NOVATEUR PUBLICATIONS
JournalNX- A Multidisciplinary Peer Reviewed Journal
ISSN No: 2581 - 4230
VOLUME 7, ISSUE 4, Apr. -2021

CARBON PASTE ELECTRODES MODIFIED BY VARIOUS ORGANIC REAGENTS

Gulboeva Dilafruz Ruziboyevna
Karshi State University

ABSTRACT:

A procedure is described for manufacturing a composite electrode based on carbon graphite powder and manganese dioxide nanoparticles deposited on its surface, obtained during the reduction reaction of potassium permanganate with manganese (II) ions from aqueous solutions. Using the methods of scanning microscopy and X-ray diffraction analysis, the success of the modification of carbon powder with nanoparticles of manganese dioxide with sizes of 20-55 nm was proved. For bulk modification of the electrode, paraffin was used as a binder. Design features and a method for manufacturing an electrode for determining hydrogen peroxide are described. Electrochemical studies of the behavior of the composite MnO_2/C electrode were carried out using cyclic and differential-pulse voltammetry methods.

Keywords: inversion voltamperometriy, tin, carbon-paste sensors, three distilled water, differentiated determination, fone electrolytes, range of the current, accumulation potential on electrode

INTRODUCTION:

At the first stages of their development, inversion methods of electroanalytical chemistry owe much to the stationary mercury-dripping electrode (SRCE), which is quite widely used and operated in the IV version with anodic polarization of anions (CI, - Br-I, - CrO_4-, MoO_4^{2-}, S^{2-}), their determination and concentration in the form of poorly soluble compounds with mercury [1-3].

Despite the indisputable advantages of SRCE, such as: constantly renewed surface, high hydrogen overvoltage, formation of amalgams with many metals, small surface, etc., this electrode also has its disadvantages, one of which is the high toxicity of mercury, leading to very serious diseases and, accordingly, limited use in analytical practice, therefore, recently, interest in the practical application of SRCE, respectively, has noticeably decreased [4].

The use of indicator electrodes made of platinum metals and gold in IV is very limited, due to the low overvoltage of hydrogen on electrodes made of platinum, gold, rhodium, palladium and their alloys, as well as the formation of oxide layers of metals at potentials more positive than +0.8 V. Such layers negatively affect the course of electrode processes and require their constant removal and renewal of the working surface of the electrode when measuring AC. In addition, metal substrates can interact with emitted elements, forming solid solutions with them [5], which are incapable of conducting an electric current.

CPE is a mixture of crushed coal with an organic non-volatile and water-immiscible liquid, which is -bromonaphthalene, nujol, liquid paraffin, wax and other organic substances. The field of application of the CPE is limited by potentials not more negative - 0.3 V, which is caused by significant residual currents on such an electrode, due to the reduction of adsorbed oxygen [6].

The properties of electrodes, in addition to the nature of their basic material (graphite, carbon-ceramic, metals, their oxides, etc.), largely depend on the state of the electrode surface

itself. For the same reason, in many cases, the working surface of the electrodes is subjected to mechanical and chemical cleaning, as well as activated in various ways or coated with a layer of another electroactive metal. However, a distinctive feature of such electrodes is the nonspecificity of their electrochemical behavior in the media under study [7].

In recent years, considerable efforts have been directed towards the development of a new group of electrodes with chemically modified surfaces [8-12]. By applying a thin layer of a modifier substance that determines and determines the properties of the created electrode, fundamentally changing its electrode begins to selectively react exclusively to a specific analytical component (metal), which has various redox and complexing properties.

Manufacturing technique of carbon-paste electrode (CPE):

An analytical balance was used to weigh the exact mass of each sample of spectrally pure graphite powder (grade B-3), previously ground in a porcelain mortar to a particle size of 160 mesh (the powder was passed through a sieve with a certain pore diameter). A weighed portion of the previously purified wax was heated in a porcelain crucible in a sand bath to the melting temperature (75-85 □ C). Graphite powder was introduced into the molten wax with constant stirring of the resulting mixture. The ratio of wax to graphite was 1: 1 by weight. The resulting mixture was heated to 150 ° C and cooled rather slowly to 90 ° C with constant stirring. At this temperature, using a conventional medical syringe, the mixture was drawn into hollow polyethylene tubes, 60 mm long and 0.3 mm in diameter. Copper or silver wire with a diameter of 0.05 mm and a length of 90 mm served as a current collector. Thus prepared CPE must be left for 7-10 days for complete solidification of the carbon paste in the tube in order to stabilize the components in the paste and eliminate peeling of the electrode surface during its mechanical renewal.

Were tested electrodes having different shapes of the working surface (cuts of different types, types and shapes), conventionally designated 1, 2 and 3. Figure 1. shows the types and shapes of three types of surface cuts of the manufactured electrodes as an example, and Table 3.1. the data obtained in the determination of indium using modified electrodes of different nature, depending on the geometric shape of the working surface of the electrode, are presented.

As can be seen from table 1, the best results were obtained with the electrode of the "3" type, having the shape of a drop, in appearance theoretically approaching a mercury drop, which is a reference working surface, and therefore it is this electrode that is characterized by high electrochemical characteristics and analytical parameters.

Table 1 Results of IV determination of indium by CPE, modified EDTA with a working surface of various types of cuts

Introduced metal, mcg (analysis conditions)	Electrode types	Found Me, $(\bar{x} \pm \Delta X; P = 0.95)$	n	S	S_r
In 1,0 mkg/ml (fon 0,1M HCl; d.t. = 1,0 mkA; Yen = -0,35 V; tn=60 s)	1	0,32±0,14	4	0,09	0,281
	2	0,64±0,10	5	0,08	0,125
	3	0,97±0,06	5	0,05	0,051

It has been established that it is precisely this shape of the working surface of the electrode that provides higher operational and physicochemical characteristics and, accordingly, causes a high current density at the end of the working surface of the electrode, which is especially important and is the main and determining criterion for electroanalytical determination of depolarizers (metals), in especially during IV, where the surface of the working electrode is an indicator (sensor)

showing the exact content of the electroactive substance.

As is known [9], chemically modified electrodes (CME) provide a different characteristic, compared to conventional electrodes, the rate of a heterogeneous electrochemical reaction, which has achieved high selectivity and sensitivity, along with the ability to isolate the working electrode from the influence of foreign substances present in the test solution. ... In some special and specific cases, CMEs exhibit electro-optical properties, which are also necessary for their use in electroanalytical chemistry.

As modified CPEs, the following were tested: electrodes modified with EDTA, dithizone, 8-hydroxyquinoline, tributyl phosphate, thiourea, thioacetamide, and thionalide [10].

The properties of solid modified electrodes, first of all, depend on the ratio of the components that make up the carbon paste, therefore, mixtures were first prepared, consisting of various proportions of graphite powder, wax and modifier (by weight). It was found that with an increase in the content of graphite in the mixture, the electrical conductivity of the electrode increases, and in this regard, it was necessary to achieve optimal ratios of the components of the carbon paste (Table 2.).

Table 2. Results of tests of the created electrodes made on the basis of different contents of the modifier in the carbon paste (CIn = 0.5 μg)

Modifier mass EDTA, g	The composition of the paste mixture, the masses. %			Peak height, mm
	Modifier EDTA	Wax	Graphite	
No modifier	0	50	50	9
0.1	2.5	50	47.5	16
0.2	5.0	50	45	25
0.3	7.5	50	42.5	70
0.4	10.0	50	40	77
0.5	12.5	50	37.5	35
0.6	15.0	50	35	21
0.7	17.5	50	32.5	9
0.8	20.0	50	30	7

The optimal amount of the modifier introduced into the coal paste was selected on the basis of our experimental data. Under optimized conditions, electrodes were manufactured containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g of the modifier. The results obtained when testing the electrodes made in this way are presented in Tables 2, 3 and 4, as well as in Fig. 2.

Table 3. Test results of the created electrodes made on the basis of different contents of the modifier in the carbon paste (CTh = 7.0 μg)

Modifier mass EDTA, g	The composition of the paste mixture, the masses. %			Peak height, mm
	Modifier EDTA	Wax	Graphite	
No modifier	0	50	50	10
0,1	2,5	50	47,5	15
0,2	5,0	50	45,0	25
0,3	7,50	50	42,5	35
0,4	10,0	50	40,0	14
0,5	12,5	50	37,5	11
0,6	15,0	50	35,0	7
0,7	17,5	50	32,5	3
0,8	20,0	50	30,0	1

Table 4. Results of tests of the created electrodes made on the basis of different contents of the modifier in the carbon paste (CSb = 2.5 μg)

Modifier weight -8-hydroxyquinoline, g	The composition of the paste mixture, masses. %			Peak height, mm
	Modifier-8-hydroxyquinoline	Wax	Graphite	
No modifier	0	50	50	15
0,1	2,5	50	47,5	20
0,2	5,0	50	45,0	49
0,3	7,5	50	42,5	41
0,4	10,0	50	40,0	34
0,5	12,5	50	37,5	28
0,6	15,0	50	35,0	23
0,7	17,5	50	32,5	19
0,8	20,0	50	30,0	16

From the data obtained, it can be seen that the optimal amount of the modifier in the paste is at the level of 2.5-10 wt. %, since with an increase in its content in a mixture of carbon paste and wax, the electrical conductivity of the entire system (electrode) decreases, and its sensitivity also decreases, due to the absence of its own electrical conductivity of the modifier, and therefore its introduction into the composition of the paste causes the electrical conductivity of the entire system. With a modifier content of 10 wt. % there is a slight decrease in the electrical conductivity of the electrode, compensated by an increase in its selectivity and sensitivity, which makes it especially important, necessary and expedient to introduce modifier different in nature and concentration into the created electrode [15].

It was also found that the nature of the CPE equipment also has a significant effect on the metrological characteristics and operating modes of the created electrodes. Of the variety of studied non-electroactive insulating materials used as a tooling for the created electrode that meets all the necessary modern requirements and parameters (chemical resistance, electrochemical inertness, water resistance, absence of impurities of foreign interfering components, thermal stability up to 100 □C) is polyethylene. When collecting carbon paste in polyethylene tubes, first of all, it is necessary to achieve good wettability of the walls of the polyethylene tube used by the paste, for this it was necessary to remove foreign substances present on the surface of the polyethylene equipment, which significantly reduce the electrical conductivity and sensitivity of the created electrodes due to the formation of air voids in them, which increase total resistance (reducing electrical conductivity) of the manufactured electrode. This preparation is achieved by treating the tubes with inorganic acids and alkalis, followed by boiling them in distilled water.

For the maximum filling of the electrode tooling, the carbon paste must be set into the polyethylene tubes at a strictly set optimized set speed. Experiments have shown that when the paste is rapidly typed into the tubes, air also enters the electrode material system, which is extremely undesirable, since it causes a decrease in the metrological characteristics and operational parameters of the manufactured electrode. And, on the contrary, with a slow set, the carbon paste quickly solidifies, which also significantly complicates its further set into the electrode being created. Therefore, it is necessary to set the optimum speed of the carbon paste in the tubes in strict accordance with their diameters, nature and other characteristics.

Figure 3 shows the volt-ampere curves of indium, taken using various types of modified CPE, and Table 5. shows the results of the determination of indium, thorium and antimony obtained after their mathematical processing.

Table 5. Comparative results of the determination of indium, thorium and antimony depending on the nature of modifiers in the manufacture of CPE (P = 0.95)

Introduced metal, mcg (analysis conditions)	h, mm	The nature of the modifier	Found metal, mkg	n	S	S_x
In 5,0 mkg/ml (fon 0,1 M HCl; d.t. = 1,0 mkA; Yen = -0,35 V; tn=60 s)	65	EDTA	4,9±0,25	5	0,14	0,028
	30	8-hydroxyquinoline	4,5±0,31	5	0,25	0,055
	25	Dithizon	5,4±0,23	5	0,19	0,035
	15	Kupferon	4,8±0,26	5	0,21	0,043
	10	Thiourea	3,9±0,18	5	0,15	0,038
Th 16,0 mkg/ml (fon 0,3 M HCl; d.t. = 0,5 mkA; Yen = -0,63 V; tn=60 s)	50	EDTA	15,9±0,25	5	0,20	0,012
	55	Kupferon	15,1±0,34	5	0,28	0,018
	-	Thiourea	-	-	-	-
	20	8-hydroxyquinoline	16,4±0,35	4	0,22	0,013
	25	Dithizon	15,3±0,40	4	0,25	0,016
Sb 3,0 mkg/ml (fon 0,2 M $H_2C_2O_4$; d.t. = 0,5 mkA; Yen = +0,65 V; tn=60 s)	45	EDTA	2,7±0,13	5	0,11	0,040
	65	8-hydroxyquinoline	2,9±0,09	4	0,06	0,020
	38	Dithizon	3,3±0,14	4	0,09	0,027
	23	Kupferon	2,2±0,15	5	0,12	0,054
	18	Thiourea	2,6±0,17	5	0,14	0,053

From the figure and the data in the table, it can be seen that the best results were obtained with the use of CPEs, modified and manufactured using EDTA for indium and thorium, and for antimony - 8-hydroxyquinoline.

The assessment of the reproducibility and correctness of the determination of the studied metals using the manufactured UET was carried out by comparing the established data with those obtained by the modified electrodes. As an example, Figure 4 shows the results of establishing the reproducibility of antimony peaks, obtained by various CPEs, modified, various organic complexing reagents.

It can be seen from the figure that the height of the peaks obtained with the CPE modified with 8-hydroxyquinoline fluctuates in a smaller range of concentrations of the metals to be determined than during the operation of other AEC modified with other organic reagents, which indicates a more stable operation of the manufactured electrode. The influence of the nature of the material after stripping (exposure) of the working surface of the electrode on its operation was also studied. Experiments have shown that the more and better the working surface of the electrode is polished, the more stable its work. The surface of the electrode was polished with glossy paper, leaving a minimum number of grooves on the carbon paste.

The results of testing the manufactured CPE samples showed that the properties of the electrodes strongly depend on the temperature of the paste set in the polyethylene tooling, therefore, the temperature regime of the carbon paste set was optimized. In addition, it is important and necessary to take into account the fact that when recruiting a mixture of graphite powder, modifier and wax, it is necessary to bring the temperature only to 100 □C, since at a higher value, thermal decomposition of the introduced organic modifier can occur only after observing these rules. and as it cools down comparatively, you can draw the paste into polyethylene tubes - accessories. Otherwise, the working surface of the electrode created in this way becomes unsuitable for mechanical renewal and does not have a mirror-like shine, which is especially important and necessary when regenerating the surface of the CPE. In this case, after the paste is set, in order to avoid the formation of voids in the tube, the manufactured electrodes must be left until the paste has completely solidified in a vertical position for 10-15 days, which is associated with the flow of coal paste in a liquid state to the bottom of the polyethylene equipment due to gravitational forces.

Establishment of metrological characteristics and analytical parameters of the created carbon-paste electrodes:

One of the most important tasks of creating CPE modified with various organic complexing reagents, which determine their metrological characteristics and analytical parameters, is the nature and concentration of the modifier. As is known, the electrochemical accumulation (concentration) of the analytes to be determined occurs on the working surface of the electrode due to the occurrence of redox and complexing reactions, as a result of which the reduction of the determined metal and its release occurs quite easily and in a free state.

At the same time, the introduction of organic modifiers into the carbon paste should significantly increase the rate of electrodeposition of heavy toxic metals on the working surface of the created electrode by increasing the number of active centers on the CPE, directly related to organic reagents in a complex with the metal being determined.

Determination of various heavy toxic metals using the electrodes created by us is a completely natural, justified, logical and final stage of our research, without which it is impossible to have complete information on the

prediction and establishment of the true picture of the metrological characteristics and analytical parameters of the manufactured EECs modified with organic complexing reagents of different nature.

From an analytical point of view, it is important and necessary to know how the presence of small amounts of mercury (II) affects the metrological characteristics and analytical parameters, as well as the useful AS [16], since, as is known, its small concentrations increase the sensitivity and the lower limit of the determined contents the method itself.

To increase the detection limit and lower the lower limit of the determined metal contents, small amounts of mercury (II) were also introduced into the analyzed solutions. To confirm this fact, IW curves (peaks) of indium, thorium and antimony were recorded in the presence of 3-4 drops of a 0.003 M solution of mercury (II) nitrate. The obtained experimental results justified our assumptions and confirmed the well-known fact in the literature [17], increasing the sensitivity of the method by 2-3 orders of magnitude.

The size and number of mercury droplets on the CPE, with each determination, as a rule, always remain the same, and the electrode process actually proceeds on the surface of the mercury droplets. Delivery-transport (mass transfer) of ions of the metal being determined to the surface of mercury drops occurs under conditions of limited spherical diffusion. Therefore, in all ratios and calculations, it is necessary to use the averaged radius of mercury drops, and the mutual distortion of diffusion fields on them should not be taken into account.

On the basis of the experimental data obtained, it can be concluded that the CPEs we have created, modified by various organic complexing reagents, are in no way inferior in their metrological characteristics and operational parameters to the widely used graphite, carbon-ceramic, platinum, mercury-dropping, sol-gel, impregnated with various reagents and other electrodes. Found wide practical application in electroanalytical and physical chemistry.

The use of the created electrodes has a rather wide range of practical use in the framework of physical and electrochemistry due to the possible selection of an appropriate selective organic complexing reagent as a selective modifier introduced into the coal paste, depending on the intended purpose and tasks of the research, as well as the nature and concentration of the analytes to be determined. ... At the same time, the indisputable advantages of the electrodes created by us are the availability, simplicity of their manufacture, low cost and the use of import-substituting local materials (ingredients) for their manufacture, as well as a long service life due to the possibility of mechanical renewal (regeneration) of the working surface, the absence of expensive equipment and devices, as well as those that do not require the training of highly qualified personnel and specialists for the creation and subsequent operation, as well as other parameters and characteristics that favorably distinguish the created modified CPE from the existing and widely used electrodes of a similar type and class in the analytical practice of various industries and institutions.

REFERENCES:

1) Toropova VF, Polyakova Yu. N. Mercury electrodes used in electroanalytical chemistry. / M., Science. 1973.S. 186 - 194.
2) Fadeeva V.I., Zolotov Yu.A., Shekhovtsova T.N., Ivanov V.M., Barbalat Yu.A., Prokhorova G.V., Pasekova N.A., Zheleznova A.A., Dolmanova I.F.,. Gormash A.V., Brykina G.D. Fundamentals of Analytical Chemistry. In 2 volumes, 2nd book. M., High School. 2001.463 p.
3) Otter F., Shtulik K., Yulakova E. Stripping voltammetry. / M., Mir. 1980.278 p.

4) Ziyaev D.A., Dadomatov A.L. Influence of the nature and concentration of modifiers on the modes and resources of work of the carbon-paste electrodes created by us. // Kimyo faculty prof. Kituvchilari va yosh olimlarning ilmiy-amaliy conf. materiallari. Tashkent-2010. S.19-21.
5) Gevorgyan A.M., Ziyaev A.L., Nagaev R.N. Optimization of the ratio of the components of the mixture of coal paste and modifier when creating electrodes used in the stripping voltammetric determination of indium and thorium. ЎZMU Yosh olimlarning ilmiy amaliy conf.
6) "Biology of va kimöning dolzarb muammolari". Toshkent. 2009.S. 156-158.
7) Gevorgyan AM, Ziyaev DA, Kalyadin VG Inversion-voltammetric determination of antimony in real objects using carbon-paste electrodes modified with oxyquinoline.
8) Brainina Kh.Z., Neiman E.Ya., Slepushkin V.V. Inversion electroanalytical methods. // M., Chemistry. 1988.239 s.
9) Plambek J. Electrochemical methods of analysis. // M .. World. 1985.504 p.
10) Gevorgyan A.M., Ziyaev D.A., Asrarov A.S, Karaev R.M. Stripping voltammetric determination of indium. Uzbek. chem. zhurn. 2008. No. 1. S.55-59.
11) Gevorgyan AM, Ziyaev D.A., Nagaev R.R. On the question of stripping voltammetric determination of indium in individual acids and their mixtures. Dokl. AN RUz. 2009. No. 6. S.56-58.
12) Gevorgyan A.M., Ziyaev D.A., Dushanov R.O. Analytical determination of thorium by stripping voltammetry. // Uzbek. chem. zhurn. 2009. No. 2. S.25-27.
13) Gevorgyan A.M., Ziyaev D, A., Kalyadin V.G., Kireev G.V. Analytical capabilities of stripping voltammetry in the determination of indium. Uzbek. chem. zhurn. 2009. No. 5. S.61-64.
14) Gevorgyan A.M., Ziyaev D.A., Kireev G.V. Analytical capabilities of stripping voltammetry in the determination of antimony in industrial materials. Chemical industry. T.87. No. 5. 2010.S. 261-264.
15) Ziyaev D.A. Stripping voltammetric determination of indium in the presence of cadmium and zinc. // Chemistry and Chemical Technology. 2011. No. 4. S. 70-72.
16) Aleksander, G., Anna, T, Boris, K, Anna, G., Nikolay, S., Alexander, V. (2018). Direct Quantification of Major and Trace Elements in Geological Samples by Time-of-Flight Mass Spectrometry with a Pulsed Glow Discharge. Analytical Letters, Vol. 15, p. 835-850.
17) Shaidarova, L.G., Chelnokova, I.A., Ilyina, M.A., Gedmina, A.V., Budnikov, G.K. (2017). Amperometric detection of hydroxypurines on an electrode modified with a composite based on mixed-valent oxides of ruthenium and cobalt under conditions of flow-injection analysis. Journal. Analyte. chemistry, T.72, No. 1, S. 91-96.