA)
2. Lewatit TP 207 (Lanxess, Germany)
3. Lewatit TP 208 (Lanxess, Germany)
4. Purolite S 930 (Purolite, UK)
5. Dowex A1 (Dow Chemical Company, USA)

Iminodiacetate chelating sorbents of this class show positive results in the extraction of nickel [4-8]. The 5 brands of sorbents selected by us are produced on an industrial scale. The parameters of the sorbents are given in Table 1. No characteristics were found for Dowex A1 sorbent.

It is known that nickel ore leaching solutions are characterized by high acidity (pH = 0.3-0.5). In the strongly acidic region, sorbents containing weakly acidic groups are in an undissociated state and have a low capacity with respect to metal cations. At these pH values, the solution also contains a significant amount of ferric and aluminum ions, which have a competing effect on the sorption of nickel and cobalt, reduce the selectivity of extraction and contaminate sorbents, since they are difficult to desorb. In this regard, the sorption extraction of target components should be carried out after removing the main amount of interfering impurities by bringing the pH of the solution to 3.8-4.6 and precipitation. To oxidize iron, a small amount of hydrogen peroxide is preliminarily introduced into the solution. The most accessible substances for neutralization are lime, limestone, caustic, soda ash, ammonium hydroxide. By this operation, up to 95% of iron, copper, aluminum (if present in the solution) can be removed from solutions.

Typical components of leach solutions such as magnesium, manganese and calcium are not removed during the precipitation process and are recovered to a small extent by this type of sorbent.

For the initial experiments on the sorption of nickel and cobalt from salt solutions, a model solution with a pH of 4.5 was prepared (Table 2). These metals are always present in leaching solutions and can have a competing effect on the sorption process of the target components.

The kinetic curves of the sorption of nickel and cobalt from a given solution by the studied sorbents in the Na^+-form is shown in Figure 1 and Figure 2.

The time to reach equilibrium during sorption in a static mode for the studied sorbents is about 5 h. During this time, all sorbents come into equilibrium with the solution and no further increase in capacity is observed. In Table 3, values of the equilibrium capacity for nickel and cobalt, achieved at a sorption time of 5 h in a static mode.

Table 1 – Characteristics of sorbents

Parameter	Amberlite IRC 748	Lewatit TP 207	Lewatit TP 208	Purolite S 930
Capacity, eq/L	1.35	2.0	2.9	1.8
Water content, %	60-65	55-60	55-60	55-65
Particle density, g/mL	1.7	1.1	1.17	1.13
Shipping weight, g/L	750	720	740	710-745

Table 2 – Composition of the model solution

Element	Ni	Co	Fe	Al	Mg	Ca
Concentration, g/L	0.378	0.030	0.025	0.044	3.500	0.580

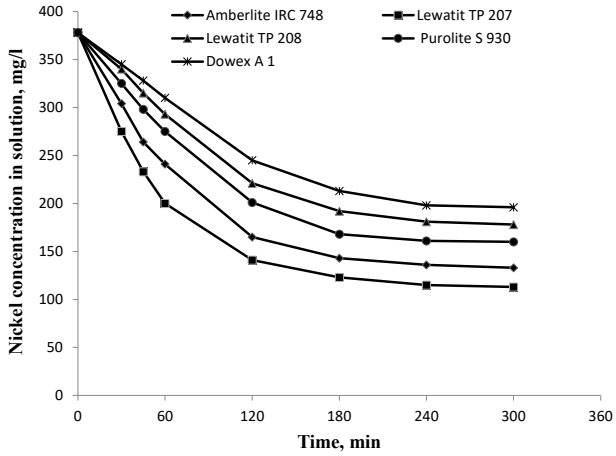

Figure 1 – Kinetic curves of nickel sorption by sorbents in Na^+-form

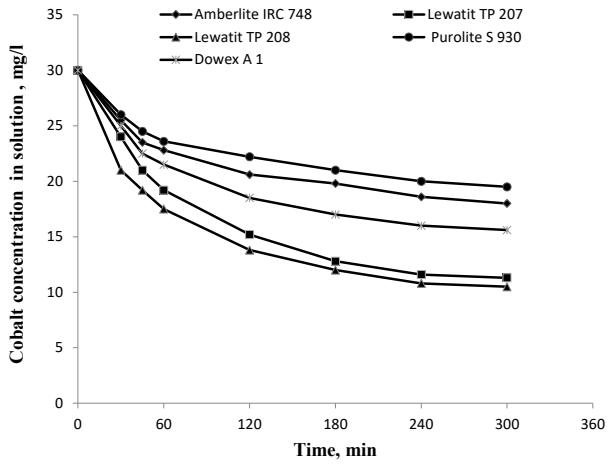

Figure 2 – Kinetic curves of cobalt sorption by sorbents in Na^+-form

According to the values of the equilibrium capacity for nickel from a solution of the investigated composition, the sorbents can be arranged in the following row:

Lewatit TP 207>Amberlite IRC 748>Purolite S 930>Lewatit TP 208>Dowex A1.

For the sorption of cobalt, the following dependence on the values of the equilibrium capacity is observed:

Lewatit TP 208>Lewatit TP 207>Dowex A1>Amberlite IRC 748>Purolite S 930.

At the same time, it can be noted that under the studied conditions all sorbent samples show similar characteristics. The highest sorption capacity for nickel is observed for AmberliteIRC

Table 3 – Equilibrium capacity of the studied sorbents for nickel and cobalt

Sorbent model	A, mg/g	
	Nickel	Cobalt
Amberlite IRC 748	24.5	1.2
Lewatit TP 207	26.5	1.9
Lewatit TP 208	20.0	2.0
Purolite S930	21.8	1.1
Dowex A1	18.3	1.4

Table 4 – Results of desorption of nickel and cobalt from the saturated sorbent AmberliteIRC 748 with acid solutions

Acid	Concentration, M	Specific volume	Degree of desorption, %	
			Nickel	Cobalt
HNO_3	0.5	1	61	56
		2	74	68
		4	90	84
	1	1	94	88
		2	95	95
		4	95	99
	2	1	100	100
	4	1	100	100
HCl	0.5	1	54	61
		2	68	83
		4	77	89
	1	1	65	87
		2	72	91
		4	89	95
	2	1	93	97
		2	95	100
		4	98	100
	4	1	98	100
		2	100	100
H_2SO_4	0.25	1	64	67
		2	69	74
		4	81	80
	0.5	1	79	75
		2	82	84
		4	85	87
	1	1	91	95
		2	93	98
		4	93	100
	2	1	95	100
		2	100	100

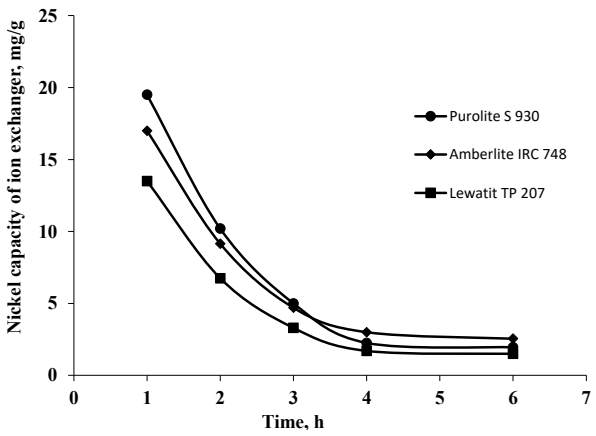

Figure 3 – Kinetic curves of nickel desorption by solution 1 M sulfuric acid

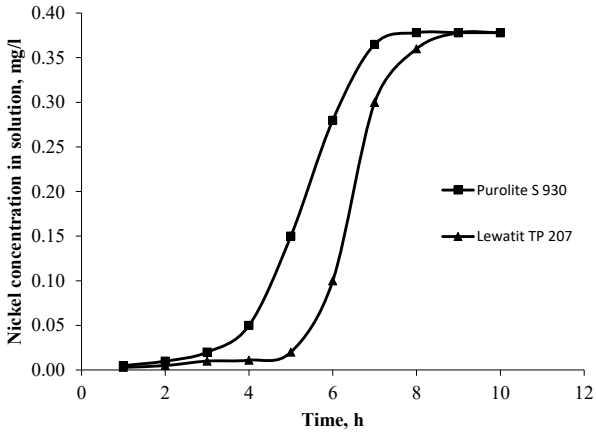

Figure 4 – Output curves of nickel sorption in dynamic mode

748 and LewatitTP 207 ion exchangers, for cobalt – for LewatitTP 208 and LewatitTP 207 ion exchangers. Analysis of resin samples after sorption does not reveal significant amounts of aluminum and iron.

The dependence of the degree of desorption of nickel and cobalt on the nature of the eluent for the Amberlite IRC 748 sorbent was studied (Table 4).

As shown by the results, the quantitative desorption of nickel and cobalt occurs when they are eluted from the sorbent 1sp.vol.2 M HNO_3, 4 sp.vol. 2 M HCl, 2 sp.vol. 2M H_2SO_4. The degree of desorption in these cases is 98-100%.

Next, we studied the kinetics of nickel desorption from samples of saturated sorbents AmberliteIRC 748, LewatitTP 207, PuroliteS 930, which showed the best performance at the sorption stage. In Figure 3 shows the kinetic curves of nickel desorption with a 1 M sulfuric acid solution.

The residual concentration of nickel in the sorbent is about 2 mg/g. According to this indicator, the studied sorbents are arranged in a row:

LewatitTP 207 >PuroliteS 930 >AmberliteIRC748.

A more substantiated answer about the parameters of the sorption extraction of nickel from solutions can be obtained from the results of an experiment carried out under dynamic conditions. Dynamic studies were carried out for two sorbents PuroliteS 930 and LewatitTP 207 and included the process of sorption until the equilibrium concentration for nickel was reached and the process of desorption with a sulfuric acid solution.

The experimental data were used to plot the output sorption curves (Figure 4).

The capacity of the studied sorbents when studying the sorption of nickel in a dynamic mode from a solution of this composition was 25.5 g/l for Purolite S 930 and 29.2 g/l for Lewatit TP 207. At the end of saturation, the sorbent was also analyzed for the cobalt content. The following data were obtained: for Purolite S 930 – 1.4 g/L, for Lewatit TP 207 – 1.8 g/L.

Next, we studied the desorption of nickel in a dynamic mode with a sulfuric acid solution with a concentration of 120 g/L. The output desorption curves are shown in Figure 5

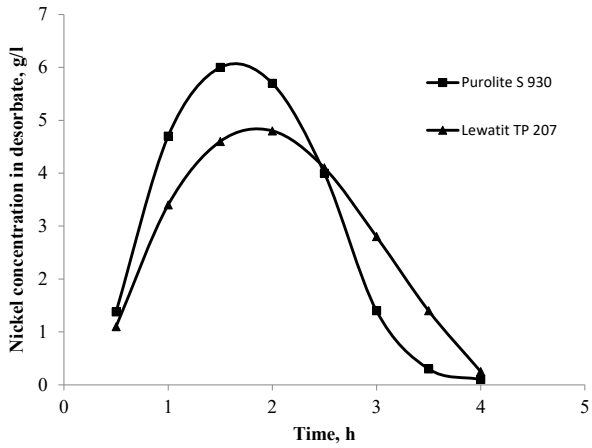

Figure 5 – Output curves of nickel desorption in dynamic mode

Tabe 5 lists some parameters of the dynamic desorption process.

Thus, in the dynamic mode, the best sorption indices were obtained for the Lewatit TP 207 sorbent, and for the desorption, for the Purolite S 930 sorbent.

The sorbent Lewatit TP 207 was subsequently used for the sorption extraction of nickel from a real solution of leaching ore from the Gornostaevskoyedeposit after a solution of hydrolytic cleaning (Table 6) in a closed cyclic mode.

The hydrometallurgical processing scheme included 5 cycles of sorption and desorption in a closed dynamic mode.

Table 5 – Nickel desorption parameters in dynamic mode

Sorbent	Maximum concentration of nickel in the desorbate, g/L	Residual concentration of nickel in the sorbent, g/L	Degree of desorption, %
Purolite S 930	5.7	1.5	94
Lewatit TP 207	4.8	2.9	90

Table 6 – The composition of the solution for leaching nickel ore after hydrolytic cleaning

Element	Ni	Co	Fe	Al	Cr
Content, g/L	1.38	0.055	0.014	<0.005	<0.005

Two series of experiments were performed. In the first series, the desorption of nickel in each cycle was carried out with a new solution of sulfuric acid; in the second series, a part of the commercial desorbate obtained in the previous cycle was used for desorption, backed up to an initial sulfuric acid concentration of 120 g/L. Table 7 and 8 show the main parameters of the investigated processes.

In the second series of experiments, after five cycles, a commercial desorbate with a sufficiently high nickel content was obtained. However, in this case, after desorption, a more significant accumulation of nickel, cobalt and iron is observed in the sorbent than in the first series of experiments. As one of the factors that can limit the process of nickel desorption, an increase in the concentration of nickel in the desorbate can be considered when the process is carried out in a closed mode.

Table 7 – Parameters of sorption-desorption processes for the extraction of nickel and cobalt in the first series of experiments (desorption with sulfuric acid solution)

№ cycles	Content in sorbent, g/L						Content in commercial desorbate, g/L	
	Ni		Co		Fe		Ni	Co
	Sorption	Desorption	Sorption	Desorption	Sorption	Desorption		
1	39.4	3.7	2.58	0.33	0.28	0.031	8.92	0.56
2	39.4	3.9	2.57	0.35	0.30	0.039	8.89	0.56
3	39.1	3.9	2.57	0.37	0.33	0.045	8.80	0.55
4	39.0	4.2	2.55	0.39	0.33	0.042	8.70	0.54
5	38.7	4.4	2.51	0.39	0.34	0.048	8.58	0.53

Table 8 – Parameters of sorption-desorption processes for the extraction of nickel and cobalt in the second series of experiments (desorption with an additional fortified commercial desorbate)

№ cycles	Content in sorbent, g/L						Content in commercial desorbate, g/L	
	Ni		Co		Fe		Ni	Co
	Sorption	Desorption	Sorption	Desorption	Sorption	Desorption		
1	39.4	3.7	2.58	0.33	0.28	0.031	8.92	0.56
2	39.7	3.9	2.66	0.38	0.32	0.039	10.80	0.77
3	39.8	4.6	2.70	0.41	0.34	0.052	12.65	0.89
4	39.8	5.1	2.74	0.43	0.39	0.061	15.14	1.05
5	40.2	6.4	2.70	0.49	0.45	0.069	18.21	1.24

To study the effect of the accumulation of nickel in the solution on the desorption indices, experiments were carried out on model solutions with a nickel content from 3 to 12 g/L (sulfuric acid concentration of 120 g/Ll). Nickel was desorbed from a saturated sorbent containing 39.5 g/L of nickel at a solution/sorbent ratio of 100/1 and stirring for 2 h. The experimental results are shown in Table 9.

The accumulation of nickel in the desorption solution up to 12 g/L leads to a decrease in the degree of its desorption from 90 to 58%.

Table 9 – Influence of the nickel content in the desorbate on the indicators of its desorption from the saturated sorbent

Nickel content in desorption solution, g/L	Residual nickel content in sorbent, g/L	Degree of desorption, %
0	3.7	90.6
3	6.4	83.8
4	8.7	78.0
6	10.5	73.4
8	13.7	65.3
10	15.0	62.0
12	16.4	58.0

4. Conclusion

All the sorbent brands studied in this work belong to the same class of materials –iminodiacetate chelating ion-exchange sorbents, which are used for selective concentration and separation of components by adjusting pH and sorption conditions. During the study, such parameters as the time required for sorption extraction, the equilibrium capacity of the sorbents, and the degree of desorption were determined. Under the conditions of sorption of nickel and cobalt from the model solution, all sorbents exhibit similar kinetic and thermodynamic properties. The highest sorption capacity for nickel is observed for AmberliteIRC 748 and LewatitTP 207 ion exchangers, for cobalt – for LewatitTP 208 and LewatitTP 207 ion exchangers. DowexA1 resin exhibits the worst kinetic and capacitive characteristics. Desorption of nickel with a solution of sulfuric acid with a concentration of 120 g/L for Purolite S 930 yielded a commercial desorbate with a maximum nickel content of 5.7 g/L (desorption degree 94%).

The use of the Lewatit TP 207 sorbent for the sorption extraction of nickel from the leaching solution of nickel ore from the Gornostaevskoyedeposit in 5 cycles made it possible to obtain a commercial desorbate with a nickel content of 18.2 g/L. However, when the process is conducted cyclically, a deterioration in desorption characteristics is observed. This is confirmed by an additional experiment on desorption by solutions containing nickel in different concentrations. An increase in the concentration of nickel in the desorbate during the process in a closed mode leads to a decrease in the degree of its desorption from 90 to 58%. Therefore, after several cycles of desorption, it is necessary to remove the commercial desorbate from the process and supply a new solution of sulfuric acid for desorption, which makes it possible to restore the sorption parameters. The use of this technique in the 6th cycle of the second series of experiments made it possible to restore the sorption properties of the sorbent and to obtain the sorption indices comparable with the 1st cycle.

Further experiments should be aimed at the selection of sorbents that provide the best indicators for the recovery of nickel and cobalt, and optimization of the parameters of sorption-desorption processes.

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Synthesis of nanocomposite material through modification of graphene oxide by nanocellulose

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Intensive research of nanocomposites contributes to the development of new materials in the fields of medicine, nanoelectronics, energy, biotechnology, information technology. Therefore, the synthesis of new materials by modifying of graphene oxide (GO) with nanocellulose and the study of its properties are of great interest. In this study synthesized nanocomposite material by modifying of graphene oxide (GO) from activated carbon (BAU-A) in a 1:1 volume ratio with nanocellulose (NC) from hemp stems belonging to the annual plant, and their chemical structure was studied by FTIR and UV-spectroscopy. The results of the study showed the absorption of the etheric bond C = O in the UV spectrum at full length 243 nm. The IR spectrum showed all the new etheric bonds O = C - OH at a wavelength of 1625 cm^{-1}. The average particle sizes of GO was 352 nm and NC was 470 nm in length and 80 nm in width. The SEM analysis indicating the NC as a contact layer between ultralow thicknesses of the GO layers. The XRD analysis indicated GO-NC composite film is a substance comprising GO and NC. According to the results, modification of graphene oxide showed that its scope can be expanded as much as possible.

Keywords: graphene; graphene oxide; activated carbon; nanocellulose; nanocomposite.

Графен оксидін наноцеллюлоза көмегімен модификациялау арқылы нанокомпозиттік материал синтездеу

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Нанокомпозиттер саласының интенсивті зерттелуі медицина, наноэлектроника, энергетика, биотехнология, информациялық технология салаларында жаңа материалдар жасалуына әсер етеді. Сондықтан графен оксидін (ГО) наноцеллюлозамен (НЦ) модификациялау арқылы жаңа материалдар синтездеу және оның қасиеттерін зерттеу барынша қызығушылық тудыруда. Бұл зерттеуде белсендірілген көмірден (БАУ-А) алынған графен оксидін біржылдық өсімдікке жататын қарасора сабағынан алынған наноцеллюлозамен 1:1 көлемдік қатынасында модификациялау арқылы нанокомпозиттік материал синтезделді. Алынған нанокомпозиттің химиялық құрылысындағы ерекшеліктері ультра күлгін (УК) және инфрақызыл (ИҚ) спектроскопия әдістерімен зерттелді. Зерттеу нәтижесі бойынша УК спектрінде 243 нм толық ұзындығында эфирлік С=О байланыстың жұтылуын көрсетті. Ал ИҚ спектрінде 1625 $см^{-1}$ толқын ұзындығында О=С–ОН жаңа эфирлік байланыстың бар екендігін көрсетті. ГО бөлшектерінің орташа өлшемдері 352 нм, ал НЦ ұзындығы 470 нм және ені 80 нм болды. SEM талдаулары бойынша НЦ ГО ультра қалыңдықтағы қабаттары арасындағы байланыс қабаты ретінде болатындығын көрсетті. Рентгендік талдау бойынша ГО-НЦ композициялық пленкасының құрамы жағынан ГО және НЦ тұратындығын көрсетті. Алынған нәтижелер бойынша графен оксидін модификациялау оның қолданылу аясын барынша кеңейтуге болатындығын көрсетті.

Түйін сөздер: графен; графен оксиді; белсендірілген көмір; наноцеллюлоза; нанокомпозит.

Синтез нанокомпозитного материала путем модификации оксида графена наноцеллюлозой

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Интенсивные исследования в области нанокомпозитов способствуют разработке новых материалов в области медицины, наноэлектроники, энергетики, биотехнологий, информационных технологий. Поэтому синтез новых материалов путем модификации оксида графена (GO) наноцеллюлозой и изучение его свойств представляет большой интерес. В этом исследовании был синтезирован нанокомпозитный материал путем модификации оксида графена (GO) из активированного угля (БАУ-А) в объемном соотношении 1:1 с наноцеллюлозой (NC) из стеблей конопли, принадлежащих однолетнему растению. Их химическая структура была изучена с помощью FTIR и УФ-спектроскопия. Результаты исследования показали поглощение эфирной связи С=О в УФ-спектре при полной длине 243 нм, а в ИК-спектре обнаружены новые эфирные связи О=С-ОН на длине волны 1625 $см^{-1}$. Средний размер частиц GO составлял 352 нм, а NC - 470 нм в длину и 80 нм в ширину. Анализ SEM показывает NC как контактный слой между сверхмалыми толщинами слоев GO. Рентгеноструктурный анализ показал, что композитная пленка GO-NC представляет собой вещество, содержащее GO и NC. По результатам модификация оксида графена показала, что область его применения может быть максимально расширена.

Ключевые слова: графен; оксид графена; активированный уголь; наноцеллюлоза; нанокомпозит.

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Synthesis of nanocomposite material through modification of graphene oxide by nanocellulose

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1. Introduction

Recently, graphene, graphene oxide (GO) and carbon materials have attracted the attention of scientists, due to their unique physical-mechanical, electronic characteristics, high thermal conductivity, hardness and strength and excellent adsorption properties [1]. One of the main reasons is that the membrane made of graphene oxide is widely used in the production of sensors, sensors, supercapacitors sensitive to moisture, temperature, organic gases [2].

Currently, graphite is used as a raw material in the synthesis of GO. However, as a result of comparative studies, the value of the fixed layer diameter of 78-92% of activated carbon is on average L_a = 0.75 nm, and the number of carbon atoms in each layer is 15-18. When the carbon content exceeds 92%, the diameter of the stable layer immediately increases by 1 nm, and the number of carbon atoms in each layer becomes more than 30. Also, the structure of activated carbon differs from graphite in that it is not crystalline, but mesomorphic, it is a flat hexagonal lattice of carbon atoms with open carbon chains connected peripherally to conduct functional groups. This allows the scattered carbon atoms to combine during strong oxidation to form closed-chain, crystalline layers [3]. Activated carbon is also the most suitable source of raw material for the synthesis of graphene oxide due to its low cost compared to graphite, high adsorption capacity and high surface area.

Despite the universal nature of GO, the main disadvantage is that the structure is unstable in a humid environment [4,5]. To eliminate this shortcoming, at present, the modification of graphene oxide with various substances is widespread.

The production of graphene with bio-tribological properties necessary for the biomedical industry was studied by chemical modification of GO using hydrazine hydrate [6], dimethylhydrazine [7], hydroquinone [8], $NaBH_4$ [9].

Recently, the production of new nanocomposites by modification of GO with nanocellulose has become an important area of research of nanomaterials. [10-12] studies have shown that the dielectric constant of the nanocomposite obtained by ultraviolet reduction of cellulose nanoparticles films and GO in a nitrogen medium has increased to 88.9. It is known that the adsorption capacity of nanocellulose and graphene oxide membrane for RhB textile dye is 86.4 mg/g [13].

In the study, the chemical structure of the nanocomposite synthesized by mixing GO from BAU-A activated carbon and NC from hemp stalks in a ratio of 1: 1 (volume) was studied by FTIR and ultraviolet spectroscopy.

2. Experiment

2.1 Materials

The study included activated carbon of BAU-A brand (GOST ST 6217-74), sulfuric acid (H_2SO_4) 94% (GOST ST 4204-77), sodium nitrate ($NaNO_3$) (GOST ST 4168-79), potassium permanganate ($KMnO_4$) (GOST ST 5777-84), hydrogen peroxide (H_2O_2) (GOST ST 50632-93), hydrochloric acid (HCl) (GOST ST 3118-77) and all reagents were used without additional purification.

2.2 Methods

2.2.1 Synthesis of GO from activated carbon

GO is synthesized from activated carbon by the Hammers method. Preparation of GO consists of the following sequence: the flask is filled with 6 g of activated carbon, which is placed in an ice bath with a temperature of 0°C and stirred continuously

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for 15 min, dripping 23 ml of 94% H_2SO_4. To the resulting suspension is added 3 g of $NaNO_3$, then during the stirring the mixture gradually is added 18 g of $KMnO_4$ with maintaining the temperature below 20°C for 2 h, after then temperature is raised to 35°C and keep for 30 min. Then after adding the deionized water, the temperature of the mixture rose to 90°C. Finally, 30% H_2O_2 is added until the mixture changes color to light yellow. At the end of the reaction, the product is filtered and washed several times in 5% HCl solution to remove residual metal ions. Finally, neutralized with deionized water until pH = 6-7.

2.2.2 Extraction of cellulose from hemp stalks

The cellulose used for modification was isolated from hemp stalks (Cannabis Ruderalis Janisch) on the basis of organosolvent oxidation [14].

2.2.3 Synthesis of nanocellulose

To obtain NC, the 1 g of the original cellulose was weighed, cellulose with 64% H_2SO_4 acid was obtained as a ratio of 1:10 (g/mL) and was titrated gradually at 0-5°C. After complete mixing of the cellulose and acid, heat the mixture at 40°C in a water bath, stirring vigorously for 1 h. The resulting suspension is separated in a centrifuge (OPn-8, Russia) with a speed of 6000 rpm, stirring for 15 min. The obtained nanocellulose is dialyzed in deionized water until the pH is 5-7.

2.2.4 The particle size of NC and GO suspensions

The average particle size was determined by Zetasizer NanoZS 90 (Malvern, UK) Dynamic laser light scattering. To do this, aqueous suspension was processed at 30 kHz for 10 min using an ultrasonic dispersant U-sonic UZTA-0.15/22-0 (Alena, Russian).

2.2.5 Modification of GO with NC

To synthesize of GO modified with NC (GO-NC), the two are combined in an equimolar ratio of 50:50 mL:mL and processed by ultrasound at a frequency of 45 kHz (UZTA-0.15 / 22-0, Russia) at a temperature of 25°C for 30 min (Figure 1). The fully mixed mixture was poured into a flat plastic surface and dried at room temperature for 48 h. As a result, a film with a thickness of 38 µm was formed. The samples were stored in the crystallizer to prevent sorption of water vapor and carbon dioxide in the air.

2.2.6 UV spectroscopy

The absorption characteristics of the obtained GO, NC and GO/NC nanocomposite in the UV region were recorded on a spectrometer PE5400-UF at a temperature of 25°C in the range of 190-1100 nm (cuvette thickness 10 mm) every 5 nm.

2.2.7 FTIR spectroscopy

FTIR analysis was performed on a spectrometer FTIR FT-801 (Simex, Russian), with a resolution of 1 cm^{-1} and a wavelength 450-4700 cm^{-1} according to the standard method using a single-use universal full internal reflection and mirror-diffuse reflection with the upper position of the model, at a temperature of 25°C and the number of scans 100.

2.2.8 SEM

The morphology of GO/NC nanocomposite was examined under a scanning electron microscope. The surface morphology of GO/NC nanocomposite was examined by SEM Quanta 200i 3D (FEITM Netherlands). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. The surface of GO/NC nanocomposite is coated with aluminum to improve the transfer of electrons. The specimens were mounted on aluminum pins with carbon tape.

2.2.9 XRD

The crystal structures of GO/NC nanocomposite was studied by X-ray diffraction on X´PertPRO diffractometer (Malvern Panalytical Empyrean, Netherlands) using monochromatized copper (CuKα) radiation with a scan step of 0.02°, K-Alpha1 [Å] 0.1542. The measurement angle was 10-45°, the X-ray tube voltage was 45 kV, the current intensity was 30 mA, and the measurement time at each step was 0.5 s and an aluminium rectangular multi-purpose sample holder (PW1172/01) was used for the measurmentin reflection mode.

3. Results and Discussion

3.1 The particle size of NC and GO suspensions

In Figure 2, it can be seen that the average particle size of the GO was 352 nm (Figure 2a), average particle size of NC was 470 nm in length and 80 nm in width (Figure 2b).

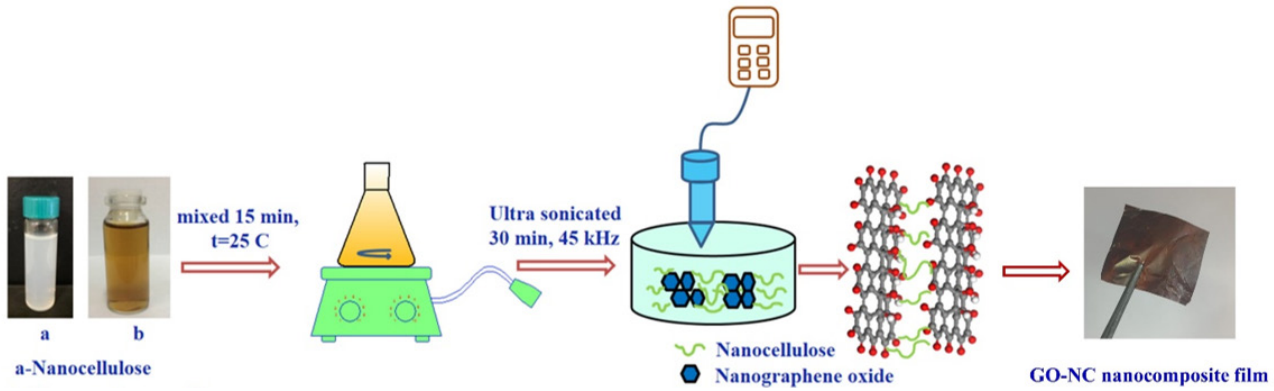

Figure 1 – Scheme of obtaining GO-NC nanocomposite film

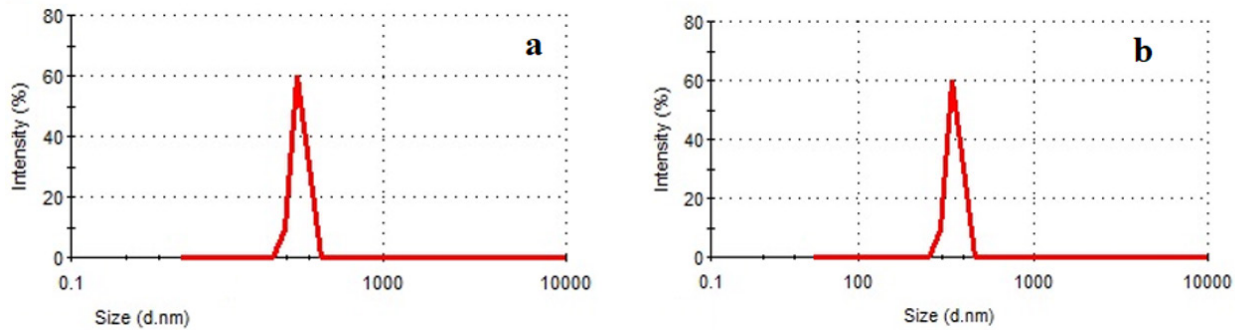

Figure 2 – The particle size of GO (a) and NC (b) suspensions

3.2 UV spectroscopy

Figures 3a-3b show the absorption spectra of GO and NC in the ultraviolet region. In Figure 2a, under the influence of π-π * bonding of aromatic rings in the chemical structure of GO, UV has an absorption of 204 nm in the region. This was found to be well consistent with the research results [15-16]. The absorption spectrum in the UV region of 231 nm, shown in Figure 2b, confirms the synthesis of cellulose nanoparticles. The study [17-18] corresponds to the indicators given in the works. Absorption of GO-NC nanocomposite in the UV region was observed at a wavelength of 243 nm (Figure 2c). This indicates that the ether C=O carboxyl bond is associated with valence stretching [19-20].

3.3 FTIR spectroscopy

Figure 4a shows FTIR of the initial GO. The FTIR spectrum of GO in Figure 4, shows a broad peak appeared at 3226 cm^{-1} and at 1420 cm^{-1} attributed to the stretching vibration mode of O-H bond. The band observed at 1723 cm^{-1} was assigned to the stretching vibration of C=O bonds in the carbonyl and carboxyl groups. The band at 1585 cm^{-1} corresponds to the stretching vibration and deformation peaks of the aromatic ring C=C bonds. The epoxy functional groups are shown at 1249 cm^{-1} as C–O stretching vibration and at peak 1054 cm^{-1} is attributed as stretching vibration of C–O alkoxy bonds [21-23].

Figure 4a shows the IR spectrum of nanocellulose. The absorbance region in the wavenumber 900 cm^{-1} is assigned to

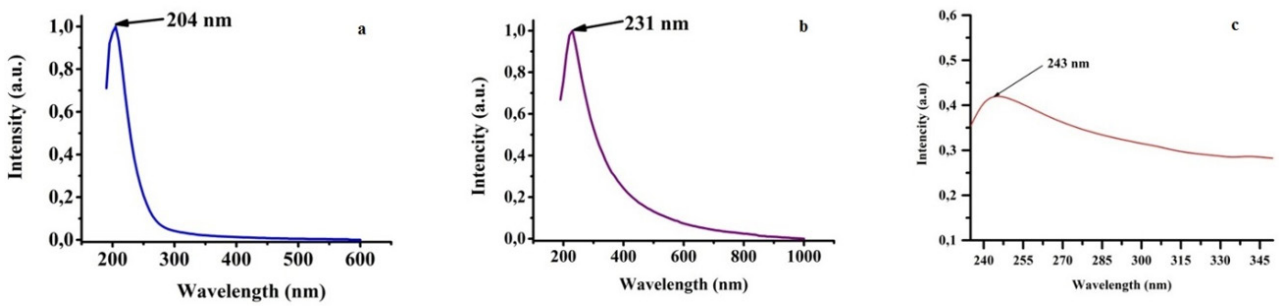

Figure 3 – Absorption spectra of GO (a), NC (b) and GO-NC (c) nanocomposites in the ultraviolet region

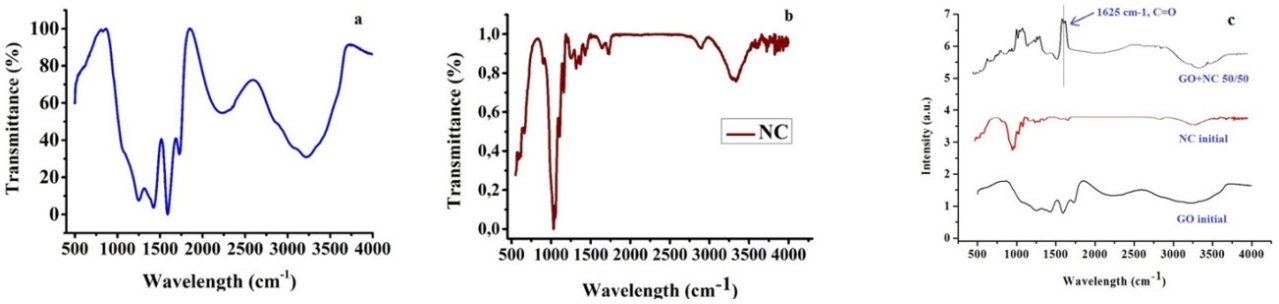

Figure 4 – FTIR spectra of GO (a), NC (b) and GO-NC (c) nanocomposites

the deformation of glycoside C–H bond. The absorption peaks in the cellulose molecule, which are observed at 1100 cm^{-1}, 1430 cm^{-1}, 2880 cm^{-1}, consequently, they are associated with the symmetrical and asymmetric signals stretching vibration of the C-O, CH_2, C–H groups. The broad absorbance band appearing in the range from 3300 cm^{-1} to 3500 cm^{-1} is characterized to the valence stretching vibration of the O–H groups. It can be seen that the results of the study are in good agreement with the work [24,25].

Figure 4c shows the IR spectra of the GO-NC nanocomposite. One of the significant changes in the IR spectrum is the occurrence of valence stretching vibration of the ether carboxyl C=O bond in the absorption region of 1625 cm^{-1}. That is, an etheric O=C–OH bond is formed between the OH group in the cellulose molecule and the carboxyl groups in the GO molecule. This is consistent with the results of the study [19-21].

3.4 SEM analysis

Figure 5 shows surface morphology of the GO-NC nanocomposite film. The SEM images indicating the CNF as a contact layer between ultralow thickness of the GO layers. Some of the GO sheets were inserted perpendicular (standing) to the membrane surface, while most of the GO assem horizontally on top of the CNF. It can be seen that the results of the study are well consistent with the literature [26].

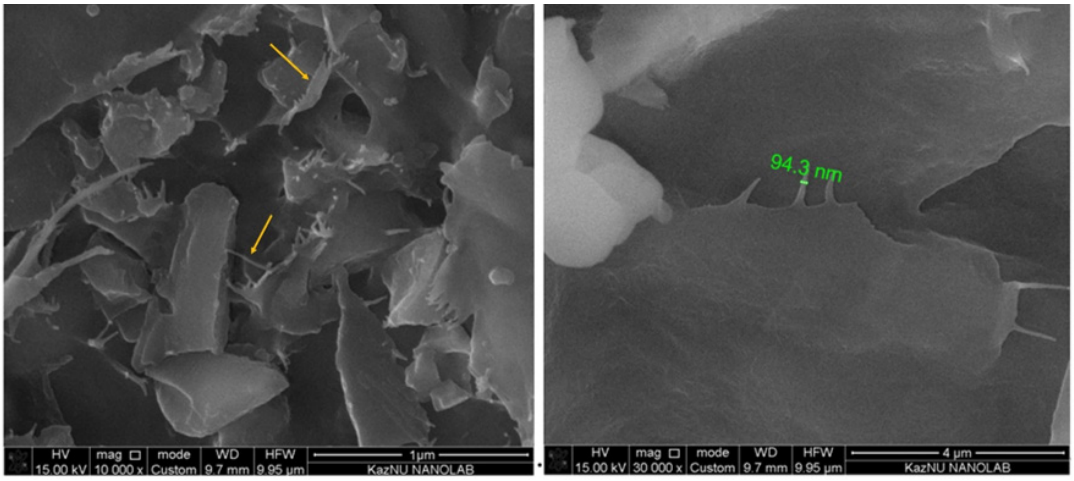

Figure 5 – SEM images of GO-NC nanocomposite film

3.5 XRD analysis

Figure 6 shows the changes of crystal structures of GO, NC and GO-NC composite films were also characterized by XRD. Figure 4a four diffraction peaks detected from all X-ray diffractograms. The 2θ = 10.5° corresponds to the characteristic peak of GO (001) lattice plane (Figure 4a) [27]. In the figure 4b, they are equal to 2θ =15.8 (1-10), 16.2 (110), 22.5 (200), 34.2 (004), and the crystal structure of the molecule is characteristic of two chains monoclinic unit per unit cell cellulose I β [28]. Additionally, in the figure 4c GO-NC composite film exhibited the (200) crystal plane of NC at 2θ=22.5°, Further, the peak occurring at 2θ = 10.21° (001) indicates that the composite film also retains the characteristics of GO. It can be proven that the GO-NC composite film is a substance comprising GO and NC.

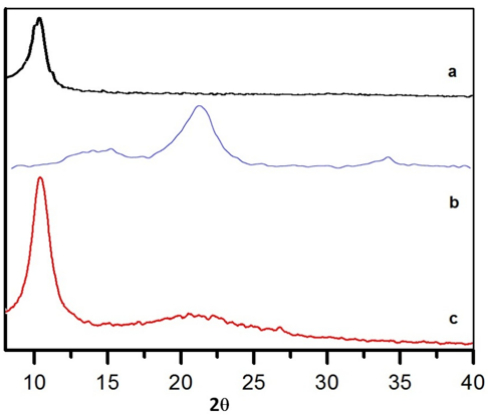

Figure 6 – XRD patterns of the GO (a), NC (b) and GO-NC composite film (c)

4. Conclusion

Based on the obtained results, for the first time GO was synthesized from activated carbon-BAU-A and modified with NC to obtain the nanocomposite GO-NC. The obtained GO and NC average particle sizes of the GO and NC were 352 nm, 470 nm in length and 80 nm in width. According to the FTIR spectrum, an etheric O = C – OH bond between the OH group in the NC molecule and the carboxyl groups in the GO molecule formed. The absorption signal at 243 nm in the ultraviolet region observed in the GO-NC nanocomposite showed that the

IR spectrum is associated with C=O stretching vibration of carboxyl groups characterized by a wavelength of 1625 cm^{-1}. The SEM analysis showed the NC as a contact layer between ultralow thickness of the GO layers. The XRD analysis indicated GO-NC composite film is a substance comprising GO and NC.

Conflict of interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgment

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Preparation and study of the physicochemical characteristics of multilayer polymer composites based on poly(ethyleneimine)-stabilized copper nanoparticles and poly(sodium 2-acrylamide-2-methyl-1-propanesulfonate)

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Multilayer films were synthesized from a complex of branched polyethyleneimine (PEI) with copper nanoparticles (PEI-CuNPs) and sodium poly-2-acrylamide-2-methyl-1-propanesulfonate (PAMPSNa), applied layer-by-layer (LbL) on a solid support in an acidic medium. Protonation of the amino groups of PEI in an acidic medium increases the positive charge of the PEI-CuNPs system to +43.5 mV and promotes the formation of an interpolyelectrolyte complex between the positively charged PEI-CuNPs and the highly charged anionic polyelectrolyte PAMPS, the ζ-potential of which was -141 mV. AFM images and SEM micrographs showed a uniform distribution of spherical copper nanoparticles in the homogeneous structure of the multilayer film. The optical characteristics and hydrodynamic dimensions of PEI-CuNPs indicate the formation of PEI-CuNPs nanoparticles with sizes of 60-300 nm, with an average size of up to 100 nm. Copper nanoparticles distributed uniformly in a multilayer PEI-CuNPs/PAMPS film may be of interest for applications in the field of membrane catalysis, biochips, sensor membranes, and controlled drug delivery.

Keywords: polyethylenimine; sodium poly-2-acrylamide-2-methyl-1-propanesulfonate; complexes of PEI-Cu^{2+} and PEI-CuNPs; layer-by-layer (LbL) deposition; multilayered thin films of PEI-CuNPs/PAMPS.

Поли (этилениминде) тұрақтандырылған мыс нанобөлшектері және поли (2-акриламидо-2-метил-1-натрий пропансульфонаты) негізіндегі мультиқабатты полимерлік композит алу және оның физикалық-химиялық сипаттамаларын зерттеу

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Қышқыл ортада қатты субстратқа layer-by-layer (LbL) әдісімен қабатпен жағылған мыс нанобөлшектері (PEI-CuNPs) және поли-2-акриламид-2-метил-1-натрий пропансульфонаты (PAMPSNa) бар тармақталған полиэтиленмин (PEI) кешенінің қатысуымен мульти қабатты пленкалар синтезделді. PEI амин топтарының қышқыл ортада протондалуы PEI-CuNPs жүйесінің зарядын +43,5 mV-ге дейін арттырады және зарядталған PEI-CuNPs жоғары зарядталған анионды PAMPS полиэлектролит арасындағы интерполиэлектролит кешенінің пайда болуына ықпал етеді, ζ-potential -141 mV-ге тең. АСМ суреттері мен микрофотографиялары көп қабатты пленканың біртекті құрылымында мыстың сфералық нанобөлшектерінің біркелкі таралуын көрсетті. PEI-CuNPs оптикалық сипаттамалары мен гидродинамикалық өлшемдері нанобөлшектерінің пайда болуын көрсетеді. Өлшемдері 60-300 нм, орташа мөлшері 100 нм дейін. Pei-CuNPs/PAMPS көп қабатты пленкасында біркелкі бөлінген мыс нанобөлшектері мембраналық катализ саласында, биочиптерді, сенсорлық мембраналарды және дәрі-дәрмектерді жеткізуді басқаруда қолдануға қызығушылық тудыруы мүмкін.

Түйін сөздер: полиэтиленимин; поли-2-акриламид-2-метил-1-натрий пропансульфонаты; PEI-Cu^{2+} және PEI-CuNPs кешендері; қабатты тұндыру (LbL); көп қабатты жұқа PEI-CuNPs/PAMPS қабықшалары.

Получение и изучение физико-химических характеристик мультислойных полимерных композитов на основе стабилизированных поли(этиленимином) наночастиц меди и поли(2-акриламид-2-метил-1-пропансульфоната натрия)

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Синтезированы мультислойные пленки с участием комплекса разветвленного полиэтиленимина (PEI) с наночастицами меди (PEI-CuNPs) и поли-2-акриламид-2-метил-1-пропансульфонатом натрия (PAMPSNa), нанесенные послойно методом layer-by-layer (LbL) на твердую подложку в кислой среде. Протонирование аминогрупп PEI в кислой среде увеличивает положительный заряд системы PEI-CuNPs до +43,5 mV и способствует образованию интерполиэлектролитного комплекса между положительно заряженным PEI-CuNPs и сильнозаряженным анионным полиэлектролитом PAMPS, ζ-potential которого равен -141 mV. АСМ-изображения и микрофотографии СЭМ показали равномерное распределение сферических наночастиц меди в однородной структуре мультислойной пленки. Оптическая характеристики и гидродинамические размеры PEI-CuNPs указывают на образование наночастиц PEI-CuNPs с размерами 60-300 нм, со средним размером до 100 нм. Наночастицы меди, равномерное распределенные в мультислойной пленке PEI-CuNPs/PAMPS могут представлять интерес для применения в области мембранного катализа, в создании биочипов, сенсорных мембран и контролируемой доставки лекарственных препаратов.

Ключевые слова: полиэтиленимин; поли-2-акриламид-2-метил-1-пропансульфонат натрия; комплексы PEI-Cu^{2+} и PEI-CuNPs; послойное осаждение (LbL); мультислойные тонкие пленки PEI-CuNPs/PAMPS.

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Preparation and study of the physicochemical characteristics of multilayer polymer composites based on poly(ethyleneimine)-stabilized copper nanoparticles and poly(sodium 2-acrylamide-2-methyl-1-propanesulfonate)

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1. Introduction

One of the promising and intensively developing areas is the production of multilayer membranes and films by the layer-by-layer (LbL) method, by embedding metal nanoparticles into their matrix to give them the desired properties and functions. Such thin-layer films have found wide application in the creation of biochips, sensor membranes, membrane nanocatalysts, for the stabilization of nanoparticles and controlled delivery of drugs, etc. The successful use of polyelectrolytes forming a complex due to covalent and hydrogen bonds, electrostatic interactions, and also due to molecular recognition made it possible to obtain new materials with unique physicochemical properties, for example, controlled thickness and morphology, uniform distribution of metal nanoparticles in the volume [1-3]. The purposeful introduction of metal nanoparticles into multilayer films makes it possible to use them as membrane nanocatalysts [4-6].

In [7-10], immobilization of mono- and bimetallic nanoparticles in the bulk of multilayer films was carried out to obtain effective nanocatalysts. It was found that the individual physicochemical properties of multilayer polymer composites depend on the choice of optimal blocks for assembling LbL capsules, the manufacturing technique, and the method of immobilization of various nanoparticles in the bulk of the films [7].

Pd nanoparticles attached to magnetic ferrite nanoparticles, supported on PAA and PEI, were used for the hydrogenation of olefin alcohols [8], and multilayer systems PAA/PVP-Au, ethyl-3-thiophene acetate/PVP-Au [9] were used for the reduction of nitrophenol [10]. The regularities of the growth of multilayers of PEI/PAA, PEI/PSS, quaternized QPEI/PAA and QPVP/PSS based on a polymer-metal complex (PMC) with copper and cobalt ions were determined, and the effect of the nature of polymers, pH of the medium, temperature, conditions of layer formation and absorption of metals on their surfaces for the formation of nanocatalysts were studied [11-13].

Of great scientific and practical interest are synthetic polyampholytes capable of existing in various conformational and phase states, depending on the change in temperature, pH of the medium, the type and concentration of low-molecular-weight salt, and the thermodynamic quality of the solvent. Depending on the nature of the acidic and basic monomers, polyampholytes are divided into: weakly charged, highly charged polyampholytes and betaines. Representatives of fully charged macromolecules, highly charged polyampholytes, consist of charged cationic and anionic monomers and have the ability to retain charges in a wide range of pH values [14,15]. The behavior of highly charged polyampholytes depends on the composition of the copolymers and the distribution of monomer units [16]. The presence of permanent charges promotes the effective binding of metal ions, dyes and surfactants.

Copolymer of sodium 2-acrylamido-2-methylpropanesulfonate (AMPSNa) is a typical representative of highly charged polyampholytes, which belongs to the less studied polymers. Recent studies show that the use of AMPSNa and ARTAC as a monomer makes it possible to synthesize

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polymer matrices with unique properties [17-20]. The importance of studies of polymers based on highly charged polyampholytes, in particular AMPSNa, is evidenced by a number of studies devoted to nanocomposite materials [21-25].

Studies on the complexation of highly charged polyelectrolytes with metal ions and the preparation of multilayer catalytic films by the LbL method have not been studied sufficiently and publications are of an episodic nature. Despite the wide range of polyelectrolytes, not all potentially applicable polymers are used to obtain multilayer nanocatalysts by LbL method.

In this work, a study was carried out on the creation of multilayers of a positively charged PEI-CuNPs complex and a negatively charged PAMPS polyelectrolyte. It is assumed that copper nanoparticles immobilized in PEI-CuNPs/PAMPS multilayers can be used as a catalytic center in the oxidation of organic substrates.

2. Experiment

2.1 Materials

Branched poly(ethylenimine) (PEI) with average-weight molecular weight M_w ~25 000 and number-average molecular weight M_n ~10 000 was purchased from Sigma-Aldrich GmbH (Figure 1).

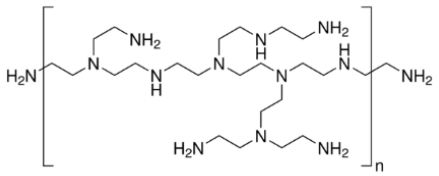


Figure 1 – Branched PEI

2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (AMPS) (50 wt. % in aqueous solution) is the product of Sigma-Aldrich GmbH (Figure 2).

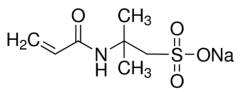


Figure 2 – AMPSNa

Copper (II) acetate monohydrate $[Cu(COOCH_3)_2 \times H_2O]$ and ammonium persulfate (APS) were purchased from Sigma-Aldrich GmbH and Changzhou Qi Di Chemical Co (China) and used without further purification.

2.2 Methods

2.2.1 Preparation of PEI-Cu^{2+} and PEI-CuNPs complexes

PEI-Cu^{2+} and PEI-CuNPs complexes were obtained according to the method described in [26]. When the solution of copper (II) acetate was poured into the PEI solution slowly, with constant stirring, the solution acquired a dark blue color (Figure 3, a). This indicated the formation of a 4:1 polymer-metal complex PEI-Cu^{2+} which means that 4 monomer units of PEI coordinate with one copper ion. When sodium borohydride interacted with PEI-Cu^{2+}, the solution changed color from dark blue to dark brown (Figure 3b). The reduction of copper ions coordinated with PEI was accompanied by a short-term evolution of gaseous hydrogen. The resulting dark brown solution of PEI-CuNPs was dialyzed for 24 hours to remove low molecular weight impurities (Figure 3, c).

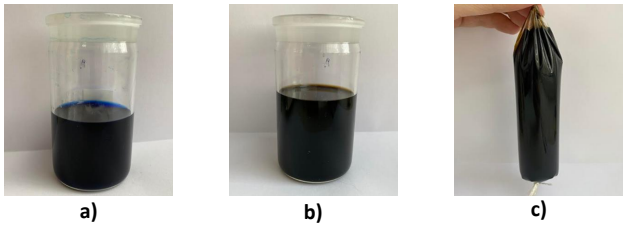
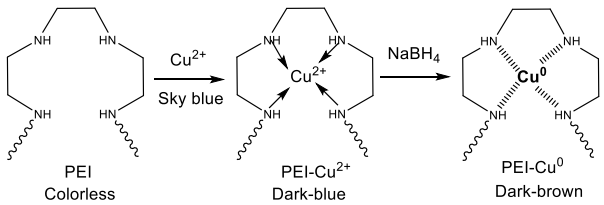


Figure 3 – PEI - Cu^{2+} complex (a); PEI-CuNPs nanoparticles (b), dialysis of PEI-CuNPs nanoparticles (c)

The formation of four coordination complexes between the repeating units of PEI and bivalent copper ions, as well as the reduction of the PEI-Cu^{2+} complex with sodium borohydride to the formation of Cu^0 nanoparticles stabilized by PEI, can be represented by the following scheme



Scheme 1 – Scheme of the formation of the PEI-Cu^{2+} coordination complex and its reduction with sodium borohydride to the zero-valence state

2.2.2 Preparation of SiO_2 substrate - SurfusNanoLane for the deposition of PEI-CuNPs/PAMPS multilayers

For the deposition of multilayers, a SiO_2-SurfusNanoLane substrate was used, which was kept in Piranha solution (a mixture of hydrogen peroxide and sulfuric acid in a ratio of 1:4) for 24 hours to remove organic contaminants and increase the surface hydrophilicity. Then the substrate was washed with water and dried in a stream of nitrogen.

2.2.3 Layer-by-layer (LbL) deposition

The LbL assembly process was performed by immersing a solid base in a dilute solution of a positively charged

polyelectrolyte to adsorb the first monolayer, then immersing it in a negatively charged polyelectrolyte to obtain a second monolayer [27-29]. The multilayer deposition was carried out using ND-DC DipCoater Nadetech (Spain) rotary spray gun (Figure 4). Multilayers were formed on the surface of the substrates using PEI-CuNPs and PAMPS solutions with a concentration of 10^{-2} mol/L at pH 4. The dipping procedure was carried out in the following order: 1) PEI-CuNPs solution; 2, 3) rinsing with distilled water; 4) PAMPS solution. In this way, PEI – CuNPs/PAMPS multilayers were obtained, consisting of 50 and 100 bilayers.

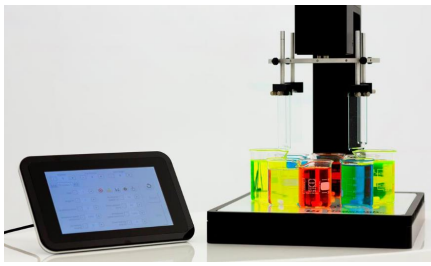


Figure 4 – Preparation of PEI–CuNPs/PAMPS multilayers using Rotary DipCoater

2.2.4 Determination of the optical characteristics of PEI-CuNPs solutions

The absorption spectra of PEI-CuNPs solutions in the ultraviolet and visible regions were measured on Specord 210 plusBU spectrophotometer (Germany, 2012). The quartz cells had an optical path length of 5 and 10 mm. All measurements were carried out at 25°C and atmospheric pressure, at a wavelength of 200-800 nm. In the spectrophotometric experiment, measurements were taken into account with a relative error of no more than 3%.

2.2.5 Determination of the average hydrodynamic dimensions and zeta potential of PEI-Cu^{2+} and PEI-CuNPs solutions

The average hydrodynamic dimensions and zeta potential of PEI-Cu^{2+} and PEI-CuNPs solutions were determined by dynamic laser light scattering on Malvern Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., UK). In the dynamic light scattering method, measurements were taken into account with a relative error of no more than 5%.

2.2.6 PAMPS identification

The identification of PAMPS obtained by the method of radical polymerization was carried out by means of IR and NMR spectroscopy. IR spectra of PAMPS were recorded on Cary 660 FTIR IR Fourier spectrophotometer (Agilent Technologies, USA) in the frequency range 400-4000 cm^{-1}. The limit of permissible error of the wave number scale is ± 0.1 cm^{-1}.

^{1}H NMR spectra were recorded on Bruker BioSpinAvance III 500 MHz NMR spectrometer (500 MHz, Germany) using deuterated water as a solvent. Chemical shifts are measured relative to the residual proton signals of the deuterated solvent.

2.2.7 Study of morphological, topographic and structural characteristics

SEM JSM-6390LV scanning electron microscope (Jeol, Japan) was used to study the surface morphology of the obtained multilayers deposited on SiO_2-SurfusNanoLane substrate. The measurements were carried out in a high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. Carbon was sprayed onto the surface of the samples using magnetron sputtering of carbon fiber to increase conductivity. The samples were mounted on aluminum rods with conductive carbon tape.

The topographic characteristics of the multilayer were obtained using scanning probe microscopy SmartSPM-1000 (Russia) with a scanning range of 100x100x15 microns. Scanner resonant frequencies> 7 kHz in XY and> 15 kHz in Z.

3. Results and Discussion

3.1 Synthesis and characterization of PAMPS

PAMPS was obtained by radical polymerization of a 30% aqueous AMPS solution in the presence of 0.25% APS at 50°C for 4 h. Unreacted monomers were removed by dialysis through a membrane in a container with distilled water with a volume of 5 L, followed by drying in an oven for 5 h, in a refrigerator for 3 h, and in a lyophilic unit for 3 h. Figure 5 shows the IR spectrum of PAMPS obtained by the method of radical polymerization.

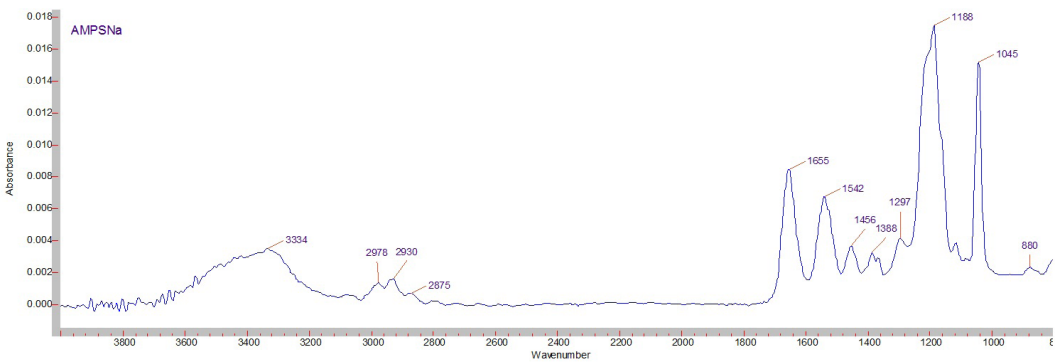


Figure 5 – IR absorption spectrum of PAMPS

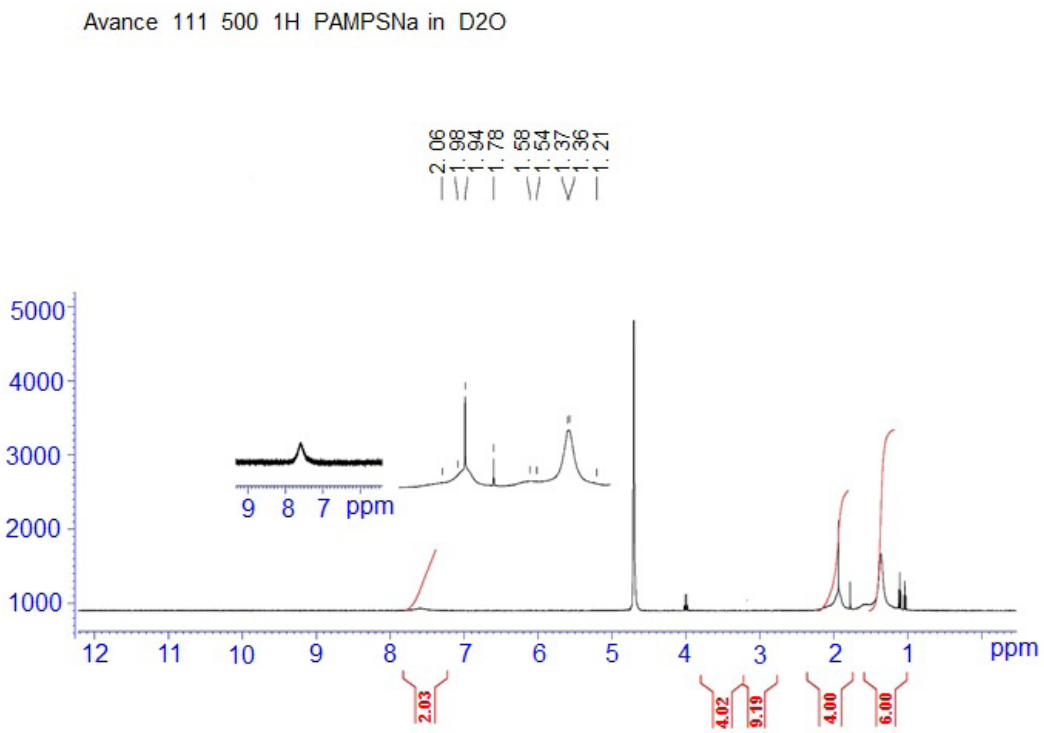


Figure 6 – ^{1}H NMR spectra of PAMPS

The absorption spectra of PAMPS are characterized by the corresponding peaks of bending and stretching vibrations of functional groups. The broad absorption band at 3334 cm^{-1} corresponds to stretching vibrations of N-H groups. Stretching vibrations of the carbonyl group of the primary amide appear at 1655 cm^{-1}. Bending vibrations of C – N and C – NH amino groups appear at 1542 cm^{-1}. The absorption bands at 1388 cm^{-1} and 1297 cm^{-1} correspond to the –CH_2- and CH groups of the polymer ridge. The characteristic S = O absorption bands appear in the regions of 1045 cm^{-1} and 1188 cm^{-1} [17,30,31].

The structure of PAMPS was also identified by ^{1}H NMR spectroscopy (Figure 6). The data obtained show the presence of 6H protons of 2 methyl groups, resonating in the region of 1.36 ppm, which confirms the linear structure of PAMPS and is in good agreement with the data of [32].

3.2 UV-Vis absorption spectra of PEI-CuNPs before and after dialysis

Figure 7 shows the results of a study of a colloidal solution of PEI-CuNPs by UV-Vis spectroscopy before and after dialysis. According to [33], the absorption spectrum of a copper acetate solution is characterized by a maximum at a wavelength of λ = 800 nm. In the spectrum of the PEI solution, no maxima are observed in the wavelength range of 200-1000 nm. When a copper acetate solution is added to an aqueous PEI solution, a maximum appears in the spectrum at a wavelength of λ = 620 nm and a maximum characteristic of a pure copper solution disappears, which indicates the formation of PEI-Cu^{2+} complex. The formation of PEI-CuNPs nanoparticles is characterized by the appearance of an absorption band at 535-540 nm. After dialysis for 24 h, the absorption spectra of PEI-CuNPs did not undergo significant changes, and the maximum of the absorption band at 540 nm remained practically unchanged for several months. This indicates the high stability of PEI-CuNPs nanoparticles. The decrease in the spectrum intensity after dialysis is associated with the removal of small nanoparticles, as demonstrated in the next section.

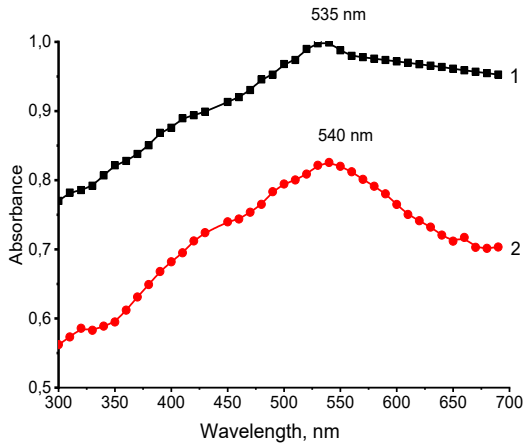


Figure 7 – UV-Vis absorption spectra of the colloidal PEI-CuNPs solution before (1) and after (2) dialysis for 24 h

3.3 Average hydrodynamic dimensions and zeta potential of PEI and PEI-CuNPs solutions

Figure 8 shows a histogram of the numerical size and ζ-potential distribution of the pure PEI solution obtained by dynamic light scattering. The histogram of the hydrodynamic particle size distribution of pure PEI is mainly divided into two ranges with an average particle size of 3-200 nm and a range of size scatter of 3-4 nm and 200 nm, respectively (Figure 8, a). More than 70% of them fall within the 3-4 nm size range. The zeta potential of the pure PEI solution is positive and is +2.95 ± 0.1 mV (Figure 8, b).

The distribution of PEI-CuNPs nanoparticles before dialysis is bimodal. The average hydrodynamic sizes of nanoparticles vary from 65 to 198 nm (Figure 9, a). In this case, particles with a size of 198 nm prevail, the amount of which is 96%. The zeta potential of the PEI-CuNPs solution before dialysis is +32.9 ± 1.6 mV (Figure 9, b).

The histogram of the hydrodynamic size distribution of PEI-CuNPs nanoparticles with an average particle size of 100 nm and a particle scatter range of 60-300 nm is shown in Figure 10, a. It can be seen that the distribution of copper nanoparticles in the PEI-CuNPs solution after dialysis became monomodal, i.e. it can be assumed that only large PEI-CuNPs nanoparticles remained in the solution, while small nanoparticles were washed out. The solution has a positive zeta potential corresponding to +43.5 - 2.04 mV (Figure 10, b), since copper nanoparticles are chemisorbed with a positively charged polyelectrolyte - PEI at pH = 4.0.

This also indicates the stability of the aqueous suspension of PEI-CuNPs, which is provided due to the prevalence of electrostatic repulsion between positively charged particles reducing the possibility of aggregation. The positive charge of the PEI-CuNPs means it will form a polyionic complex with the negatively charged PAMPS.

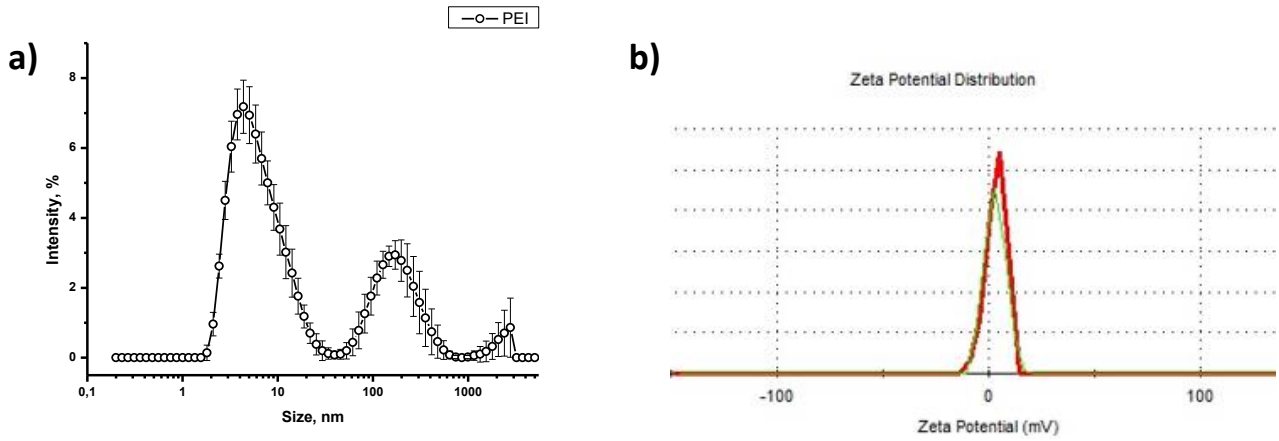


Figure 8 – Histogram of PEI distribution by hydrodynamic dimensions (a) and **ζ**-potential of the solution (b)

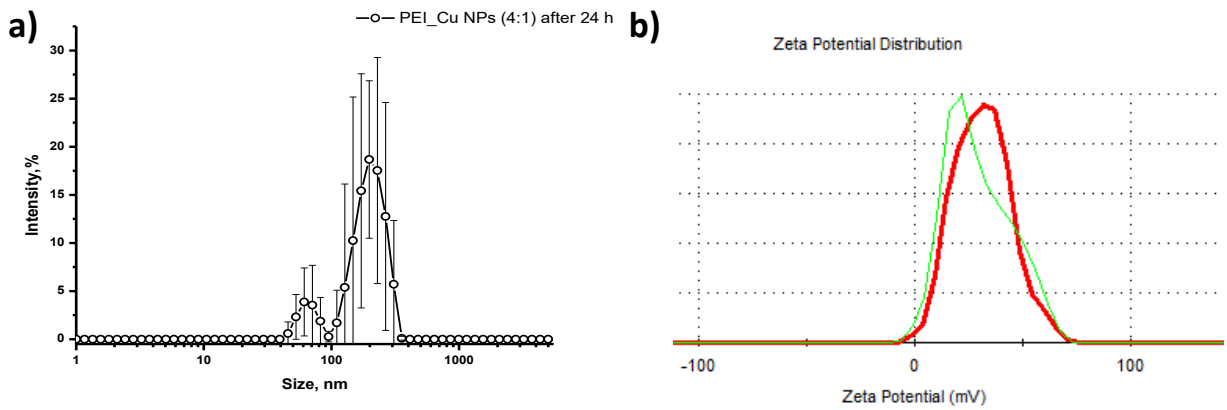


Figure 9 – Histogram of the PEI-CuNPs distribution by hydrodynamic dimensions (a) and **ζ**-potential of the solution (b) before dialysis

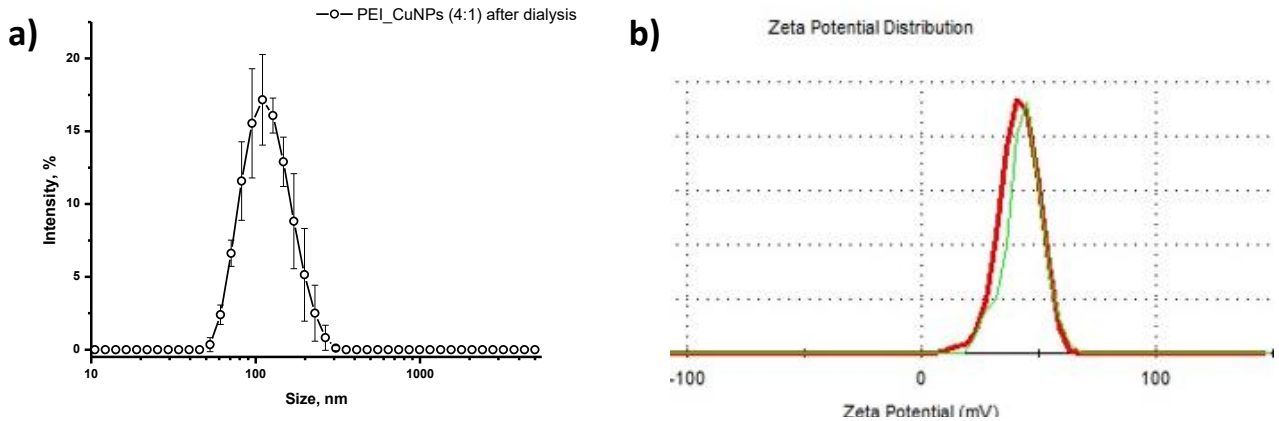


Figure 10 – Histogram of the PEI-CuNPs distribution by hydrodynamic dimensions (a) and **ζ**-potential of the solution (b) after dialysis

3.4 Preparation of PEI-CuNPs/PAMPS multilayers

In order to create multilayer films by the LbL method, we used solutions of a positively charged polyelectrolyte - PEI-CuNPs and a negatively charged polyelectrolyte - sodium poly-2-acrylamide-2-methyl-1-propanesulfonate (PAMPSNa). SiO_2-SurfusNanoLane was used as a substrate, on which positively charged PEI-CuNPs nanoparticles (ζ = + 43.5±2.04 mV) and negatively charged PAMPS (ζ = -141 ± 7 mV) were alternately deposited. As can be seen from Fig. 11, the substrate is coated uniformly with PEI-CuNPs/PAMPS multilayers, consisting of 50 (Figure 11, a) and 100 layers (Figure 11, b) painted in a saturated blue color.

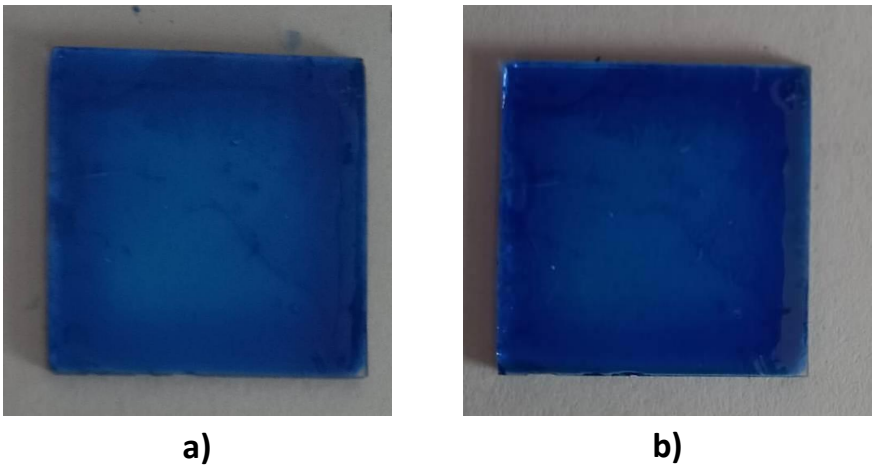


Figure 11 – Multilayers: a – PEI-CuNPs/PAMPS (50 layers); b – PEI-CuNPs/PAMPS (100 layers) applied to the plate using the layer-by-layer method

Figure 12 shows AFM images of PEI-CuNPs/PAMPSNa multilayer films (50 layers) deposited on a silicon substrate. It is seen that the surface of multilayer films is sufficiently smooth and porous. The pores are spherical. A granular morphology with a developed surface structure with a grain size of 50-130 nm is observed. The roughness of multilayer PEI-CuNPs/PAMPS films is small and averages ≥ 20 nm. The formation of a uniform surface of multilayers is apparently associated with the formation of interpolyelectrolyte complexes with positively charged PEI-CuNPs nanoparticles and negatively charged PAMPS macromolecules stabilized by polyionic contacts.

The data of the atomic force microscopy are confirmed by the results of the scanning electron microscope (Figure 13). In homogeneous multilayers, evenly distributed and isolated copper nanoparticles, which have a spherical shape, can be seen.

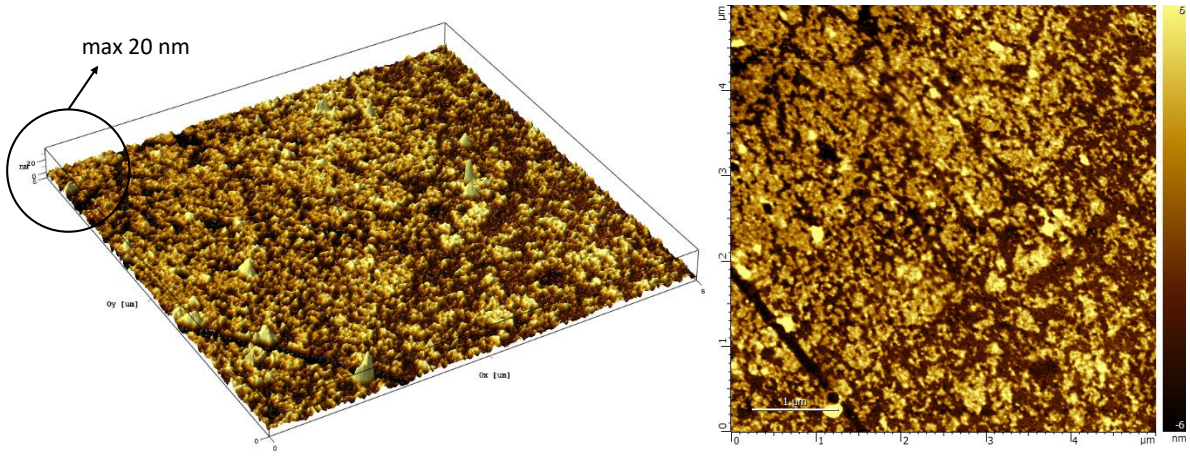


Figure 12 – Surface topography of PEI-CuNPs/PAMPS multilayer film (50 layers)

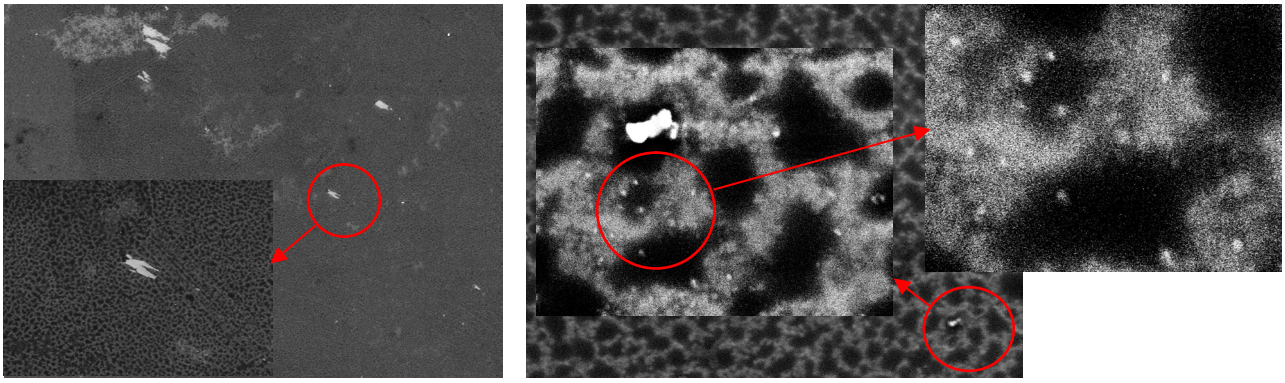


Figure 13 – SEM micrographs of PEI-CuNPs/PAMPS multilayer film

4. Conclusion

Multilayered thin films composed of PEI-CuNPs/PAMPS have been obtained by layer-by-layer deposition of positively charged PEI-CuNPs and negatively charged PAMPS on the surface of SiO_2. In aqueous solution PEI, PEI-Cu^{2+} and PEI-CuNPs were characterized by UV-Vis spectroscopy, DLS, and zeta-potential. In solid state multilayers of PEI-CuNPs/PAMPS were studied by AFM and SEM. It was found that nanoparticles of copper are uniformly distributed within multilayers and in perspective can be used as membrane catalysts for oxidation of organic substrates.

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Магний-ионды батареяға арналған ұнтақ висмут негізіндегі анодтық материал және оның қасиеттері

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Аталған жұмыста ұнтақ висмут негізіндегі интеркаляциялық анод материалы синтезделді. Сканерлеуші-электронды микроскопия көмегімен көміртек пасталы суспензияның субстрат бетінде біркелкі таралғаны анықталды. Ұнтақ висмут негізінде синтезделген электродқа 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$/ацетонитрил ерітіндісінен Mg^{2+} иондарының электрхимиялық интеркаляциясы мен деинтеркалациясының заңдылықтары зерттелді. Циклдік вольтамперометриямен бірге сканерлеуші-электронды микроскопия мен атомды-эмиссиялы спектроскопиялық талдау нәтижелері катод аймағында Mg_xBi_y интерметаллидтің түзілуімен байланысты тотықсыздану процестері, ал циклдің кері бағытында болжам бойынша магнийдің екі сатылы тотығуы жүретіні анықталды. Циклдік вольтамперограммалардан тура және кері бағыттағы шыңдарының потенциалдар айырымы арқылы магний иондарының интеркаляциялық материалға тотықсыздануының қайтымды емес екені анықталды. Электрод материалына интеркаляция және деинтеркаляция процестері үшін магний ионының диффузия коэффициенті Рендлс-Шевчик теңдеуін қолдана отырып есептелді. Олар сәйкесінше $3{,}12 \cdot 10^{-11}$ см^2/с және $1{,}85 \cdot 10^{-11}$ см^2/с тең болды. Рентген-фазалық анализ нәтижелері интерметаллид түзілуіне сәйкес келетін висмуттың кристалды торының кубты құрылымын көрсетті. 1С ток беру арқылы гальваностатикалық циклдеу кезінде синтезделген анод материалының сыйымдылығы 104 мА·сағ·г$^{-1}$ құрайтынын көрсетті. Бұл нәтижелер магний-ионды ток көздерін құрастыру үшін жақсы көрсеткіш деп есептеуге болады.

Түйін сөздер: магний; интеркаляция; висмут; циклдік вольтамперометрия; магний-ионды аккумулятор; анод.

Powder bismuth-based anode material for magnesium-ion batteries and its properties

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In this work an intercalation anode material synthesized on the base of the powdered bismuth is presented. The uniformly distribution of carbon paste suspension over the substrate surface was found out by scanning-electron microscopy. The regularities of electrochemical intercalation and deintercalation of magnesium ions into the electrode created on the base of powdered bismuth in a solution of 0.25 mol/L $Mg(N(SO_2CF_3)_2)_2$ on the base of acetonitrile were studied. The cyclic voltammograms with the results of scanning electron microscopy and atomic emission analysis indicate that in the cathode area the reduction processes proceed with the formation of an intermetallic compound – Mg_xBi_y; two peaks were observed at the reverse course which were conceivably corresponding to two-stage magnesium oxidation. According to cyclic voltammograms by the difference in the potential of peaks in the forward and reverse directions it was established that the processes of reduction and oxidation of magnesium ions into intercalation material were irreversible. The diffusion coefficients of intercalation and deintercalation into the electrode material were calculated using the Rendles-Shevchik equation; they were $3.12 \cdot 10^{-11}$ sm^2/s and $1.85 \cdot 10^{-11}$ sm^2/s, respectively. X-ray diffraction (XRD) results demonstrated the cubic structure of the bismuth crystal lattice with altered parameters corresponding to intermetallide formation. At galvanostatic cycling of the synthesized anode material a capacity of up to 104 mA·h·g^{-1} at current load 1C was achieved. Such results can be a good indicator for the development of magnesium-ion power sources.

Keywords: magnesium; intercalation; bismuth; cyclic voltammetry; magnesium-ion batteries; anode.

Анодный материал на основе порошкообразного висмута для магний-ионных батарей и его свойства

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В данной работе синтезирован интеркаляционный анодный материал на основе порошкообразного висмута. С помощью сканирующей электронной микроскопии было обнаружено, что углеродная пастообразная суспензия равномерно распределена по поверхности субстрата. Были изучены закономерности электрохимической интеркаляции и деинтеркаляции ионов магния в электрод, полученного на основе порошкообразного висмута в растворе 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$ на основе ацетонитрила. Циклические вольтамперограммы вкупе с результатами сканирующей электронной микроскопии и атомно-эмиссионного анализа свидетельствуют о том, что в катодной области протекают процессы восстановления с образованием интерметаллида – Mg_xBi_y, а на обратном ходе наблюдаются два пика, соответствующие предположительно двухстадийному окислению магния. По циклическим вольтамперограммам через разность потенциалов пиков на прямом и обратном направлениях установлено, что процессы восстановления и окисления ионов магния в интеркаляционный материал являются необратимыми. Коэффициенты диффузии интеркаляции и деинтеркаляции в электродный материал были рассчитаны с использованием уравнения Рендлса-Шевчика, которые составили $3{,}12 \cdot 10^{-11}$ см^2/с и $1{,}85 \cdot 10^{-11}$ см^2/с, соответственно. Результаты РФА показали кубическую структуру кристаллической решетки висмута с измененными параметрами, соответствующими образованию интерметаллида. При гальваностатическом циклировании синтезированного анодного материала была достигнута емкость до 104 мА·ч·г$^{-1}$ при токовой нагрузке 1С. Полученные результаты могут служить хорошим показателем для разработки магний-ионных источников тока.

Ключевые слова: магний; интеркаляция; висмут; циклическая вольтамперометрия; магний-ионные батареи; анод.

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ХАБАРШЫ
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Магний-ионды батареяға арналған ұнтақ висмут негізіндегі анодтық материал және оның қасиеттері

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1. Кіріспе

Электрондық технологияның дамуы және сұраныстың тұрақты артуы арзан әрі қауіпсіз энергия түрлендіргіштерін зерттеуге және құрастыруға көбірек көңіл бөлуді талап етеді. Қазіргі қажеттіліктерді қанағаттандыратын барлық заманауи батарея жүйелерінің ішінде литий-ионды батареялар (ЛИБ) энергияны сақтаудың ең қолайлы жүйесі болып табылады. Алайда литий жер қыртысында сирек кездесетін элемент болып табылады. Сонымен қатар, литийге поляризация кезінде анодтың бетіне ине тәріздес дендрит түзу қасиеті тән, бұл ЛИБ-тің қауіпсіздік жағынан қызып кету, жарылыс сияқты бірнеше күрделі мәселелерді туындатады [1-4]. Сондықтан, осы қиындықтарды еңсеру үшін магний ток көздерін литийлі электрхимиялық жүйелерге балама ретінде ұсынылады. Магний, литий иондарымен салыстырғанда дендритсіз тотықсыздануына байланысты қауіпсіздігінің жоғары болуы, жер қыртысында кеңінен таралуы, төмен құны және жоғары сыйымдылығы (3833 мА·сағ·см$^{-3}$) сияқты айтарлықтай артықшылықтарға ие [5-7]. Сондай-ақ, литий металына қарағанда, магнийдің екі валентті катионы екі есе жоғары көлемдік энергия тығыздығын қамтамасыз етеді. Осы артықшылықтарға қарамастан, магний бірқатар кемшіліктерге ие. Қарапайым электролиттерде металл магнийдің бетінде магнийдің ионының қайтымды тотықсыздануы мен тотығуына кедергі болатын пассивті қабат пайда болады, бұл магний-иондық батареяларының циклденуін қиындатады. Д. Аурбах және оның зерттеушілер тобы бұл мәселені Гриньяр реактивін қолдана отырып шешті [6]. Алайда, мұндай электролиттердің ауаға жоғары сезімталдық және анодтың коррозиялық белсенділігі сияқты бірқатар кемшіліктері бар, бұл оның тұрақсыздығына әкелуі мүмкін. Қазіргі уақытта идеалды электролиттер жоқ, сондықтан көптеген ғалымдар металл күйіндегі анод материалын басқа да балама материалға ауыстыруына назар аударуда.

Магнийді кремний, көміртек, фосфор сияқты бейметалл элементтерге енгізу бойынша зерттеулер бар, бірақ бұл элементтердің аморфты құрылымына байланысты магний ионының интеркаляциясы кезінде кристалдық тор бұзылуы мүмкін, ал деинтеркаляция кезінде тор толығымен қайта қалпына келмейді. Төмен потенциалдар аймағында элементтер магниймен қайтымды әрекеттесетіні белгілі [8-12]. Атап айтқанда, Mg_3Bi_2 интерметалидін құрайтын висмут белгілі бір теориялық сыйымдылыққа ие болуы мүмкін. Оны магний-иондық батареялар үшін теріс электрод ретінде қолданылуын Т. Артур және оның тобы алғаш рет зерттеп [11], магний металымен қайтымды электрхимиялық интеркаляциялану/деинтеркаляциялану қабілетін және қарапайым электролиттермен үйлесімділігін анықтаған. Сонымен қатар, висмут оңай иілгіш металл, көптеген циклдан кейін құрылымы тұрақты болып қалады, ал бұл қасиеті оны анод материалы ретінде пайдалану кезінде сыйымдылықты сақтау үшін өте маңызды. Висмуттың басқа үміткерлермен салыстырғанда тағы бір артықшылығы – оның төмен диффузиялық кедергісі [8].

Осылайша, әдеби шолу мен анодтың ең қолайлы түрін таңдау бойынша жасалған зерттеулердің нәтижелеріне сүйене отырып [12], берілген жұмыста интеркаляциялық материал ретінде ұнтақ висмут таңдалды және оның негізінде дайындалған электрод материалына Mg^{2+} иондарының электрхимиялық интеркаляциясы мен деинтеркаляциясының заңдылықтары зерттелді.

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Таңдалған висмут ұнтағының микродисперсті өлшемі, белсенді бетті ұлғайтып, магний ионының интеркаляциялық қабілетін жақсартуға мүмкіндік береді.

2. Тәжірибелік бөлім

2.1 Ұнтақ висмут негізінде интеркаляциялық анодты материалды жасау

Висмут негізіндегі анодты материалдар 11% поливинилиденфторидті (ПВДФ) N-метил 2-пирролидонда (НМП, 99,8%, Sigma-Aldrich) ерітіп, одан кейін 90% висмут ұнтағын (орташа мөлшері 74 мкм) және 3% техникалық көміртекті қосу арқылы дайындалды. Біртекті қоспаны алу үшін суспензия 8 сағат бойы араластырылды. Дайын суспензия мыс фольгасының бетіне Doctor Blade ракельжүзімен жағылды. НМП артық мөлшерін кетіру үшін материал пеште 60°С температурада шамамен 12 сағат кептірілді, диаметрі 10 мм электродты дискілерді кесіп алғаннан кейін, вакуум пешінде 24 сағат бойы 100°С температурада қайта кептіру жүргізілді. Белсенді массаны анықтау үшін электродтар өлшеніп, жоғарыда сипатталған жағдайларда қайтадан кептірілді. Электродтардың соңғы меншікті массасы 1,8-ден 2,1 мг/см^2-ге дейін болды.

2.2 Жасалған интеркаляциялық анод материалды физика химиялық әдістермен зерттеу

Электролит пен электрхимиялық ұяшықты дайындау оттегі мен су мөлшері 1 ppm-нен аспайтын аргонмен толтырылған қолғап боксында жүргізілді. Электролитті дайындау үшін бис(трифторметилсульфонил)магний имиді ($Mg(N(SO_2CF_3)_2)_2$, 99,5%, Solvionic) және ацетонитрил (АН) еріткіші CH_3CN (сусыз, 99,8%, Sigma Aldrich) қолданылды. Қолданар алдында $Mg(N(SO_2CF_3)_2)_2$ тұзы вакуумда кептіріліп, бірнеше күн бойы молекулалық електе (0,4 нм) сусыздандырылды.

Барлық электрхимиялық сынақтар Swagelock үш электродты ұяшығында жүргізілді. Жұмысшы электрод ретінде синтезделген висмут электроды, көмекші және салыстырмалы электрод ретінде магний металы (99,9%) қолданылды. Көмекші және салыстырмалы электродтардағы тотыққан магний қабатын кетіру үшін беті алдынала тазартылып, майсыздандырылды. Полипро-пилен материалдан жасалған сепаратор (Wattman FS 2190) $Mg(N(SO_2CF_3)_2)_2$/АН сусыз электролитіне батырылды.

Циклдік вольтамперлік (ЦВ) өлшеулер және гальваностатикалық циклдеу Solartron Analytical XM MTS потенциостат/гальваностат көмегімен жүргізілді. ЦВ үшін 0,1-1,0 мВ/сек аралығында сканерлеу жылдамдығында және заряд/разряд циклденуі 0,1С, 1С, 10С ток мәндерінде жүргізілді.

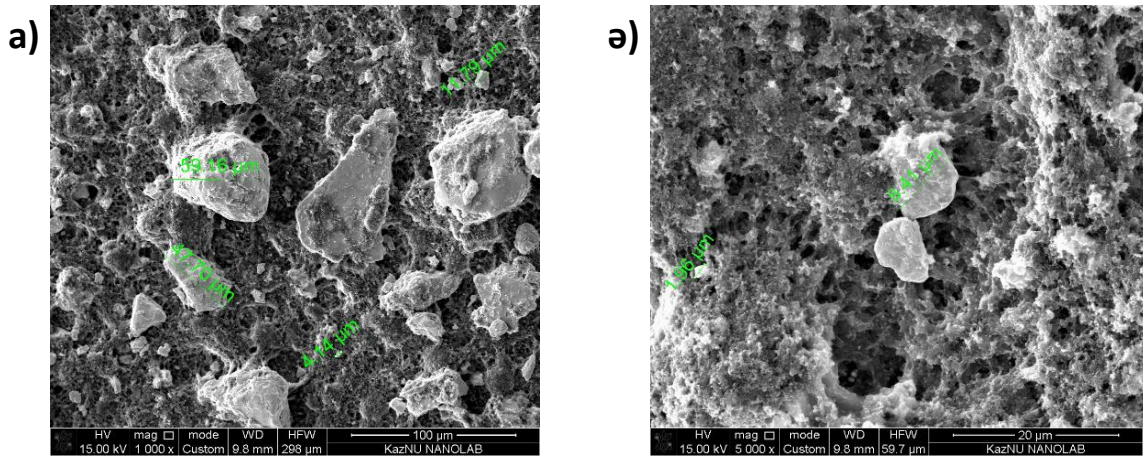
Электрхимиялық сынақтарға дейін және одан кейінгі висмут электродтарының морфологиясы Rigaku Miniflex 600ge (РСА) энергодисперсиялық рентген аппаратымен жабдықталған Quanta 200i 3D сканерлеуші-электронды микроскоптың (СЭМ) көмегімен зерттелді. Морфологиялық зерттеуге дейін электролит қалдықтарын кетіру үшін пайдаланылған электродтар ацетонмен жуылды.

Интеркаляцияланған және деинтеркалирленген висмут анодтарын рентген-фазалық анализ (РФА) Bruker D8 дифрактометрінде жүргізілді (Cu-Ka-сәулелену, дифракция диапазоны 10-нан 80-ге дейін, қадам 0,02, сканерлеу жылдамдығы: 0,1-0,2 с/қадам).

3. Зерттеу нәтижелері және оларды талдау

1 суретте мыс төсемесіне жағылған ұнтақ висмут негізінде синтезделген анод материалының СЭМ көмегімен алынған суреттері келтірілген. Ұнтақ висмуттың көміртекпен қоспасының беті біркелкі таралған әртүрлі пішіндегі бөлшектерден тұратынын байқауға болады. Бөлшектердің өлшемі 10-50 мкм тең. 1ә суретте масштабты арттырған кезде, электрод бетінде дөңгелек түйірлерге ұқсас өлшемі шамамен 400 нм-ге жуық ұсақ бөлшектер көрінеді.

Синтезделген электрод материалының электрхимиялық сипаттамаларын анықтау үшін вольтамперлік

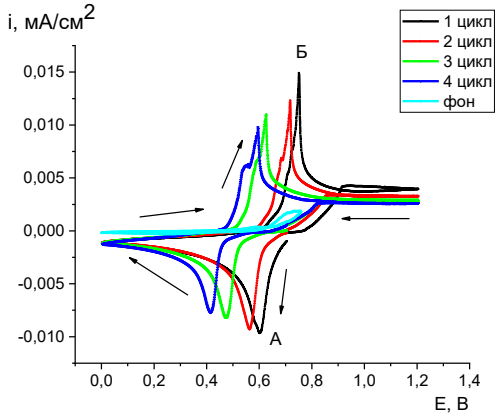


1-сурет – Синтезделеген ұнтақ висмут негізіндегі анод материал бетінің морфологиясы

өлшеулер жүргізілді. 2-суретте әртүрлі циклдарда 0,5 моль/л $Mg(N(SO_2CF_3)_2)_2$/АН ерітіндісіндегі висмут электродының циклдік вольтамперограммалары келтірілген. Вольтамперлік қисықтарда бір шың байқалады: бірінші циклде 0,71 В потенциалындағы ток тығыздығының күрт артуы (салыстырмалы Mg электродына қатысты) Mg_xBi_y қорытпасының түзілуімен жүреді (А шыңы). Тотықсыздану потенциалдары цикл саны артқан сайын теріс мәндер аймағына жылжиды. 1-ші циклдегі тотығу процесі 0,62 В потенциалынан басталып, шыңның түбі 0,75 В-қа дейін жетеді (Б шыңы), ол түзілген интерметаллидтің тотығу процесіне сәйкес келеді. Циклдар саны артқан сайын шыңдардың катодтық (i_p^k) және анодтық (i_p^a) ток тығыздығының абсолютті мәндері төмендейді, ал магнийдің тотықсыздану және тотығу шың потенциалдары теріс аймаққа ығысады. Поляризациялық қисықтың кері бағытында анодтық шыңдарының да қосарлануы жүреді, бұл магнийдің тотығуының екі сатылы процесін көрсетуі мүмкін [13]. Катодтық және анодтық процестер үшін потенциалдар мәндері цикл саны өскен сайын теріс аймаққа ауысады.

Сонымен қатар 2 суретте ашық көк түспен ацетонитрилдің поляризациялық қисығы келтірілген. Еріткіштің тотықсыздану процесінде айқын шың жоқ. Ал кері бағытта 0,6 В потенциалдан тотығу толқыны байқалады.

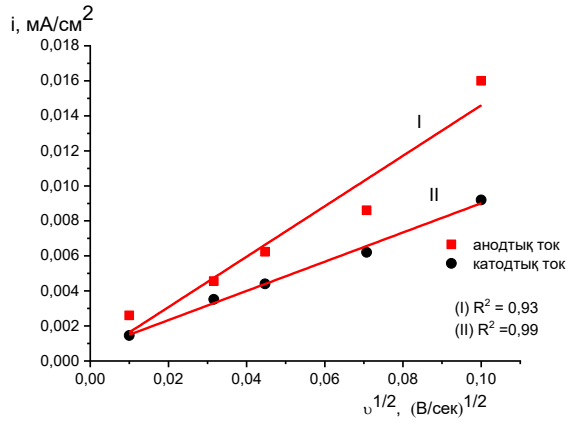
Классикалық электрхимия заңына сәйкес, егер тура және кері бағыттағы шыңдардың жартылай потенциалдарының қосындысы E^0-ға, ал осы шыңдардың потенциалдар айырмасы 2,2 RT/F 25˚С температурада бір электронды электрхимиялық реакция үшін 56,5 мВ шамасына тең болса, жүйеде реакция қайтымды болып саналады. Біздің жағдайда, бірінші циклда потенциалдар айырымы 150 мВ құрайды. Сонымен қатар, аталған өлшем потенциал беру жылдамдығына тәуелді емес. Бұл анод



2-сурет – 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$/АН ерітіндісіндегі және таза АН еріткішіндегі ұнтақ висмут негізіндегі анодқа магний иондарының интеркаляция/деинтеркаляциясының циклдік вольтамперограммалары, υ = 0,1 мВ/с Mg/Mg^{2+} қатысты, Т=25˚С

материалына магний иондарының интеркаляциясы мен деинтеркаляциясының қайтымсыздығының белгісі.

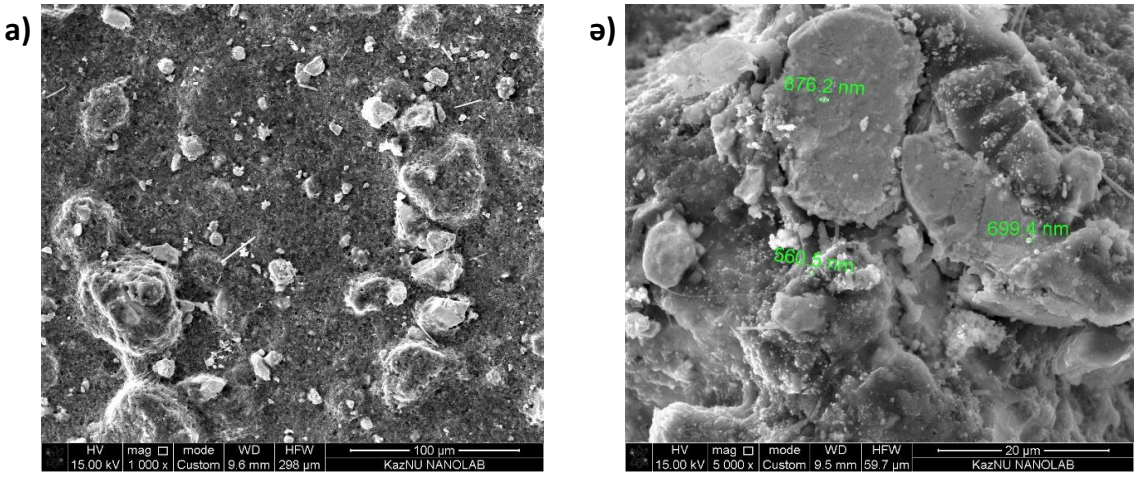
Висмут электродындағы Mg^{2+} иондарының диффузиясын түсіндіру және магнийдің диффузия коэффициентін (D_{Mg}) бағалау үшін әр түрлі потенциал беру жылдамдығында циклдік вольтамперометрия қисықтарынан анодтық және катодтық шыңдарының ток тығыздық мәндері анықталып, олардың потенциал беру жылдамдығының түбір асты мәніне тәуелділік графиктері тұрғызылды (сурет 3).



3-сурет – 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$/АН ерітіндідегі анодтық және катодтық шыңдар тогының потенциал беру поляризация жылдамдығының түбір асты мәніне тәуелділігі, Т=25˚С

3-ші суретте келтірілгендей $I_{p-}\upsilon^{1/2}$ тәуелділігі сызықтылыққа бағынатынын көреміз. Сканерлеу жылдамдығы неғұрлым жоғары болса, шыңның ток тығыздығының мәні соғұрлым жоғары болатындығы анықталды. Электродтық реакцияның диффузия коэффициенті (D_{Mg}) Рендлс-Шевчик теңдеуін [14] қолдана отырып есептелінді. Циклдік вольтамперограммалар бойынша есептелген D_{Mg} диффузия коэффициенті сәйкесінше интеркаляция және деинтеркаляция үшін $3{,}12\cdot10^{-11}$ см²/с және $1{,}85\cdot10^{-11}$ см²/с құрайды. Диффузия коэффициенттерінің мәні Mg^{2+} иондарының ұнтақ висмут электродындағы миграция кинетикасы қайта зарядталатын магний батареялары үшін салыстырмалы түрде [15] жоғары екенін көрсетеді.

4 суреттерінде 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$/АН ерітіндісінде магний интеркаляциядан кейін ұнтақ висмут негізінде синтезделген электродтар бетінің морфологиясы келтірілген. Таза висмут анодымен салыстырғанда, интеркаляциядан кейін айқын жиектерге ие ірі түзілімдердің жиынтығы байқалады, алайда висмут электродының жалпы бетінің морфологиясы біркелкі болып қалады (сурет 4 а). Микросуреттерде көрсетілгендей интеркаляцияға дейін және одан кейінгі бөлшектердің пішіні мен көлемі өзгермейді.



4-сурет – Магний иондарының интеркаляциядан кейінгі висмут электродының бетінің морфологиясы

Электродтың бетін талдау нәтижелері бойынша (1-кесте) магний мен күкірттің пайыздық қатынасы магний интеркаляциясынан кейін жоғарылайтынын көруге болады.

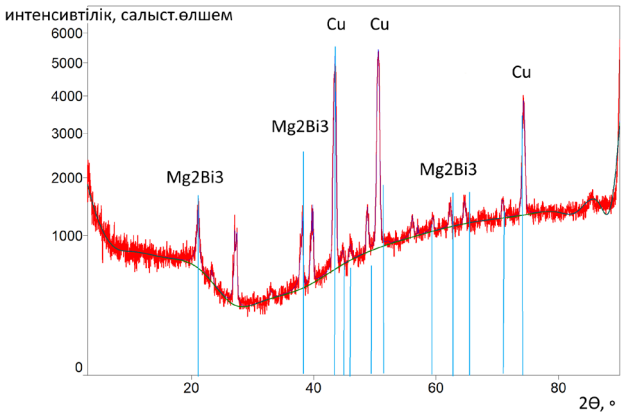
1-кесте – Ұнтақ висмут негізіндегі интеркаляциялық анодты материалға магний иондарының интеркаляциясына дейінгі және кейінгі атомдық эмиссиялық спектроскопияның нәтижелері

Элемент	W, %	
	Интеркаляцияға дейін	Интеркаляциядан кейін
Mg	0,00582	2,94
Si	-	0,72
P	2,00	1,04
S	0,64	4,17
Ca	0,82	0,47
Cu	83,09	74,59
Bi	13,46	15,11

Магний висмутидінің түзілуін дәлелдеу үшін рентгенфазалық талдау жүргізілді (сурет 5). Рентгенограммада висмут пен мыстың дифракциялық сызықтары бар. Сондай-ақ, магний висмутидына немесе кристалдық тор параметрінің едәуір ұлғайғандағы висмуттың кубтық модификациясына сәйкес келетін 0,269 нм жазықтықаралық қашықтығы бар өте әлсіз қарқындылықтағы сызық көрінеді. Висмутты одан әрі өңдеу кезінде оның қасиетін бақылау үшін субстрат пен оған жағылған висмуттан тұратын фазаға жартылай сандық талдау жүргізілді. Талдау нәтижелері бойынша, висмутқа сәйкес келетін сызықтардың қарқындылығының төмендеуі байқалады. Бұл висмут фазасының мөлшерінің азаюы және соған сәйкес интерметаллид фазасының көбеюіне алып келеді.

2-кестеде магний иондарының интеркаляцияға дейінгі және кейінгі анодтың кристалдық торының теориялық параметрлері, сондай-ақ РФА нәтижелерінен алынған эксперименттік анықталған мәліметтері келтірілген [16]. Аталған кестеде, ұнтақ висмут негізінде синтезделген анодтың және магний ионын интеркаляцияғаннан кейін түзілген материалдың кристалдық торының теориялық және практикалық өлшемдері бір-біріне жақын екенін көруге болады.

Синтезделген анод материалының электрлік сипаттамаларын анықтау үшін, теориялық материал сыйымдылығынан ток тығыздығы есепетеліп, оның гальваностатикалық циклдену қисықтары түсірілді.



5-сурет – Магний иондарының интеркаляциясынан кейінгі висмут негізіндегі электрод бетінің рентгенфазалық талдауы және оған сәйкес теориялық шыңдар

2-кесте – Ұнтақ висмут негізіндегі синтезделген және магний ионымен интеркаляцияланған анод материалы кристалдық торының өлшемдері

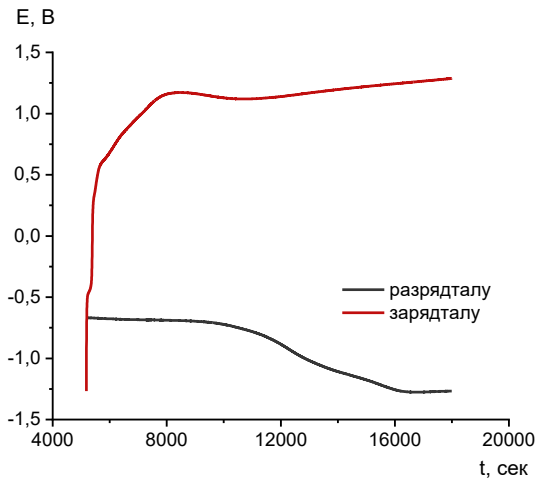
Фаза	Пішіні	Мәндері	Кристалдық торының бүйірлерінің өлшемдері			
			a, нм	b, нм	c, нм	V, нм^3
Синтезделген анод	Ромбоэдрлі (R-3m)	Теориялық	0,4596	0,4596	1,2033	0,2542
		Тәжірибелік	0,4540	0,4540	1,1844	0,2441
Магний иондарымен интеркаляцияланған анод	Гексагональді (P-3m1)	Теориялық	0,4720	0,4720	0,7445	0,1659
		Тәжірибелік	0,4675	0,4675	0,7416	0,1621

Алынған қисықтарды өңдеу арқылы тәжірибелік сыйымдылық мәндері келесі теңдеу арқылы есептелді:

$$C = \frac{I \cdot \tau}{m}$$

мұндағы, C – сыйымдылық (А·сағ·г$^{-1}$), I – ток тығыздығы (А), τ – уақыт (сағ), m – масса (г).

6-суретте 1С ток тығыздығы кезіндегі гальваностатикалық заряд-разряд типтік қисықтары көрсетілген. 1С ток тығыздығын беру кезінде максималды сыйымдылық 104 мА·сағ·г$^{-1}$-ге дейін қол жеткізуге болады және 10 циклден кейін 94 мА·сағ·г$^{-1}$деңгейінде сақталады, бұл бір цикл үшін сыйымдылықтың тек 0,96%-ға орташа төмендеуіне сәйкес келеді (сурет 6).



6-сурет – 0,25 моль/л $Mg(N(SO_2CF_3)_2)_2$/АН ерітіндідегі ұнтақ висмут негізінде синтезделген анодының гальваностатикалық циклдену қисықтары

10С ток тығыздығында он циклден кейін сыйымдылық шамамен 73 мА·сағ·г$^{-1}$ дейін төмендейді. Сыйымдылықтың әртүрлі ток тығыздығы кезінде сақталуы осы интеркаляциялық материалдың разрядқа қабілеттілігін көрсетеді. Ең жоғары меншікті сыйымдылық 1С кезінде 104 мА·сағ·г$^{-1}$ тең. Бұл теориялық мәннің (298 мА·сағ·г$^{-1}$) шамамен 40%-ын құрайды.

4. Қорытынды

Зерттеу жұмысы барысында келесідей нәтижелер алынды:

— Ұнтақ висмут негізіндегі интеркаляциялық анодтық материал синтезделді. СЭМ нәтижелері матрица компонентінің біркелкі таралуын көрсетті.

— Циклдік вольтамперометрияның нәтижелері катодты аймақта магний висмутидінің түзілуіне сәйкес келетін шыңдарды, ал анодтық аймақта магний иондарының екі сатылы тотығуы жүретіні дәлелдеді. Магний иондарының синтезделген анодқа интеркаляция/деинтеркаляциясы қайтымды емес екені анықталды. Осы процестердің магний иондарының диффузия коэффициенті есептелді ($3{,}12 \cdot 10^{-11}$ см^2/с және $1{,}85 \cdot 10^{-11}$ см^2/с).

— Магний иондарымен интеркаляцияланған анодқа жүргізілген рентгенфазалық талдау нәтижелері құрылымы кубтық Mg_3Bi_2 құрамды интерметаллидтің түзілетінін дәлелдеді. Кристалды құрылымның теориялық және тәжірибелік параметрлері өзара ұқсас екені анықталды.

— Ұнтақ висмут негізінде синтезделген материал жоғары ток тығыздығында «ұзақ» цикл жұмыс жасау қабілетін көрсетті. 1С ток шамасында максималды сыйымдылығы 104 мА·сағ·г$^{-1}$ дейін жетті.

Алғыс білдіру

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МАЗМҰНЫ – СОДЕРЖАНИЕ

Y. Panova, Y. Aubakirov, H. Arbag
Selection of sorption materials for the extraction of nickel and cobalt from the ore of the Gornostaevskoye deposit 4-12

K. Akatan, T.K. Kuanyshbekov, S.K. Kabdrakhmanova, A.A. Imasheva, A.K. Battalova, R.B. Abylkalykova, A.K. Nasyrova, Zh.E. Ibraeva
Synthesis of nanocomposite material through modification of graphene oxide by nanocellulose 14-20

B.S. Selenova, A.Ye. Ayazbayeva, A.V. Shakhvorostov, S.K. Kabdrakhmanova, S.Z. Nauryzova, S.E. Kudaibergenov
Preparation and study of the physicochemical characteristics of multilayer polymer composites based on poly(ethyleneimine)-stabilized copper nanoparticles and poly(sodium 2-acrylamide-2-methyl-1-propanesulfonate) 22-31

А.К. Абильдина, Р.Ж. Джуманова, Г.С. Рахымбай, А.Н. Бейсеева, А.М. Аргимбаева
Магний-ионды батареяға арналған ұнтақ висмут негізіндегі анодтық материал және оның қасиеттері.....32-39

CONTENTS

Y. Panova, Y. Aubakirov, H. Arbag
Selection of sorption materials for the extraction of nickel and cobalt from the ore of the Gornostaevskoye deposit 4-12

K. Akatan, T.K. Kuanyshbekov, S.K. Kabdrakhmanova, A.A. Imasheva, A.K. Battalova, R.B. Abylkalykova, A.K. Nasyrova, Zh.E. Ibraeva
Synthesis of nanocomposite material through modification of graphene oxide by nanocellulose 14-20

B.S. Selenova, A.Ye. Ayazbayeva, A.V. Shakhvorostov, S.K. Kabdrakhmanova, S.Z. Nauryzova, S.E. Kudaibergenov
Preparation and study of the physicochemical characteristics of multilayer polymer composites based on poly(ethyleneimine)-stabilized copper nanoparticles and poly(sodium 2-acrylamide-2-methyl-1-propanesulfonate) 22-31

A.K. Abildina, R.Zh. Dzhumanova, G.S. Rakhymbay, A.N. Beiseyeva, A.M. Argimbayeva
Powder bismuth-based anode material for magnesium-ion batteries and its properties.....32-39