KAUNAS UNIVERSITY OF TECHNOLOGY

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THE MODIFICATION AND PROPERTIES OF GRAPHITE FELT ELECTRODES

Summary of Doctoral Dissertation
Technological Sciences, Chemical engineering (05T)

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

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INTRODUCTION

Relevance of the work. Recently, fundamental investigations of various carbon-based materials (graphene and its oxide, carbon nanotubes, graphite, etc.) have been conducted in search of the application for these materials in different fields, such as medicine, biotechnology, chemical and electrochemical catalysis, photochemistry, energetics, etc. One of these carbon-based materials is graphite felt (GF) which is produced from polyacrylonitrile fiber and is light-weight, has a large specific surface area, is permeable to gas and liquids in all directions, chemically and thermally stable, and electrically conductive. Due to these properties, it can be used for the production of electrodes for various electrochemical devices (flow batteries (FB), fuel cells, reactors for electrochemical synthesis, etc.). In order to make the GF electrodes suitable for conduction of electrochemical processes, they are often additionally treated thermally and modified with functional substances by using chemical and electrochemical methods, i.e. various functional groups are formed and metals and their derivatives possessing catalytic properties are deposited on the surface of GF filaments.

Aim of the work. To investigate the potential of graphite felt modification with Co, Co-Ni, Ni, and Ag by electroless deposition and to evaluate the electrochemical properties of the modified graphite felt with the aim to use it in the electrochemical polysulfide and bromide/bromobromide flow energy storage devices for the more effective conduction of oxidation-reduction reactions.

In order to reach the aim of the work we had to complete the following goals:

1. To find a simple and effective method for hydrophilization of GF.
2. To choose solutions for electroless deposition of metals (Co, Co-Ni, Ni, and Ag) and modify the GF in them under different mixing conditions of the solutions (hydrodynamic modes).
3. To investigate the morphology, elemental composition, structure, liquid permeability, and specific electrical conductivity of the GF modified with metals (Co, Co-Ni, Ni, and Ag). To compare the above-mentioned properties of the modified GF with the respective ones of the non-modified GF.
4. To investigate the electrochemical properties of GF-Co, GF-Co-Ni, and GF-Ni by carrying out redox reactions of polysulphides in an aqueous sodium polysulfide Na_2S_x (x=2−5) solution, and the ones of GV-Ag by carrying out redox reactions of bromide/bromobromide ions in an aqueous solution containing NaBr and Br_2.
5. To propose the flow chart for the production of electrodes from GF modified with metals, choose suitable equipment and determine optimal parameters of technological process.

Scientific novelty of the work. The modification of GF with Co, Co-Ni, Ni, and Ag coatings by using the electroless (chemical) deposition method with stirring of solutions with a magnetic stirrer, ultrasound stirring (ultrasonication), and continuous circulation in flow-through reactor was investigated. The influence of different hydrodynamic conditions on the distribution of metals in the whole volume of the modified GF was determined. The electrochemical properties of electrodes from GFs modified with the respective metals in aqueous solutions of polysulphides and bromide/bromobromide were determined.

Practical value of the work. The results presented in the thesis are important for further development of GF modification technology and the application of electrodes from the modified GFs in flow batteries for a more effective conversion of electrical energy to chemical energy and vice versa. It has been demonstrated that GFs modified with Co, Co-Ni, and Ni are promising materials for application in the production of electrodes for polysulphides-bromide/bromobromide flow batteries.

Approval and publication of research results. Results of the research have been presented in nine publications: two were published in journals included into the Institute for Scientific Information (ISI) database; one was published in a Lithuanian Journal Approved by the Department of Science and Studies; six publications were reported in the proceedings of conferences.

Structure and content of the dissertation. The dissertation consists of an introduction, a literature review, the experimental part, results and discussion, conclusions, lists of references and publications on the topic of the dissertation. The list of references includes 160 bibliographic sources. The results are discussed on 113 pages, illustrated in 15 tables and 45 figures.

Statements presented for the defence:

1. Aqueous solutions of lower alcohols and acetone are suitable for efficient hydrophilization of GF.
2. During GF modification by using the electroless deposition method, an even distribution of metals (Co, Ni, and Co-Ni) in the whole volume of modified GF and mass fraction of the deposited metals depend on the hydrodynamic mode and duration of the modification process.
3. High electrochemical activity in aqueous polysulfide solutions is characteristic of electrodes made from GFs modified with Co, Co-Ni, and Ni by using the electroless deposition method at room temperature, thus indicating that these GFs are promising materials for the production of FB electrodes.

1. EXPERIMENTALSETUP

The graphitized polyacrylonitrile fiber felt, simply named as graphite felt (GF), purchased from Wale Apparatus (USA) was used in this work. GF samples of 25±0.5mm length and 10±0.5mm width were cut out from a GF sheet of 4±0.2mm thickness. All chemicals of analytically pure grade were purchased from Reakhim, Sigma-Aldrich and Lachema. Double-distilled water (specific resistivity of > 6 MΩcm) was used for the preparation of all solutions. All experiments were carried out at room temperature (20±1°C). GF samples before modification were pre-treated and wet with aqueous solutions of organic solvents, such as ethanol C_2H_5OH, methanol CH_3OH, propanone (acetone) $(CH_3)_2CO$, isopropanol $(CH_3)_2CHOH$ and n-propanol C_3H_7OH (assay >99.8%). The sequence, conditions of each pre-treatment deposition procedure are described in detail in chapter "Results and discussion".

The modification of GF samples with Ag was carried out by using the electroless deposition process, immediately after pre-treatment and wetting with aqueous solution of ethanol. Two separate aqueous solutions **A** and **B** were prepared for electroless Ag deposition. Solution **A** was a source of Ag^+ ions and contained 0.25 M $AgNO_3$, 0.5 M KOH and a proper quantity of concentrated ammonia solution for a complete dissolution of the formed Ag_2O (pH>13). Solution **B** contained 0.25 M D-glucose as the reducing agent. The GF sample was impregnated in 10 cm^3 of solution **A** while simultaneously being exposed to ultrasonication for 6 min. Then, an equal volume of solution **B** was added to solution **A** and electroless Ag deposition on the surface of GF filaments started. It lasted for another 3, 6, 12 and 24 minutes under ultrasound action. GF modified with Ag in the absence and presence of ultrasound action are hereinafter referred to as GF-Ag and GF-Ag-us, respectively. The electroless deposition-obtained GF-Ag and GF-Ag-us samples were thoroughly rinsed with water and dried in an oven at 80°C for 10 h.

The sequence of procedures applied for low-temperature and high-temperature modification of GF with electroless Co, Ni, Co-Ni alloy and specific parameters of each stage is:
1. Wetting in aqueous solutions of C_2H_5OH (25%, v/v), 3 min
2. Rinsing with distilled water, 3 times with a new portion of water, 1 min for each rinse
3. Sensitilization in aqueous solutions of $SnCl_2$ (40 g/dm^3) acidified with concentrated HCl (40 cm^3/dm^3), 3 min
4. Rinsing with distilled water, 3 min
5. Catalysing in aqueous solutions of $PdCl_2$ (1 g/dm^3) acidified with concentrated HCl (1 cm^3/dm^3), 3 min
6. Rinsing with distilled water, 3 min
7. Electroless deposition

8. Rinsing with distilled water, 3 times with a new portion of water, 1 min for each rinse
9. Drying in laboratory oven at 80°C, 4–6 h

The volume of used solutions (or distilled water) in each stage of modification was 50 cm^3 for low-temperature deposition and 20 cm^3 for high-temperature deposition. The composition of the solution for electroless deposition of Co, Ni, Co-Ni alloy at room temperature (20±1°C) is presented in Table 1 and the composition of the solution for electroless deposition of Co, Ni, Co-Ni alloy at high temperature (50±1°C, 70±1°C, 90±1°C) is presented in Table 2. The last component NaH$_2$PO$_2$ as reducing agent was dissolved in electroless deposition solution immediately before the deposition process.

The pH of solutions were measured with the pH-meter WTW330 (Portugal). The solutions were stirred (to improve pre-treatment and modification processes) in three ways: with a magnetic stirrer MM-5 (GF samples modified in such a way are referred to as GF-Co-m, GF-Co-Ni-m, or GF-Ni-m), using an ultrasonic bath VTUSC3 (Vellman) with the ultrasound frequency of 42 kHz (GF samples modified in such a way are referred to as GF-Ag-us, GF-Co-us, GF-Co-Ni-us, or GF-Ni-us) and with the flow-through reactor (FTR). GF samples modified in such a way are referred to as GF-Co-ft, GF-Co-Ni-ft, or GF-Ni-ft.

The FTR was made of PTFE (polytetrafluoroethylene) plastic. A schematic view of this equipment is presented in Figure 1. The average flow rate of 100 cm^3/min of liquid circulated throughout the FTR and then lengthwise GF sample was incorporated by using the peristaltic pump.

Table 1. The composition of aqueous solution used for low-temperature (20±1°C) electroless deposition of Co, Co-Ni and Ni onto GF filaments

Component	Concentration of electroless solutions		
	Co solution	Co-Ni solution	Ni solution
Tetrasodium pyrophosphate decahydrate Na$_4$P$_2$O$_7$·10H$_2$O	70 g/L	70 g/L	70 g/L
Aqueous ammonia NH$_3$·H$_2$O (concentrated, 25 %)	75 cm^3/L	75 cm^3/L	75 cm^3/L
Cobalt sulphate heptahydrate CoSO$_4$·7H$_2$O	23.8 g/L (Co^{2+}–5 g/L)	11.9 g/L (Co^{2+}–2,5 g/L)	-
Nickel sulphate heptahydrate NiSO$_4$·7H$_2$O	6.4 g/L (Ni^{2+}–1,34 g/L)	11.9 g/L (Ni^{2+}–2,5 g/L)	23.8 g/L (Ni^{2+}–5 g/L)
Sodium hypophosphite monohydrate NaH$_2$PO$_2$·H$_2$O	26 g/L	26 g/L	26 g/L

Table 2. The composition of the aqueous solution used for high-temperature (50±1°C, 70±1°C, 90±1°C) electroless deposition of Co, Co-Ni and Ni onto GF filaments

Component	Concentration of electroless solutions		
	Co solution	Co-Ni solution	Ni solution
Sodium citrate dihydrate $Na_3C_6H_5O_7 \cdot 2H_2O$	100 g/l	100 g/l	100 g/l
Ammonium chloride NH_4Cl	100 g/l	100 g/l	100 g/l
Aqueous ammonia $NH_3 \cdot H_2O$ (concentrated, 25%)	Corrective by $pH = 8–9$	Corrective by $pH = 8–9$	Corrective by $pH = 8–9$
Cobalt sulphate heptahydrate $CoSO_4 \cdot 7H_2O$	80 g/l	40 g/l	-
Nickel sulphate heptahydrate $NiSO_4 \cdot 7H_2O$	-	40 g/l	80 g/l
Sodium hypophosphite monohydrate $NaH_2PO_2 \cdot H_2O$	40 g/l	40 g/l	40 g/l
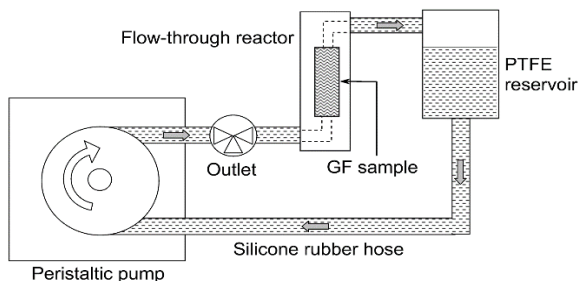
Fig. 1. A schematic diagram of the equipment used for GF modification with electroless Co, Ni, Co-Ni alloy under flow-through conditions.

The loading of electroless deposited Ag, Co, Ni, or Co-Ni alloy on the surface of GF filaments is expressed by the mass fraction of the deposited metal (mass %) which was calculated after gravimetrical analysis according to the following equation:

$$w_{\text{metal}} = \frac{m - m_o}{m} \cdot 100\% \quad (1)$$

where m_o and m are masses of GF samples before and after electroless deposition of Ag, Co, Ni, or Co-Ni alloy, respectively. The mass was determined with the weighing accuracy of ±0.0001 g using the analytical balance ABJ 120-4M (Kern).

The surface morphology, elemental composition, and structure of filaments taken from the external and internal parts of the modified GF samples were characterized after the proper splitting of samples using a scalpel. The surface morphology and composition of the modified GF filaments were investigated with

the Quanta FEG 200 (FEI) high-resolution SEM (scanning electron microscope), equipped with a Bruker XFlash® 4030 detector (Bruker AXS) for high-resolution EDX (energy dispersive X-ray spectroscopy). The structure of electroless deposit onto GF filaments was investigated by using XRD (X-ray diffraction). XRD measurements were performed with the Bruker D8 Advance (Bruker AXS) diffractometer in the 2θ range from 10° to 70° and with a Ni-filtered CuK_a irradiation (λ=1.54056 10^{-10} m). The identification of phases presented in the modified GF samples was performed from the characteristic peaks observed in the X-ray diffraction patterns by using the Search Match software and the PDF-2 database.

The electrical conductivity of the modified GF and, for comparison, of bare GF was determined by measuring the differential conductance dI/dE of rectangular samples. This was done by connecting to the ends of sample clips made from silvered copper foil and recording the voltammetric characteristics of each sample. The current-voltage (*I-E*) curves were recorded by applying the cyclic voltammetry technique in a potential range from -1 V to +1 V at a sweep rate of 100 mV/s using the above-mentioned potentiostat-galvanostat. The calculation of conductivity σ of GF and the modified GF samples was performed according the following formula:

$$\sigma = \frac{L}{a \cdot b} \cdot \left(\frac{dI}{dE} \right) \qquad (2)$$

where L is the distance between the two silvered copper foil clips; a and b are the width and the thickness of samples, respectively; the differential conductance dI/dE corresponds to the slope of the recorded *I-E* curves which have a straight line form.

The liquid permeability of the modified GF was determined by performing the falling head permeability test. Before starting the flow measurements, the GF sample is saturated and the standpipes are filled with distilled water to a given level. The test then starts by allowing water to flow through the sample until the water in the standpipe reaches a given lower limit. The time required for the water in the standpipe to drop from the upper to the lower level is recorded. Often, the standpipe is refilled and the test is repeated twice. On the basis of the test results, the permeability of the sample was calculated as:

$$K = \frac{a \cdot L}{A \cdot \Delta t} \cdot \ln \left[\frac{h_{max}}{h_{min}} \right] \qquad (3)$$

where L is the height of the soil sample column, A – the sample cross section, a – the cross section of the standpipe, Δt – the recorded time for the water column to flow though the sample, h_{max} and h_{min} – the upper and lower water level in the standpipe measured using the same water head reference.

CV (cyclic voltammetry), chrono-techniques and EIS (electrochemical impedance spectroscopy) were applied for the characterization of GF-Co, GF-Ni,

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GF-Co-Ni activity toward electrochemical oxidation and reduction of PSS in an unstirred deoxygenated aqueous solution containing 1 M Na_2S (prepared form $Na_2S \cdot 9H_2O$, assay 97.5%) 1 M NaOH (assay 99.8%) and dissolved 1 M S (assay 99.998%) powder (pH ~13.8). Hereinafter, this solution is referred to as 1 M Na_2S+NaOH+S mixture.

The electrochemical analysis of GF samples modified with Ag was performed in an unstirred aqueous solution containing 0.2 M NaBr (assay 100%) and 0,2 M Br_2 (assay 99.8%) (pH ~1.65).

All electrochemical tests were performed at room temperature (20±1°C) by means of a potentiostat-galvanostat SP-150 (BioLogic) interfaced with the EC-Lab v10.39 software and connected to the conventional three-electrode electrochemical cell. The working electrode in this cell was 6 mm in diameter and 4 mm in thickness cylinder-shaped piece of the modified GF sample which was fixed in the hole of a special holder made from PTFE plastic. Wired graphite contact on the bottom of the hole in this holder served as the current collector. The geometric surface area of approximately 12.5 mm^2 of the investigated GF electrode was limited by a 4 mm in diameter hole in a temple of the holder. A rectangular Pt plate with the total surface area of approximately 12 cm^2 and an Ag/AgCl electrode filled with a saturated aqueous KCl solution ($E° = 0.197$ V vs. SHE) were used as counter and reference electrodes, respectively. EIS results were obtained in the frequency range of 10 mHz to 50 kHz by applying a sinusoidal voltage amplitude of ±10 mV around the OCP (open circuit potential) of the investigated modified GF electrode in 1M Na_2S+NaOH+S or 0.2 M NaBr+Br_2 mixture.

The freshly prepared solution for each electrochemical test was deoxygenated by bubbling the N_2 gas (99.996 vol.%) for at least 30 min. The nitrogen atmosphere was maintained over the solution in the electrochemical cell during all electrochemical measurements.

All above-mentioned analyses were also performed with bare GF sample, for comparison.

1. RESULTS AND DISCUSSION
2.1. GF pre-treatment before modification
2.1.1. GF pre-treatment and wetting with NaOH and HCl aqueous solutions

The experiments revealed that GF is hydrophobic as it hardly got wet when it was exposed to the water-based solutions. The boiling in strong alkaline solutions and pretreatment in oxidizing inorganic acid solutions are applied for increasing the hydrophilicity of GF. The surface of GF filaments becomes more hydrophilic after electrochemical oxidation in sulphuric acid solution as well.

2.1.2. GF pre-treatment and wetting with aqueous solutions of organic solvents

The GF filaments can be wet considerably quicker by using low surface tension liquids which are well miscible with water (methanol CH_3OH, ethanol C_2H_5OH, 1-propanol (n-propanol, C_3H_7OH), 2-propanol (isopropanol, $(CH_3)_2CHOH$) and propanone (acetone, $(CH_3)_2CO$)) and later could be leached out of the GF matrix. The wetting properties of any solid substance are related to the equilibrium of interfacial forces at the boundary of surfaces of three phases, i.e. solid, liquid and vapour. A quantitative parameter of wettability is the contact angle measured between the surfaces of interacting solid and liquid.

~130°	~123°	~115°	~93°	<45°
H_2O	10% (v/v)	20% (v/v)	25% (v/v)	30% (v/v)
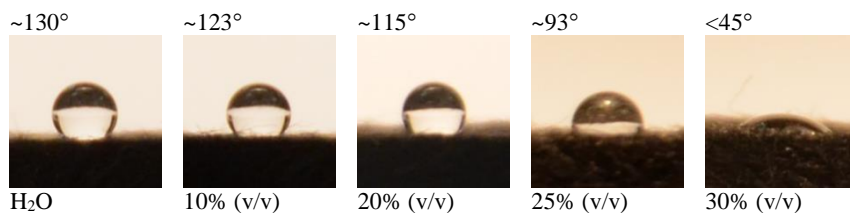
Fig. 2. Typical views of droplets of distilled H_2O and aqueous C_2H_5OH solutions of different concentrations on the surface of dry GF sample at room temperature. The values of contact angle and concentration of C_2H_5OH aqueous solutions are presented above and below the pictures, respectively

The measurement of contact angle between the flat surface of a GF sample and the above-mentioned pure organic solvents was complicated, since droplets of these solvents penetrated immediately into the GF matrix. In certain cases, the contact angles lower than 30° were observed for several seconds until penetration into GF (Fig. 2). On the other hand, this directly demonstrates a very good wettability of the GF sample with these solvents. As a result of a series of experiments, the minimum sufficient concentrations of these solvents in aqueous mixtures which show proper and fast wettability of the GF filaments matrix were determined. It is most likely that better wettability is due to the almost twice lower surface tension values of the mixtures than those of pure water. The aqueous solutions with lower concentration of these solvents demonstrate poor wetting of GF filaments (contact angle >90°) and droplets of such solutions as well as the ones of pure water remained on the surface of the GF sample for a very long time (up to few hours) (Fig. 3).

Facile and quick GF hydrophilization before other modification steps can be carried out with aqueous solutions of ethanol C_2H_5OH, methanol CH_3OH, propanone (acetone) $(CH_3)_2CO$, isopropanol $(CH_3)_2CHOH$ and n-propanol C_3H_7OH, which lowest sufficient concentrations are 25%, 30%, 35%, 10%, and 5 % (by volume), respectively.
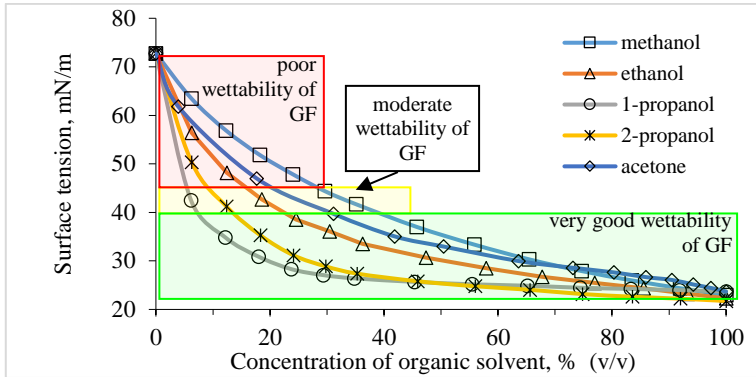
Fig. 3. A visualization of GF wettability with aqueous mixtures of some organic solvents. Data of surface tension dependence on the concentration of organic solvents-water mixtures were taken from literature.

2.2. Electroless deposition of metal coatings onto GF

2.2.1 Electroless deposition of Ag onto GF at room temperature

The processes which takes place in solution **A** during its preparation and the electroless Ag deposition process occurring after mixing solutions **A** and **B** could be described by the following reaction equations:

$$2AgNO_{3(aq)} + 2KOH_{(aq)} \rightarrow Ag_2O_{(s)} + 2KNO_{3(aq)} + H_2O_{(l)}$$

$$Ag_2O_{(s)} + 4NH_{3(aq)} + H_2O_{(l)} \rightarrow 2[Ag(NH_3)_2]OH_{(aq)}$$

$$C_6H_{12}O_{6(aq)} + 2[Ag(NH_3)_2]OH_{(aq)} + KOH_{(aq)} \rightarrow KC_6H_{11}O_{7(aq)} + 2H_2O_{(l)} + 4NH_{3(aq)} + 2Ag_{(s)}$$
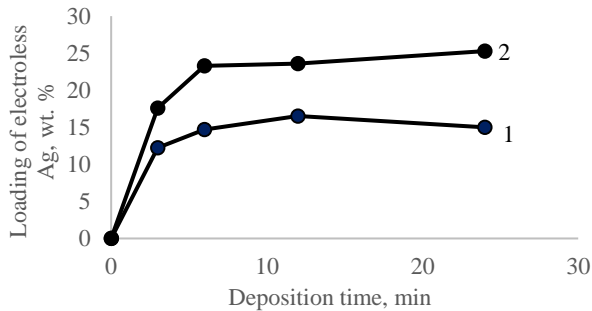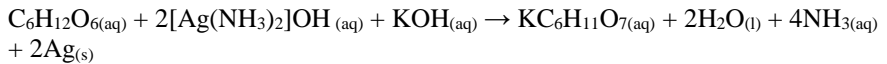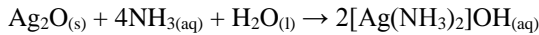
Fig. 4. Time-dependence of electroless Ag loading (wt. %) on the surface of GF-Ag (1) and GF-Ag-us (2)

Fig. 4 shows that the loading of electroless deposited Ag on the surface of GF-Ag and GF-Ag-us filaments increases most rapidly over the first 3 min. The mass fraction of deposited Ag reached 12.2 and 17.5 wt. % for GF-Ag and GF-Ag-us, respectively. In both cases, the mass fraction of Ag in GF-Ag and GF-Ag-us samples changed slightly after 6 min. This could be related to a relatively fast electroless Ag deposition reaction, when the major part of the Ag was formed within the first 6 minutes. The maximal and almost unchangeable loadings of electroless deposited Ag on the surface of GF-Ag and GF-Ag-us filaments were observed in the deposition time interval from 6 to 24 min. Additionally, it was found that constant mass fraction of deposited Ag in GF-Ag-us samples, obtained after 6, 12 and 24 min, was approximately 1.6 times greater than in the case of GF-Ag-us samples. An increase of Ag mass fraction onto the filaments of GF-Ag-us samples could be explained by increased transport rate of reactants into the internal parts of GF and by the acceleration of deposition process during the ultrasonic irradiation of electroless Ag deposition solution in general. Therefore, further morphological, compositional and structural investigations were performed only for GF-Ag and GF-Ag-us samples obtained after 6 min of electroless Ag deposition.

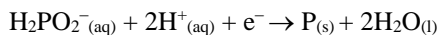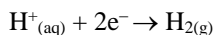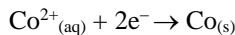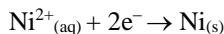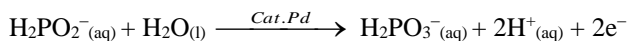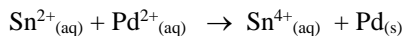### 2.2.2. Electroless deposition of Co and Ni onto GF at high temperature

Co, Ni and Co-Ni alloy coatings obtained by electroless deposition onto GF from electrolytes (Table 2) at high temperature (50–90°C) did not distinguish themselves by high mass fraction of deposited metals, therefore electrolytes for electroless deposition at room temperature were chosen (Table 1).

2.2.3. Electroless deposition of Co, Ni and Co-Ni alloy onto GF at low temperature

The uniform distribution of modifying particles or coating onto filaments in the whole volume of GF sample is essential, especially when electroless or electrochemical deposition are used for this purpose. Previous works reported that ultrasonication of electroless silvering solution ensures a better penetration of reagent into porous matrix of GF.

In order to improve this result and to achieve a completely uniform distribution of electroless Co, Ni, Co-Ni alloy deposit onto the external and internal filaments of GF sample, the modification was performed under different solution mixing modes (hydrodynamic conditions): stirring the solutions with a magnetic stirrer, ultrasonication, and continuous circulation in a flow-through reactor was investigated.

The activation and sensitization of the surface of GF filaments and successive electroless co-deposition of Co and Ni from alkaline solution could be described by the following reaction equations:

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$$Sn^{2+}_{(aq)} + Pd^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + Pd_{(s)}$$

$$H_2PO_2^-{}_{(aq)} + H_2O_{(l)} \xrightarrow{\quad Cat.Pd \quad} H_2PO_3^-{}_{(aq)} + 2H^+_{(aq)} + 2e^-$$

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$$

$$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$$

$$H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

$$H_2PO_2^-{}_{(aq)} + 2H^+_{(aq)} + e^- \rightarrow P_{(s)} + 2H_2O_{(l)}$$

Due to the last reaction, P is incorporated into electroless Co, Ni and Co-Ni alloy.
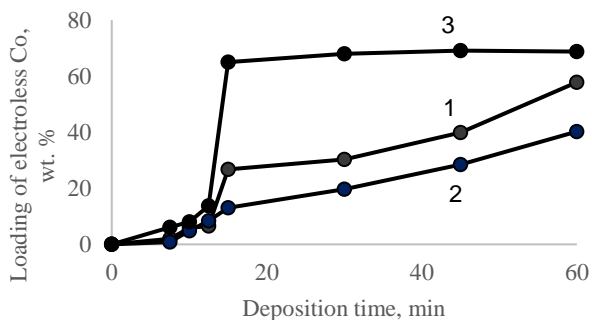
Fig. 5. Time-dependence of electroless Co loading (wt. %) on the surface of GF-Co-m (1), GF-Co-us (2) and GF-Co-ft (3)
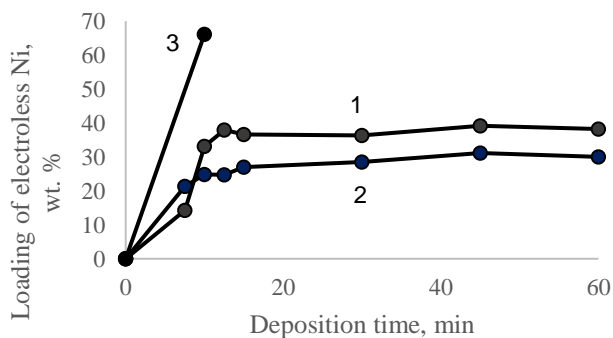
Fig. 6. Time-dependence of electroless Ni loading (wt. %) on the surface of GF-Ni-m (1), GF-Ni-us (2) and GF-Ni-ft (3)

Gravimetrical measurements revealed that stirring the solutions applied to electroless metal deposition solution enabled an increase of Co, Ni or Co-Ni alloy loading on the surface of GF filaments.The biggest mass fraction of Co, Ni, or Co-Ni alloy (68.7%, 66.2%, and 63.1%, respectively) was obtained when the solutions were mixed by continuous circulation in a flow-through reactor, and the lowest mass fraction was determined after ultrasonication (40.2%, 30.0%, and 29.9%, respectively). Gravimetrical analysis has shown that electroless Ni deposition (Fig.6) is the most intensive and ends after 10–12.5 min. However, the deposition processes for Co (Fig.5) and Co-Ni alloy (Fig.7) are slower and the metal fraction on the GF surface keeps increasing until the 60th minute, irrespective of the stirring mode.
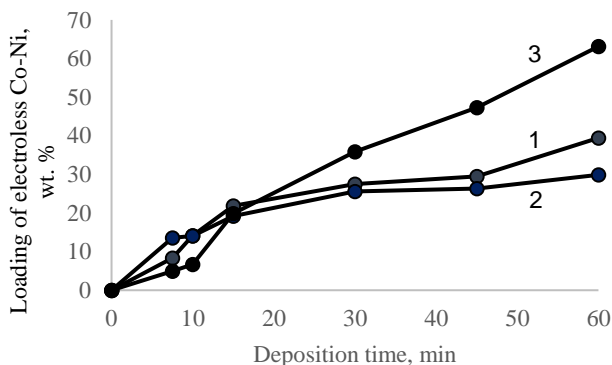

Fig. 7. Time-dependence of electroless Co-Ni loading (wt. %) on the surface of GF-Co-Ni-m (1), GF-Co-Ni-us (2) and GF-Co-Ni-ft (3)

2.3. The morphology, composition and structure of modified GF
2.3.1. The morphology, composition and structure of GF-Ag

The results of SEM analysis showed that GF-Ag sample, exposed in a non-agitated and not irradiated with ultrasound electroless Ag deposition solution for 6 min exhibit different surface morphology of Ag deposited on the filaments at the internal and external parts of the samples (Fig. 8, 1 and 2).
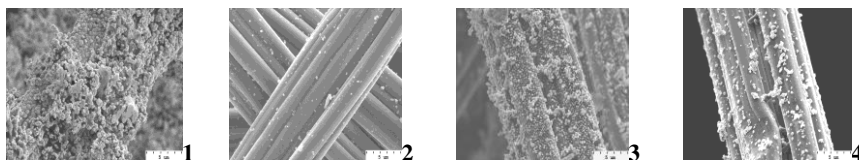

Fig. 8. SEM micrographs of filaments taken from the external (1 and 3) and internal (2 and 4) parts of GF-Ag (1 and 2) and GF-Ag-us (3 and 4) samples exposed in electroless Ag deposition solution for 6 min.

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GF-Ag filaments located at the external part of the sample are fully covered in dendritic layer of Ag, while GF-Ag filaments on the internal part of the sample exhibit only randomly dispersed individual globular Ag particles of nanometric dimensions (up to 200 nm). When electroless Ag deposition was conducted in the presence of ultrasound action, the morphological differences of Ag particles deposited on the external and internal filaments of GF-Ag-us sample have been reduced greatly (Fig. 8, 3 and 4). In both cases, the depositions of individual globular Ag particles, as well as larger conglomerates of these particles were observed on the surface of filaments of GF-Ag-us sample. However, the surface concentration of Ag particles was visibly lower on the internal filaments of the GF-Ag-us sample. Moreover, a similar distribution of Ag concentration throughout the internal and external parts of the GF-Ag and GF-Ag-us samples was observed in the results of EDX analysis. When electroless Ag deposition was performed in a non-agitated or non-ultrasonicated solution, the greatest concentration of Ag was found on the surface of external GF-Ag filaments, while the surface of internal filaments exhibited about 100 times lower concentration of Ag particles. In the presence of ultrasound action, a more uniform distribution of Ag concentration, i.e. more uniform deposition of Ag particles, on the surface of internal and external filaments of GF-Ag-us sample was obtained. In this case, Ag concentration on the surface of internal filaments is only 4.5 times lower in comparison with Ag concentration on the surface of external filaments. This is perhaps associated with the improved penetration of reactants (mass transport) to the internal filaments and a more uniform distribution of deposited Ag particles in the whole volume of GF-Ag-us sample. Furthermore, the cavitation phenomenon induced by ultrasonic irradiation causes local increases in temperature and pressure at the liquid-solid boundary of the phases. This may lead to an increased number of nucleation and crystallization centres at the surface of GF filaments, as well as the rate of Ag(I) reduction to metallic Ag.
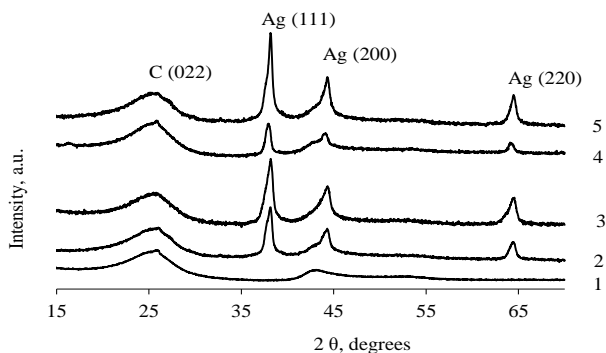

Fig. 9. XRD patterns of bare GF (1), internal (2 and 4) and external (3 and 5) filaments of GF-Ag (2 and 3) and GF-Ag-us (4 and 5) samples exposed in electroless Ag deposition solution for 6 min.

XRD analysis of samples showed a significant change in the structure of GF-Ag and GF-Ag-us samples in comparison with bare GF (Fig. 9). In the XRD pattern of bare GF, two broad peaks at 2θ equal to 26.0° and 43.1° are observed, which corresponds to (002) and (100) planes reflections of the graphitic form of carbon (Fig. 9, pattern 1). The appearance of new intense and narrow peaks of Ag phase in XRD patterns of GF-Ag and GF-Ag-us samples proves the presence of the crystalline Ag phase on GF filaments.

2.3.2. The morphology, composition and structure of GF-Co, GF-Ni and GF-Co-Ni

The morphology, chemical composition, and structure of metals deposited on the surface of the inner and external GF filaments were determined by SEM, EDS, and RDS methods, respectively. It has been observed that the distribution uniformity of Co, Ni, Co-Ni throughout the volume of the modified GF depends on the hydrodynamic mode and duration of modification process during low-temperature electroless modification of GF. It was observed that the deposition of Co, Ni, and Co-Ni coatings under different hydrodynamic modes showed that the biggest difference between the inner and external parts of GF samples were obtained under ultrasonication of modification solutions; much smaller differences were seen when the modification solutions were stirred with magnetic stirrer, and no differences were observed while circulating the solutions in the continuous flow reactor.
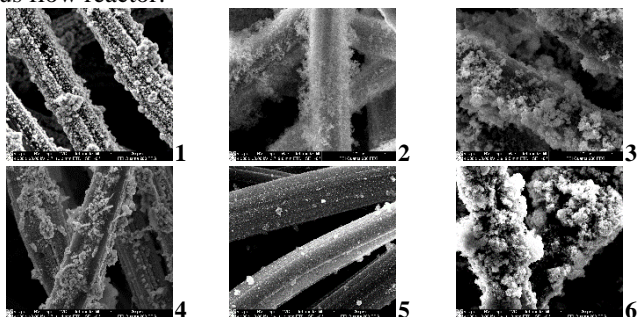

Fig. 10. SEM micrographs of filaments taken from the external (1, 2 and 3) and internal (4, 5 and 6) parts of GF-Co-m (1 and 4), GF-Co-us (2 and 5) and GF-Co-ft (3 and 6) samples exposed to electroless Co deposition solution for 60 min

SEM micrographs of bare GF filaments and those taken from the internal part of the GF-Co, GF-Ni and GF-Co-Ni samples modified using different stirring in electroless solution are presented in Figure 10, Figure 11 and Figure 12, respectively. The globules and pores of electroless Co, Ni and Co-Ni alloy deposit are clearly observed on the surface of filaments taken both from the external and

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internal parts of long-term (up to 1 h) modified GF-Co, GF-Ni and GF-Co-Ni samples, especially at GF-Co-ft sample (Fig. 10, 3 and 6), GF-Ni-ft (Fig. 11, 3 and 6) and GF-Co-Ni-ft (Fig. 12, 3 and 6). It is clear that a rather short time of nucleation, a sufficiently high deposition rate, and a uniform distribution of electroless Co and Ni deposit in the whole volume of modified GF sample were ensured by the continuous flow of electroless deposition solution throughout the modifiable GF sample.
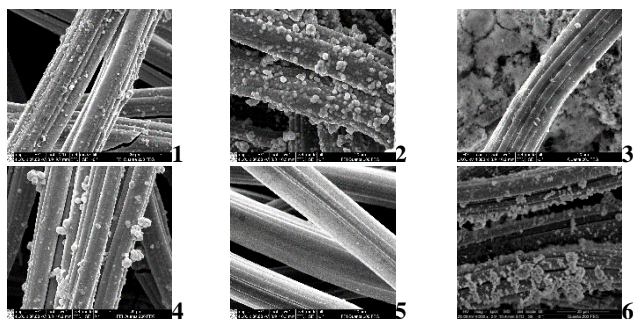

Fig. 11. SEM micrographs of filaments, taken from the external (1, 2 and 3) and internal (4, 5 and 6) parts of GF-Ni-m (1 and 4), GF-Ni-us (2 and 5) and GF-Ni-ft (3 and 6) samples, exposed to electroless Ni deposition solution for 10 min (3 and 6) and 60 min (1, 2, 4 and 5)
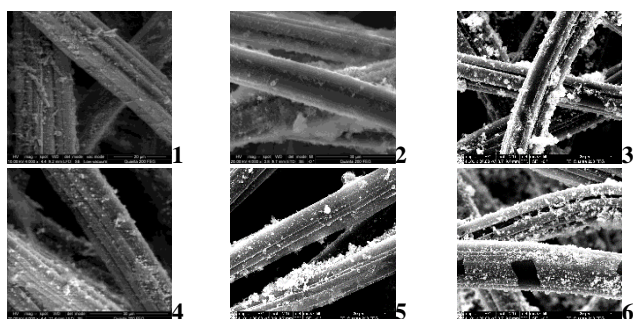

Fig. 12. SEM micrographs of filaments, taken from the external (1, 2 and 3) and internal (4, 5 and 6) parts of GF-Co-Ni-m (1 and 4), GF-Co-Ni-us (2 and 5) and GF-Co-Ni-ft (3 and 6) samples exposed to electroless Co-Ni deposition solution for 60 min

EDX analysis of GF-Co, GF-Ni and GF-Co-Ni samples revealed that beside the co-deposition of Co and Ni, the incorporation of P atoms occurs as well. The total concentration of metals and traces of incorporated P did not exceed 2 at. %.

The surface concentration of Co and Ni, or just Ni was visibly lower on the internal filaments of GF-Co-us, GF-Co-Ni-us and GF-Ni-us samples. Moreover, a similar distribution of metal concentration throughout the internal and external

parts of the modified GF samples was observed in the case of GF-Co-ft, GF-Co-Ni-ft and GF-Ni-ft samples.

Furthermore, it was noted that the even distribution of deposition leads to a complete covering of GF filaments with electroless Co, Ni, Co-Ni alloy and decreases the carbon concentration on the filaments of GF-Co-ft, GF-Co-Ni-ft and GF-Ni-ft.

A high level of oxygen concentration on the surface of bare GF filaments is very likely to be related to chemisorbed oxygen or the presence of the oxygen-containing species (e.g. OH) on the surface of graphitic carbon. Meanwhile, a relatively high concentration of oxygen determined on the surface of GF-Co, GF-Ni and GF-Co-Ni samples filaments could be related to the partially oxidized superficial layer of electroless Co, Ni and Co-Ni alloy deposits.

The XRD analysis has shown a significant change in the structure of GF-Co (Fig. 13), GF-Ni (Fig. 14) and GF-Co-Ni (Fig. 15) samples modified in electroless solution for 1 h while stirring the solutions with a magnetic stirrer, ultrasonication, and continuous circulation in flow-through reactor regimes in comparison with the bare GF sample. In the XRD patterns of bare GF, two broad peaks at 2θ equal to 26.0° and 43.1° can be observed which correspond to (002) and (100) planes reflections of the hexagonal structure of the graphitic form of carbon (JCPDS card No. 41-1487) (pattern 1).
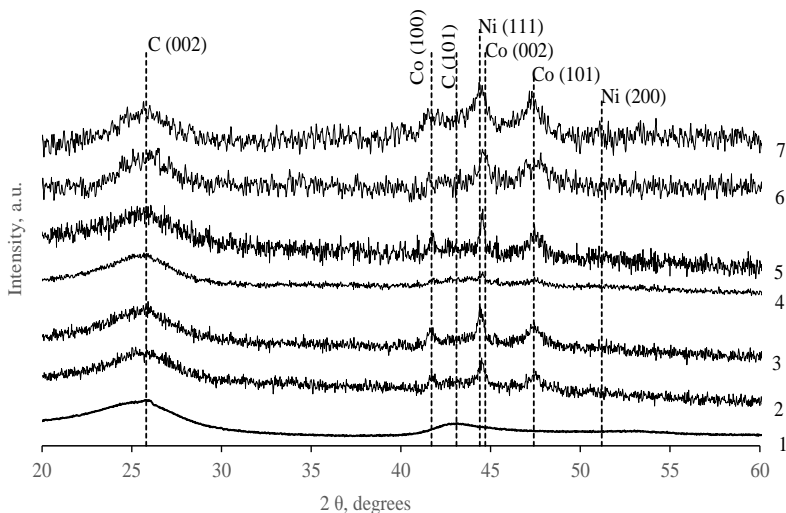

Fig. 13. XRD patterns of bare GF (1), internal (2,4,6) and external (3,5,7) filaments of GF-Co-m (2,3), GF-Co-us (4,5) and GF-Co-ft (6,7) samples exposed to electroless Co deposition solution for 60 min.
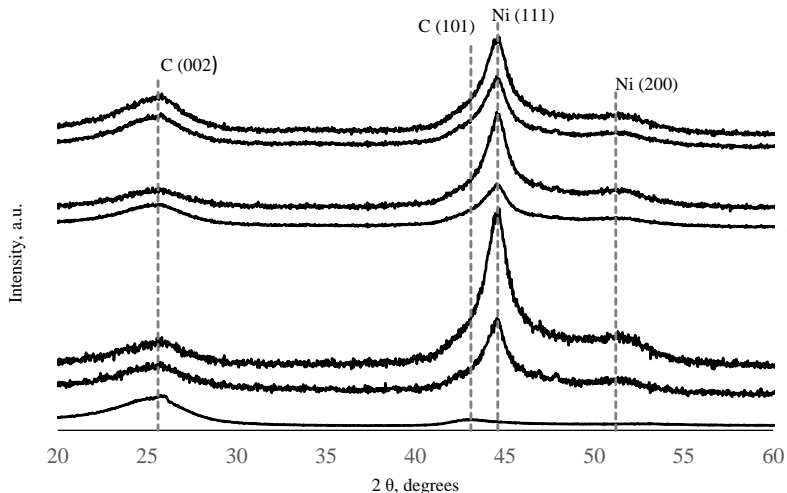
Fig. 14. XRD patterns of bare GF (1), internal (2,4,6) and external (3,5,7) filaments of GF-Ni-m (2,3), GF-Ni-us (4,5) and GF-Ni-ft (6,7) samples exposed to electroless Ni deposition solution for 10 (6,7) and 60 min (2–5)

The appearance of additional peaks in XRD patterns obtained from the internal and external parts of GF-Co and GF-Co-Ni samples indicates the presence of Co phase on the filaments of the modified GF. The diffraction peaks of hexagonal close-packed Co lattice are observed at 2θ angles equal to 41.7°, 44.8° and 47.6°, which correspond to the reflections of (100), (002), and (101) planes, respectively (JCPDS card No. 05-0727).

The individual peaks assigned to face-centred cubic (fcc) Ni lattice are clearly identified in the XRD patterns of GF-Ni samples, but are not clear in the XRD patterns of GF-Co and GF-Co-Ni samples. The presence of fcc Ni phases is suspected only due to the relatively more intensive diffraction peak at 44.6° which is determined by the overlapping of Co (002) and Ni (111) reflections. Similar XRD patterns obtained from the internal and external filaments of the modified GF in the flow-through reactor confirm the uniform distribution of electroless Co, Ni, Co-Ni alloy in the whole volume of the modified GF samples.
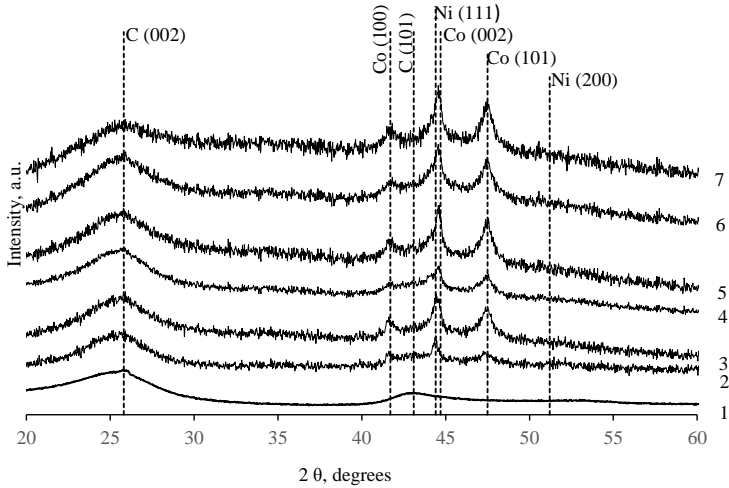
Fig. 15. XRD patterns of bare GF (1), internal (2,4,6) and external (3,5,7) filaments of GF-Co-Ni-m (2,3), GF-Co-Ni-us (4,5) and GF-Co-Ni-ft (6,7) samples exposed to electroless Co-Ni deposition solution for 60 min

2.4. Liquid permeability of modified GF

The investigation of liquid permeability of the unmodified and modified GFs has revealed that it depends on the mass fraction and distribution uniformity of metals (Ag, Co, Ni, and Co-Ni) in the whole volume of the modified GF.
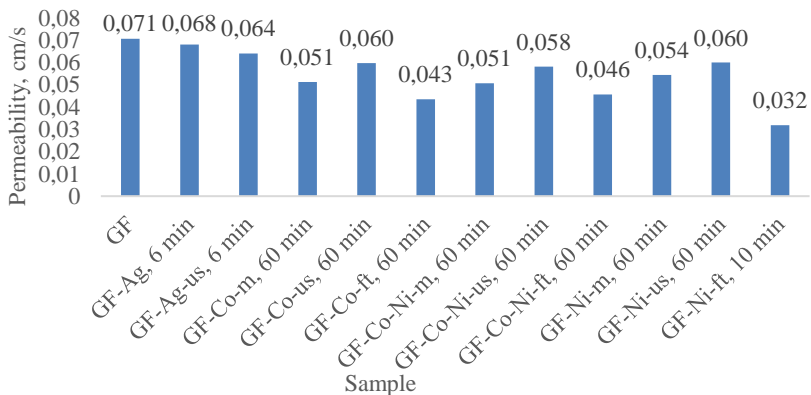

Fig. 16. Permeability analysis data of bare GF and of GF samples modified with metals

Liquid permeability was the lowest for the samples modified in the flow-through reactor when the distribution of deposited metal was the most uniform. For samples coated with Co, Ni, and Co-Ni alloy it was 0.043 cm/s, 0.046 cm/s, and 0.032 cm/s, respectively, whereas it was the highest for unmodified GF (0.071 cm/s). Theresults of liquid permeability are presented in Figure 16.

2.5. Electrical conductivity of the modified GF

As Fig. 17 shows, a uniform coverage of GF filaments with Ag in the whole volume of the sample increased its electrical conductivity up to 10.7 S/cm. This value is approx. 1.2 times larger than the electrical conductivity of unmodified GF (8.6 S/cm). This is related to the fact that Ag, being a very good conductor, deposited on the surface of GF filaments increased the overall electrical conductivity of GF-Ag and GF-Ag-us composites.
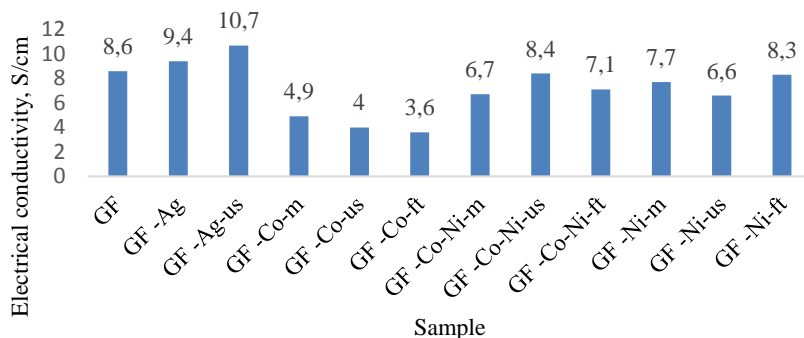

Fig. 17. Electrical conductivity analysis data of bare GF and of GF samples modified with metals

On the other hand, the electrical conductivity of GFs modified with Co, Ni, and Co-Ni alloy was lower (3.6 – 8.4 S/cm) than the one of unmodified GF, which is most likely due to the oxidation of metal surface.

2.6. Electrochemical tests of modified GF and bare GF electrodes
2.6.1. Electrochemical tests of GF-Ag and bare GF electrodes in NaBr and Br$_2$ solution

As Fig. 18 reveals, the replacement of GF electrode with GF-Ag one in 0.2 M NaBr and 0.2 M Br$_2$ solutions increased the anodic current by 1.35 times and raised the cathodic current by up to 1.4 times proving that GF-Ag possesses catalytic properties during electrochemical oxidation of Br$^-$ and reduction of Br$_3^-$ ions (this is confirmed by data in Fig. 19, Fig. 20, and Fig. 21). However, it was

observed that Ag deposited on the surface of GF filaments was not electrochemically stable with time.
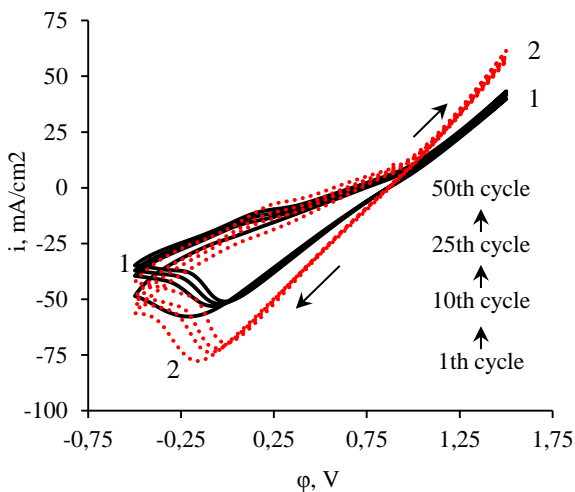

Fig. 18. The cyclic voltammograms (up to 50 cycles) recorded for bare GF (curve 1) and GF-Ag-us (curve 2) electrodes in 0.2 M NaBr and 0.2 M Br$_2$ mixture (potential scan rate 20 mV s^{-1})
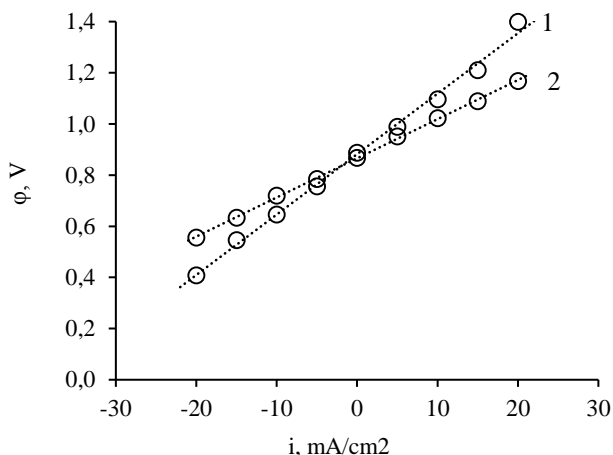

Fig. 19. Potential-current density curves recorded for bare GF (curve 1) and GF-Ag-us (curve 2) electrodes polarized in a 0.2 M NaBr and 0.2 M Br$_2$ mixture under galvanostatic conditions when the densities of anodic and cathodic currents were changed from 0 to 20 mA cm^{-2} with 5 mA cm^{-2} increment
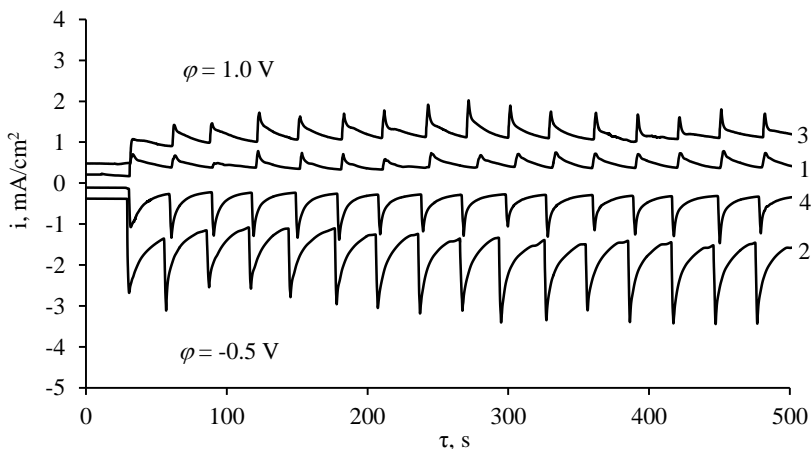
Fig. 20. The chronoamperograms recorded for bare GF (curves 1 and 2) and GF-Ag-us (curves 3 and 4) electrodes, anodically and cathodically polarized in a supporting H_2O electrolyte when the portions of ~10 μL of 0.2 M NaBr and 0.2 M Br_2 mixture were periodically injected directly into the surface of the investigated electrode. Injections started after 180 seconds and each current peak corresponds to an injection moment with the time interval of 30 seconds
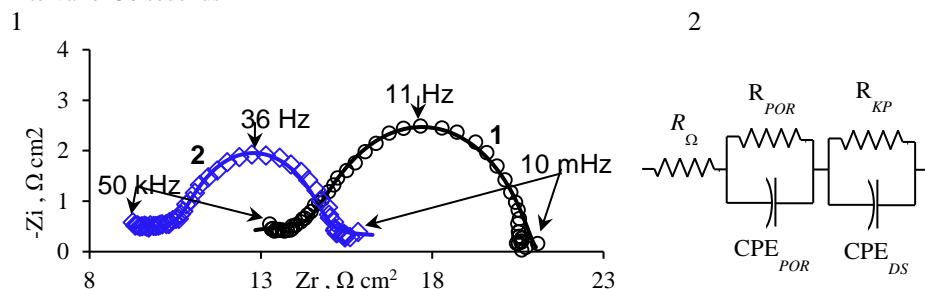

Fig. 21. Nyquist plots recorded for bare GF (curve 1) and GF-Ag-us (curve 2) electrodes in 0.2 M NaBr and 0.2 M Br_2 mixture at OCP. The open dots represent the experimental results and the solid lines are plotted from fitting results. In insertion, the equivalent circuit is presented (2).

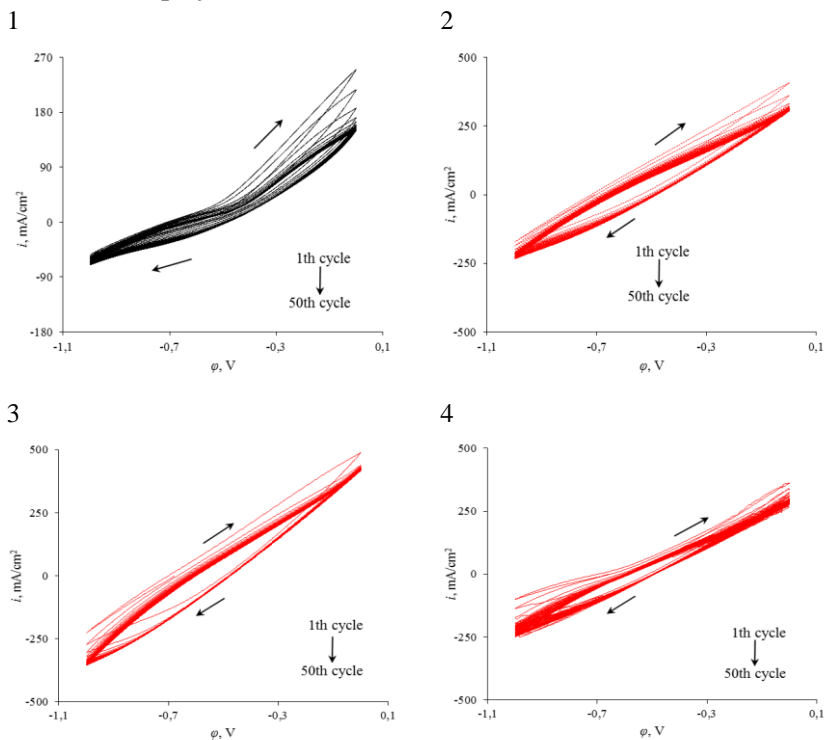## 2.6.2. Electrochemical tests of GF-Co, GF-Co-Ni, GF-Ni and bare GF electrodes in a polysulfide solution

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Fig. 22. The cyclic voltammograms (up to 50 cycles) recorded for bare GF (1), GF-Co-ft (2), GF-Co-Ni-ft (3) and GF-Ni-ft (4) electrodes in 1 M Na_2S+NaOH+S mixture (potential scan rate 20 mV s^{-1})

A replacement of the GF electrode with GF-Co, GF-Co-Ni, and GF-Ni ones in an aqueous sodium polysulfide Na_2S_x (x=2−5) solution containing 1 M of Na_2S, S, and NaOH each, led to the anodic current being increased by up to 1.9, 2.7, and 1.8 times, respectively, and cathodic current increased by up to 3.6, 5.1, and 3.4 times (Fig. 22), respectively, proving that these electrodes possess catalytic properties during electrochemical oxidation and the reduction of polysulfide ions (this is confirmed by data in Fig. 23, Fig. 24, Fig. 25). Electrodes made from GFs modified with low-temperature electroless Co, Co-Ni, and Ni deposits are also characterised by high electrochemical stability in aqueous polysulfide solutions.
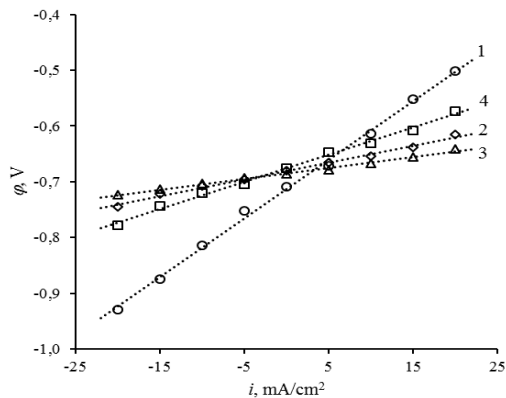
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Fig. 23. Potential-current density curves recorded for bare GF (curve 1), GF-Co-ft (curve 2), GF-Co-Ni-ft (curve 3) and GF-Ni-ft (curve 4) electrodes polarized in 1 M $Na_2S+NaOH+S$ mixture under galvanostatic conditions when anodic and cathodic current densities were changed from 0 to 20 mA cm^{-2} with 5 mA cm^{-2} increment
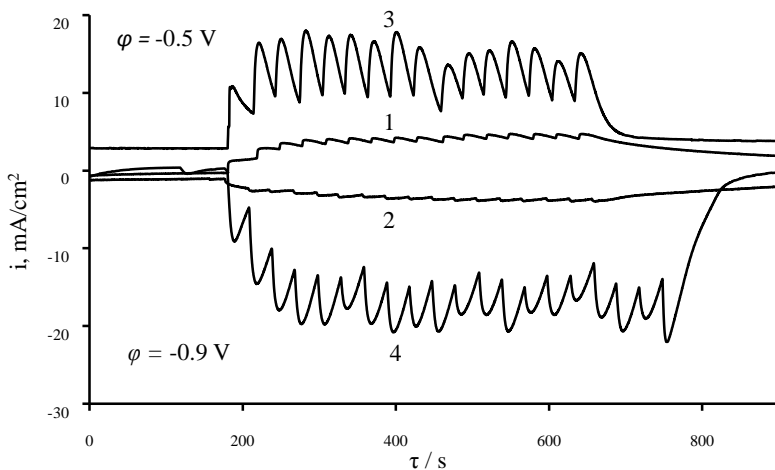
Fig. 24. The chronoamperograms recorded for bare GF (curves 1 and 2) and GF-Co-ft (curves 3 and 4) electrodes (the chronoamperograms of GF-Ni-ft and GF-Co-Ni-ft samples are similar), anodically and cathodically polarized in a supporting H_2O electrolyte when the portions of ~10 μL of 1 M $Na_2S+NaOH+S$ mixture were periodically injected directly into the surface of investigated electrode. Injections started after 180 seconds and each current peak corresponds to an injection moment with the time interval of 30 seconds

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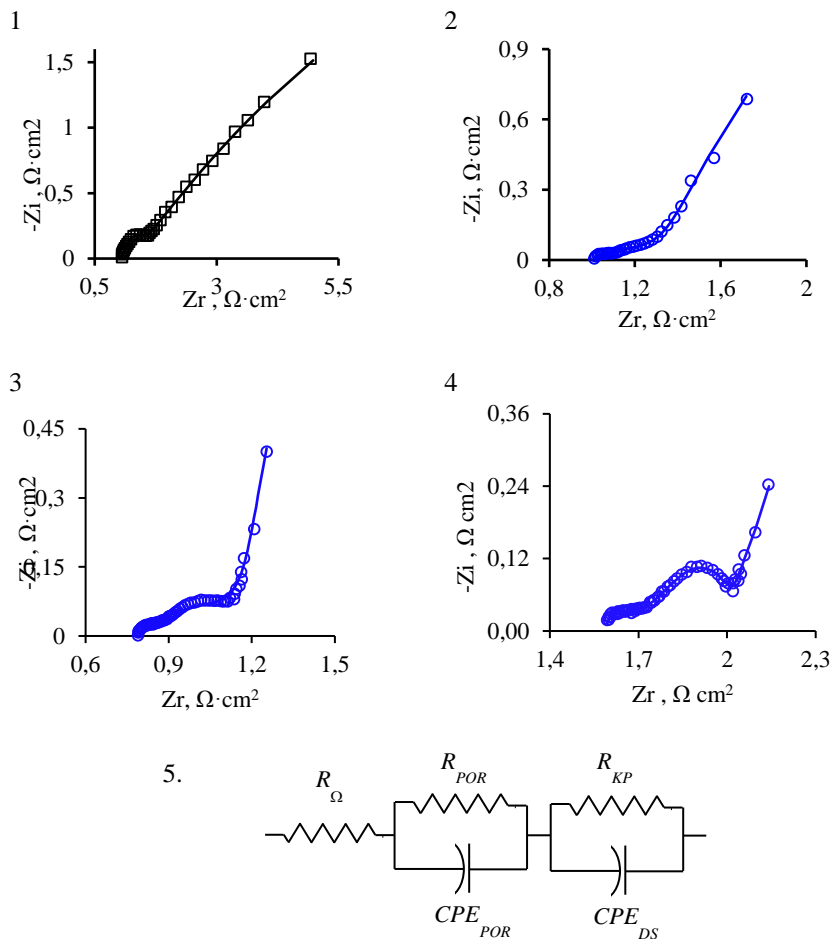
Fig. 25. Nyquist plots recorded for bare GF (1), GF-Co-ft (2), GF-Co-Ni-ft (3) and GF-Ni-ft (4) electrodes in 1 M $Na_2S+NaOH+S$ mixture at OCP. The open dots represent the experimental results and the solid lines are plotted from fitting results. In the insertion, the equivalent circuit is presented (5)

2.7. The technological scheme of intermittent operation for GF modification with electroless Co, Ni or Co-Ni alloy

The flow chart (Fig. 26) of the batch operation in the flow-through reactor for the production of electrodes from modified GF was suggested. The optimal technological process parameters were determined and the suitable equipment was chosen.
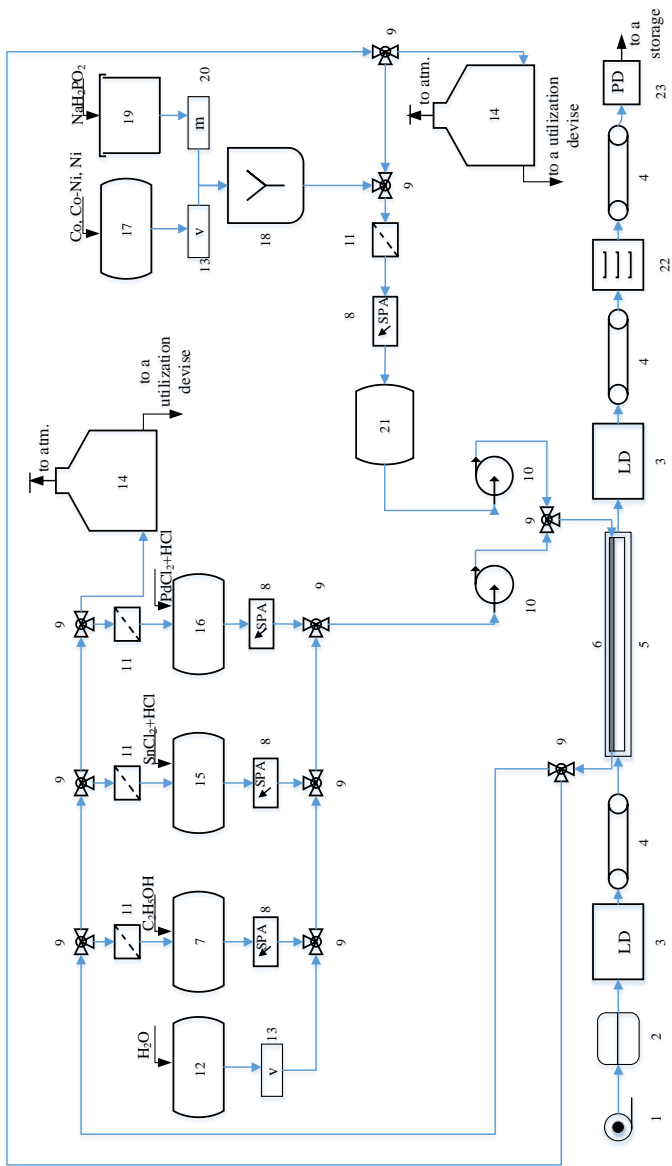
Fig. 26. A technological scheme of intermittent operation for GF modification with electroless Co, Ni or Co-Ni alloy. 1 – GF roll, 2 – cutting device, 3 – loading device, 4 – belt conveyer, 5 – flow-through reactor with interdigitated channels, 6 – network of interdigitated channels, 7, 12, 15, 16, 17 – liquid material storage tanks, 8 – spectrophotometric analyzer, 9 – three-way valve, 10 – pump, 11 – filtration unit, 13 - volumetric dispenser, 14 – tank for used chemical reagents, 18 – mixer, 19 – bulk material storage container, 20 – weight dispenser, 21 – tank for electroless deposition solution, 22 - drying chamber, 23 – packing device

CONCLUSIONS

1. Facile and quick GF hydrophilization preceding other modification steps can be carried out with aqueous solutions of ethanol C_2H_5OH, methanol CH_3OH, propanone (acetone) $(CH_3)_2CO$, isopropanol $(CH_3)_2CHOH$ and *n*-propanol C_3H_7OH; their lowest sufficient concentrations are 25%, 30%, 35%, 10%, and 5 % (by volume), respectively.

2. Ultrasound irradiation applied to electroless Ag deposition solution enabled an increase of Ag loading on the surface of GF filaments by approximately 25 wt. %, i.e. 1.6 times higher compared with the Ag mass fraction of GF sample modified without ultrasonication. A constant Ag mass in GF coated with Ag was reached after 6 min. However, the biggest mass fraction of Co, Ni, or Co-Ni alloy (60−70%) was obtained when the solutions were mixed by continuous circulation in a flow-through reactor, and the lowest mass fraction was determined after ultrasonication (30−40%). Electroless Ni deposition is the most intensive and ends after 10−12.5 min. On the other hand, the deposition processes for Co and Co-Ni alloy are slower and the metal fraction on the GF surface keeps increasing until the 60th minute irrespective of the stirring mode.

   3.1. It has been observed that during electroless modification of GF, the distribution uniformity of metal (Ag, Co, Ni, Co-Ni) throughout the volume of the modified GF depends on the hydrodynamic mode and the duration of modification process. It was observed that nanosized Ag particles of spheroid shape deposited on GF filaments by ultrasonication, distributed more uniformly in the whole GF volume. However, the deposition of Co, Ni, and Co-Ni coatings under different hydrodynamic modes showed that the biggest difference between the inner and external parts of GF samples were obtained under ultrasonication of the modified solutions; much smaller differences were seen when the modified solutions were stirred with a magnetic stirrer, and no differences were observed while circulating the solutions in the continuous flow-through reactor.

   3.2. Liquid permeability was the lowest for the samples modified in the flow-through reactor when the distribution of deposited metal was the most uniform. For samples coated with Co, Ni, and Co-Ni alloy it was 0.043 cm/s, 0.046 cm/s, and 0.032 cm/s, respectively, whereas it was the highest for unmodified GF (0.071 cm/s).

   3.3. Uniform covering of GF filaments with Ag in the whole volume of the sample increased its electrical conductivity up to 10.7 S/cm. This value is approx. 1.2 times higher than the electrical conductivity of unmodified GF (8.6 S/cm). Despite this, the electrical conductivity of GFs modified with Co, Ni, and Co-Ni alloy was lower (3.6 S/cm–8.4 S/cm) than the one of unmodified GF, which is most likely due to the oxidation of metal surface.

4.1. Replacement of GF electrode with GF-Ag one in 0.2 M NaBr and 0.2 M Br_2 solutions led to the anodic current being increased by up to 1.35 times and cathodic current increased by up to 1.4 times proving that GF-Ag possesses catalytic properties during electrochemical oxidation of Br^- and reduction of Br_3^- ions. However, it was observed that Ag deposited on the surface of GF filaments was not electrochemically stable with time.

4.2. A replacement of GF electrode with GF-Co, GF-Co-Ni, and GF-Ni ones in an aqueous sodium polysulfide Na_2S_x (x=2−5) solution containing 1 M of Na_2S, S, and NaOH each, increased anodic current up to 1.9, 2.7, and 1.8 times, respectively, and raised the cathodic current up to 3.6, 5.1, and 3.4 times, respectively, proving that these electrodes possess catalytic properties during electrochemical oxidation and reduction of polysulfide ions. Electrodes made from GFs modified with Co, Co-Ni, and Ni by electroless deposition at room temperature are also characterised by high electrochemical stability in an aqueous polysulfide solutions.

5. The flow chart of the batch operation in the flow-through reactor for the production of electrodes from GF modified with Co, Ni, and Co-Ni alloy was suggested. The optimal technological process parameters were determined and the suitable equipment was chosen.

List of Publications and proceedings on the Theme of dissertation Publications corresponding to the list of Institute of Science Information (ISI Web of Science) database

1. Macijauskienė, Brigita; Griškonis, Egidijus. Ultrasound assisted modification of graphite felt with electroless silver – Part 1: composition, morphology, structure and electrical conductivity // Chemija. Vilnius: Lietuvos mokslų akademija. ISSN 0235-7216, ISSN 2424-4538 (online). 2015, Vol. 26, No. 1, p. 1–8.

2. Macijauskienė, Brigita; Griškonis, Egidijus. Graphite felt modified with electroless Co-Ni-P alloy as an electrode material for electrochemical oxidation and reduction of polysulfide species // Chemical Papers. Bratislava: Springer. ISSN (Print) 0366-6352, ISSN (Online) 1336-9075. 2016, Vol. 70, No. 12, p. 1611–1620. DOI: https://doi.org/10.1515/chempap-2016-0094

Articles in Lithuanian Journals Approved by the Department of Science and Studies

1. Macijauskienė, Brigita; Griškonis, Egidijus; Jezerskaitė, Angelė. Grafito veltinio elektrocheminis ir cheminis modifikavimas kobaltu. // CHEMINĖ TECHNOLOGIJA. Kaunas. 2012. Vol. 2, No. 60, ISSN 1392 – 1231. p. 31–36.

Publications in conference proceedings

1. Macijauskienė, Brigita; Griškonis, Egidijus. Electrochemical modification of graphite felt with cobalt // Chemija ir cheminė technologija, KTU, sekcija – Neorganinių junginių chemija ir technologija. KTU- Kaunas. 2012. ISSN 2029-9222. p.101 – 105.
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REZIUMĖ

Temos aktualumas

Pastaruoju metu plačiai atliekami įvairių anglies darinių (grafeno bei jo oksido, anglies nanovamzdelių, grafito ir kt.) fundamentalieji ir taikomieji tyrimai siekiant panaudoti šias medžiagas įvairiose srityse (medicinoje, biotechnologijose, cheminei bei elektrocheminei katalizei, fotochemijoje, energetikoje ir pan.). Vienas tokių anglies darinių yra iš poliakrilnitrilo pluošto gaminamas lengvas, turintis didelį savitąjį paviršių, visomis kryptimis pralaidus dujoms bei skysčiams, chemiškai bei termiškai patvarus ir laidus elektrai grafito veltinis. Dėl minėtų savybių jį galima panaudoti įvairiausių elektrocheminių įrenginių (pratekančiųjų elektrolitų akumuliatorių (PEA), kuro elementų, elektrocheminės sintezės reaktorių ir kt.) elektrodų gamybai. Kad grafito veltinio (GV) elektrodai būtų tinkami tam tikriems elektrocheminiams procesams vykdyti, jie dažnai papildomai apdorojami termiškai bei modifikuojami funkcinėmis medžiagomis taikant cheminius ir elektrocheminius metodus, t. y. modifikavimo metu grafito veltinio siūlelių paviršiuje sudaromos įvairios funkcinės grupės, chemiškai bei elektrochemiškai nusodinami katalizinių savybių turintys metalai bei jų junginiai.

Darbo tikslas

Ištirti grafito veltinio cheminio modifikavimo Co, Co-Ni, Ni bei Ag galimybes ir įvertinti modifikuoto grafito veltinio elektrodų elektrochemines savybes siekiant juos panaudoti elektrocheminiame polisulfidų ir bromido/brombromido pratekančiųjų elektrolitų akumuliatoriuje efektyvesniam oksidacijos–redukcijos reakcijų vykdymui.

Siekiant darbo tikslo, reikėjo išspręsti **šiuos uždavinius**.
1. Nustatyti paprastą ir efektyvų būdą GV hidrofilizuoti.
2. Parinkti cheminio metalų (Co, Co-Ni, Ni bei Ag) nusodinimo tirpalus ir juose atlikti GV modifikavimo procesus, taikant šių tirpalų skirtingus maišymo būdus (hidrodinaminius režimus).
3. Ištirti modifikuoto metalais (Co, Co-Ni, Ni bei Ag) GV morfologiją, elementinę sudėtį, struktūrą, skysčio pralaidumą ir savitąjį elektrinį laidumą. Visas modifikuoto GV savybes palyginti su atitinkamomis nemodifikuoto GV savybėmis.
4. Ištirti GV-Co, GV-Co-Ni ir GV-Ni elektrochemines savybes vykdant polisulfidų oksidacijos–redukcijos reakcijas vandeniniame natrio polisulfido Na_2S_x (x=2–5) tirpale, turinčiame Na_2S, S ir NaOH, o GV-Ag

– vykdant bromido/brombromido jonų oksidacijos–redukcijos reakcijas vandeniniame tirpale, turinčiame NaBr ir Br_2.

5. Pasiūlyti metalais modifikuoto GV elektrodų gamybos technologinę schemą, parinkti tinkamus procesų parametrus bei įrangos tipą.

Mokslinis naujumas

Ištirtas GV modifikavimas Co, Co-Ni, Ni bei Ag dangomis taikant cheminio nusodinimo būdą, taikant tirpalų maišymą magnetine maišykle, ultragarsinį maišymą ir nuolatinę cirkuliaciją pro srautinį reaktorių. Nustatyta skirtingų hidrodinaminių sąlygų įtaka metalų pasiskirstymui visame modifikavimo GV tūryje. Nustatytos atitinkamais metalais modifikuotų GV elektrodų elektrocheminės savybės polisulfidų ir bromido/brombromido vandeniniuose tirpaluose.

Praktinė vertė

Disertacijoje pateikti darbo rezultatai yra svarbūs plėtojant GV modifikavimo technologiją bei modifikuoto GV elektrodų pritaikymą pratekančiųjų elektrolitų akumuliatoriuose efektyvesniam elektros energijos konvertavimui į cheminę energiją ir atvirkščiai. Parodyta, kad Co, Co-Ni bei Ni modifikuotas GV yra perspektyvios medžiagos panaudojant jas polisulfidų–bromido/brombromido pratekančiųjų elektrolitų akumuliatorių elektrodų gamybai. Pasiūlyti principiniai sprendimai tokiai technologijai įgyvendinti.

Darbo aprobavimas ir publikavimas

Disertacijos tema yra paskelbta 9 publikacijose: 2 straipsniai žurnaluose, įtrauktuose į Mokslinės informacijos instituto (*Clarivate Analytics Web of Science*) duomenų bazę, 1 straipsnis kitų tarptautinių duomenų bazių leidiniuose ir 6 pranešimai arba jų santraukos konferencijų pranešimų medžiagoje.

Darbo apimtis

Disertaciją sudaro įvadas, literatūros apžvalga, naudotos medžiagos bei tyrimų metodika, rezultatai bei jų aptarimas, išvados, publikacijų disertacijos tema sąrašas ir 5 priedai. Pateikiamas 160 šaltinių sąrašas. Pagrindinė medžiaga išdėstyta 113 puslapių, įskaitant 45 paveikslus ir 15 lentelių.

Ginamieji disertacijos teiginiai

1. GV efektyviam hidrofilinimui yra tinkami vandeniniai žemesniųjų alkoholių ir acetono tirpalai.

2. Cheminio nusodinimo būdu modifikuojant GV, metalų (Co, Ni, Co-Ni) pasiskirstymo tolygumas visame modifikuoto GV tūryje ir nusodintų metalų masės dalis priklauso nuo hidrodinaminio režimo ir modifikavimo proceso trukmės.

3. Kambario temperatūroje ($t=20\pm1$ °C) cheminio nusodinimo būdu Co, Co–Ni, Ni modifikuoto GV elektrodams būdingas didelis elektrocheminis aktyvumas vandeniniame polisulfidų tirpale, ir šie elektrodai yra perspektyvios medžiagos PEA elektrodams gaminti.

IŠVADOS

1. Efektyvus GV hidrofilinimas atliekamas naudojant etanolio C_2H_5OH, metanolio CH_3OH, propanono (acetono) $(CH_3)_2CO$, izopropilo alkoholio $(CH_3)_2CHOH$ ir *n*-propanolio C_3H_7OH vandeninius tirpalus, kurių pakankamos mažiausios koncentracijos atitinkamai yra: 25 %, 30 %, 35 %, 10 % ir 5 % (tūrio).

2. Nustatyta, kad GV siūlelių paviršuje nusėdusio Ag masės dalis priklauso nuo ultragarso poveikio. Taikant ultragarsinį maišymą pastovi Ag masės dalis pasiekiama jau po 6 min, ir ji yra apie 1,6 karto didesnė nei sidabruojant GV nemaišomame tirpale. GV siūlelių paviršuje nusėdusio Co, Ni, ar Co-Ni lydinio didžiausia masės dalis (nuo 60−70 %) gaunama modifikavimo tirpalus maišant srautiniame reaktoriuje, o mažiausia – maišant ultragarsu (nuo 30−40 %). Nustatyta, kad intensyviausiai vyksta cheminis Ni nusodinimas. Šis procesas įvyksta per 10 min. Co ir Co-Ni lydinio nusodinimo procesas yra lėtesnis, ir ant GV nusėdusio metalo masės dalis didėja iki 60-osios proceso minutės, nepriklausomai nuo tirpalo maišymo režimo.

   3.1. Pastebėta, kad cheminio nusodinimo būdu modifikuojant GV, metalų (Ag, Co, Ni, Co-Ni) pasiskirstymo tolygumas per visą modifikuoto GV tūrį priklauso nuo hidrodinaminio režimo ir modifikavimo proceso trukmės. Nustatyta, jog veikiant ultragarsui ant GV siūlelių nusodinamos nanometrinių matmenų Ag dalelės, kurių forma artima sferoidams, daug tolygiau pasiskirsto per visą GV tūrį. O Co, Ni ir Co-Ni dangų nusodinimo metu pastebėta, kad didžiausi skirtumai tarp GV bandinio išorinių ir vidinių dalių gaunami modifikavimo tirpalą maišant ultragarso poveikiu, gerokai mažesni skirtumai − maišant magnetine maišykle, o skirtumų nepastebima maišant srautiniame reaktoriuje.

   3.2. Modifikuojant GV srautiniame reaktoriuje, kai nusodinami metalai tolygiausiai pasiskirsto per visą GV tūrį gautų bandinių pralaidumas skysčiui yra mažiausias (Co, Ni ir Co-Ni dengtiems bandiniams atitinkamai siekė 0,043 cm/s, 0,046 cm/s, 0,032 cm/s), o nemodifikuoto GV – didžiausias (0,071 cm/s).

   3.3. Tolygus GV siūlelių padengimas Ag per visą bandinio tūrį padidino jo elektrinį laidumą iki 10,7 S/cm. Tai 1,2 karto daugiau, palyginus su nemodifikuoto GV elektriniu laidumu. O Co, Ni ir Co-Ni lydiniu modifikuotų GV bandinių elektrinis laidumas yra mažesnis (jo vertės svyruoja tarp 3,6–8,4 S/cm) nei nemodifikuoto GV (8,6 S/cm). Tai susiję su šių metalų paviršiaus oksidacija.

   4.1. 0,2 M NaBr ir 0,2 M Br_2 tirpale vietoj GV panaudojus GV-Ag elektrodą pastebėta iki 1,35 karto padidėjusi anodinės bei iki 1,4 karto – katodinės srovės vertė. Tai rodo, kad GV-Ag pasižymi katalizinėmis savybėmis elektrochemiškai oksiduojant Br^- bei redukuojant Br_3^- jonus. Tačiau

4.2. Vandeniniame natrio polisulfidų Na_2S_x (x=2–5) tirpale vietoj GV panaudojus GV-Co, GV-Co-Ni ir GV-Ni elektrodus pastebėtos atitinkamai iki 1,9, 2,7 bei 1,8 karto padidėjusios anodinės ir iki 3,6, 5,1 bei 3,4 karto – katodinės srovės vertės. Tai rodo, kad šie elektrodai pasižymi katalizinėmis savybėmis elektrochemiškai oksiduojant bei redukuojant polisulfidų jonus. Cheminio nusodinimo būdu Co, Co-Ni, Ni modifikuotiems GV elektrodams būdingas didelis elektrocheminis stabilumas vandeniniame polisulfidų tirpale.

5. Pasiūlyta Co, Ni, Co-Ni modifikuoto GV elektrodų gamybos srautiniame reaktoriuje principinė periodinio veikimo technologinė schema. Nustatyti optimalūs technologinio proceso parametrai, parinkti tinkami įrangos tipai.