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MODIFIED CARBON-CONTAINING ELECTRODES IN ELECTROANALYSIS: PAST, PRESENT AND FUTURE

Abstract. At the end of 2019, the scientific world celebrated the 60 th anniversary of the awarding of the Nobel Prize for his contribution to the development of electrochemistry to the Czech scientist Yaroslav Geyrovsky. The method of polarography developed by him opened a new page of quantitative and qualitative analysis in chemistry. This article is devoted to this event and provides brief information about the possibility of creating an alternative proposed by Geyrovsky to a dripping mercury electrode for polarographic analysis. In this context, the stages of development of electrochemical methods of analysis using carbon-containing materials will be presented here.

Keywords: Voltammetry, dripping mercury electrode, modified carbon-containing electrodes, stages of development of polarography.

Due to all its advantages: low cost, speed and simplicity, electrochemistry has always been an ideal choice for the quantitative analysis of substances of inorganic and organic nature. This was facilitated by the transition from the use of indicator dripping mercury electrodes in voltammetric analysis to solid carbon-containing ones [1].

Probably, the first idea of using carbon-graphite materials as electrodes for polarographic analysis was given by Adams, who proposed in 1959 to use a mixture of a paste-like consistency consisting of coal powder and a liquid non-electroactive binder. Since then, carbon paste electrodes (CPE) and the corresponding sensors have received attractive development in electrochemical analysis, in particular in voltammetry. The evolution of the development of voltammetry using paste and then modified electrodes is traced by the following stages [2].

- **1959–1963**: introduction of carbon paste and its first applications by Adams and his collaborators to study the mechanisms of electrode reactions of various organic compounds.
- **1964, 1965**: the first experiments on the modification of carbon pastes. The ability to vary the composition of carbon pastes and the relative ease of their preparation is a stimulating factor for changing the characteristics of the initial carbon-binder mixture by introducing other chemically active components into it, remains relevant today. It is this procedure that can lead to a purposeful improvement in the characteristics of the electrode.
- **1974:** the appearance of carbon pastes with an electrolytic binder. The replacement of conventional non-electroactive paste-like liquids with electrolyte solutions opened the

way for a certain branch of electrochemistry of electroactive electrodes made of carbon paste, which made it possible to study the redox behavior, as well as various structural and morphological changes of inorganic compounds dissolved directly in the electrolyte. Currently, such studies usually belong to a special field, the so-called solid-state electrochemistry.

- **1980–2000:** the era of chemically modified carbon pastes. Attempts to use favorable mechanical and electrochemical properties of carbon pastes for the manufacture of sensors of a new generation were crowned with success in the early 80s. Modification of carbon paste by impregnating carbon particles with a methanol solution of dimethylglyoxime represents another milestone in the history of CPE. This was the first attempt when a classical analytical reagent served as a selective modifier, thus initiating subsequent research on the development and application of chemically modified carbon paste electrodes (CMCPE) in electrochemical analysis [3].

Since then, the number of publications of works with chemically modified electrodes based on carbon-containing paste has begun to grow exponentially, including review articles. This trend continues at the present time.

In the late 80 s and early 90 s of the last century, works appeared on the modification of carbon-containing pastes with enzymes and other biologically active substances. On the basis of these pastes, enzymatic biosensors were created that allow controlling some enzymatically catalyzed reactions of biological substances. Initially, the enzyme immobilization procedure was carried out by simply adding the necessary enzyme to the carbon paste. The simplicity of making an enzyme sensor immediately attracted the attention of biochemists, and enzyme biosensors based on carbon paste quickly came to the fore. One of the first comprehensive reviews showing the entire genesis of such biosensors was presented by Gorton [4].

The 90 s and early 2000 s are characterized by the appearance of carbon-containing composites on the market, which allow replacing soft paste electrodes with hard ones. Usually, the method of manufacturing such solid electrodes differs little in simplicity from the manufacture of carbon paste electrodes, but the latter have a stronger matrix.

The 2000 s and up to the present – the period of development of methodological foundations for the modification of electrode materials; rejection of toxic mercury salts and other toxic components that pollute the environment and adversely affect human health; obtaining electrodes with a catalytic response that can significantly reduce overvoltage in the determination of a number of substances of inorganic, and especially organic nature; the use of noble metal nanoparticles and transition group metal oxides as modifying agents stimulated the development of a new direction in electrochemical analysis – nanoanalytics [5].

Carbon-containing nanomaterials based on mono- and poly-carbon nanotubes, nanopackages, graphitized nanofibers, etc., as well as nanorods made of precious metals have qualitatively new properties necessary for the creation of indicator electrodes: a large specific surface area, which determines their high electrochemical and catalytic activity, sorption properties, as a consequence of porosity and surface defects of nanomaterials, their thermal stability [6]. These properties of nanomaterials open wide horizons for further reducing the limits of determining trace amounts of matter in electroanalysis by using nanostructured electrodes, improving separation and concentration processes using nanotubes, nanostructured polymers as new selective sorbents. Currently, a series of electrochemical studies has been published in the analysis by voltammetry using various nanoparticles applied to the surface of the electrode as modifiers using physical sorption, chemisorption, laser ablation from solutions.

Such electrodes are able to exhibit an electrocatalytic effect in the redox processes of both organic and inorganic compounds by reducing the overvoltage of various electrode processes, increase the selectivity and sensitivity of electroanalysis. By sewing metal nanoparticles to DNA (an electrochemically inactive substance), pico- and nanomolar DNA concentrations can be determined [7]. Thick-film graphite electrodes modified by ex- or insitu bismuth film were used to determine trace amounts of zinc, cadmium and lead in multicomponent objects, group vitamins in pharmaceuticals [8; 9].

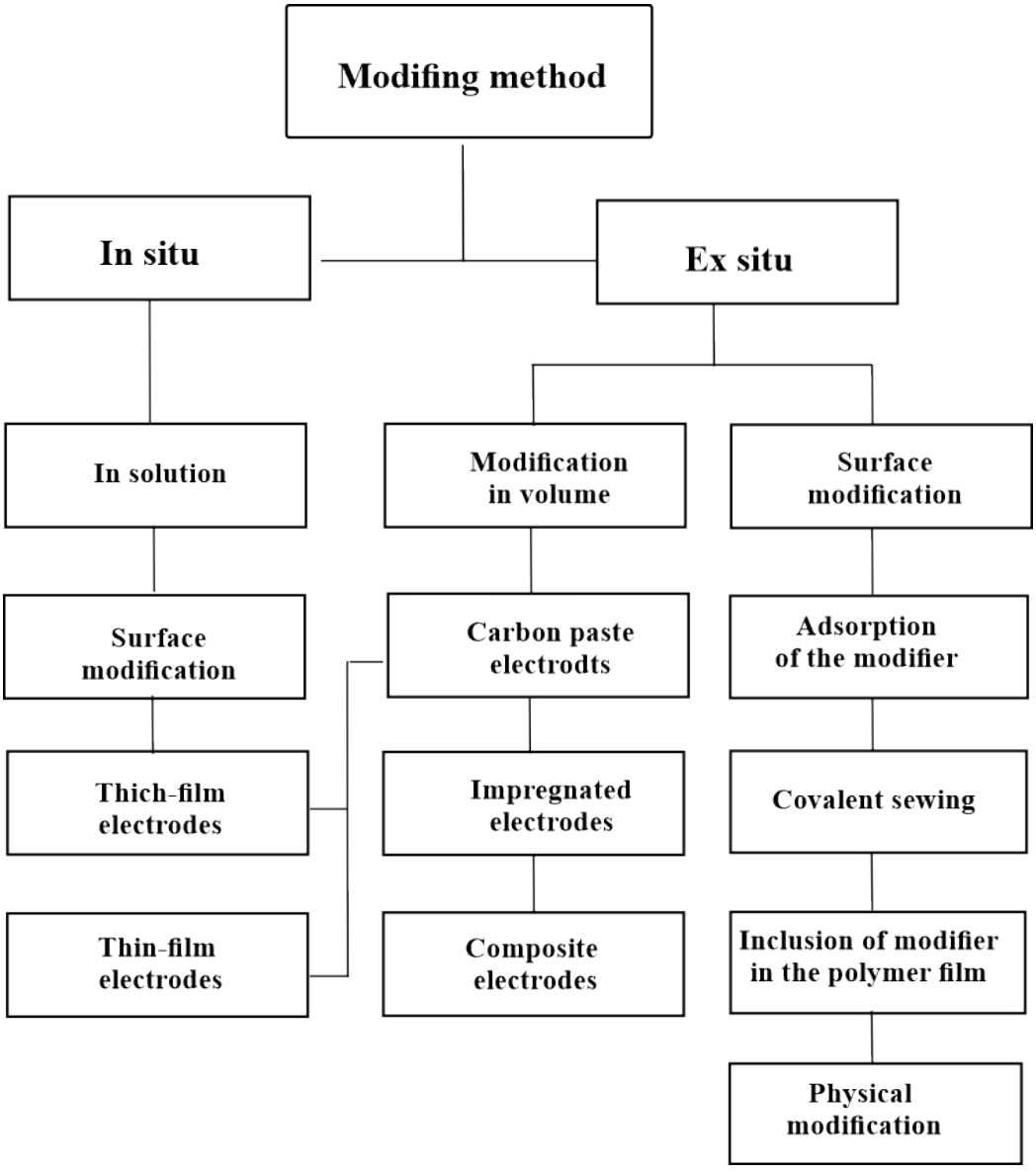

Fig.1. Methods of modification of electrodes

A thick-film carbon-containing electrode modified with silver nanoparticles was used for the inversion-voltammetric determination of sulfide ions and mercaptans in the contents of 10^{-7}–5×10^{-7} M, iodine in waters, food products and biological fluids in the concentration range of $1 \times 10^{-7} – 8 \times 10^{-7}$ M with a correlation coefficient of 0.9985. Gold and silver nanoparticles, silica gel with enzymes deposited on them, and nanotubes are used for electrochemical detection of biomolecules, including DNA in biosensors [10; 11].

Based on the specific electrochemical properties of metal nanoparticles, a new generation of highly sensitive sensors for environmental and medical purposes has recently been created. Thus, enzyme-free bio- and immunosensors based on Berlin azure nanolayers and magnetic nanoparticles have been tested [12].

The use of such biosensors opens up new possibilities for non-invasive methods of medical diagnostics [13; 14].

The main reason for the need to modify the electrode is to obtain a qualitatively new sensor with the desired, often predetermined properties. In this regard, carbon pastes can undoubtedly represent one of the most convenient materials for the manufacture of modified electrodes.

The methodology and principles of modification of carbon-containing pastes are illustrated by the scheme [7, 15] presented in (Fig. 1).

Unlike relatively complex modifications of solid substrates, the preparation of chemically modified carbon paste electrodes is very simple, usually using various alternative procedures. The modifier can be dissolved directly in the binder or mechanically mixed with the paste during its homogenization.

It is also possible to soak graphite particles with a modifier solution, and after evaporation of the solvent, use it as an impregnated carbon powder. Finally, already prepared pastes can be modified in situ.

The advantage of in situ modification methods is that they do not require the addition of modifier molecules to the electrode. It is enough to clean the surface from the products of the electrochemical reaction before modification. However, the service life of such electrodes is relatively short, since before each measurement there is a need for modification again.

As an alternative to in situ modification methods, methods of pre-immobilization of modifiers (ex situ) on electrodes made of various materials such as glass carbon, metals, pyrographite, carbon-containing composite materials, impregnated graphite, carbon mesh, carbon paste, fabrics, fibers, etc. have been developed and are widely used. The combination of their properties makes it possible to create electrodes with specified sensitivity and selectivity parameters.

Conclusion

Assessing the prospects of using modified electrodes in voltammetric analysis, it can be noted that the development of the method itself is increasingly mixed with the development of new electrodes and sensors that allow determining "cheaper, faster, easier and better". A large number of research works on the search for ways to use and select modifiers, their immobilization on the surface of electrodes, the use of electronic transfer mediators is an indisputable proof of interest in this problem, although the phenomenological stage in conducting research has not yet ended. A number of issues that prevent the widespread use of modified electrodes have not yet been resolved. In particular, this applies to the production of electrodes with a stable electrochemical response, which does not depend on the methods of preparing the electrode surface before the corresponding measurements. Attempts to replace mercury with other metals, for the most part, lead to a loss of sensitivity and selectivity of definitions.

The relatively short "life" of most electrodes, their "aging" over time, which manifests itself in changes in the composition and structure of the modifying layer and deterioration of its analytical characteristics, is another problem. The duration of operation of the electrodes is severely limited by the need to regenerate the surface after each measurement. It is the surface of the electrode that is the source of most problems. Even for a well-studied mercury film electrode (PRE), the nature of the mercury film on its surface is still being discussed – whether it is homogeneous with a thickness of 0.5 to 10 microns or Hg is released in the form of small droplets with a statistical distribution on the surface of the electrode.

When creating and using modified electrodes, it becomes necessary to answer a number of questions: how to make the surface of the modifying layer stable

and reproducible, how do the properties of the modifying layer affect the parameters of the response signal, how does electrochemical or mechanical surface treatment affect the activity of the modifier and the electrode process, how to eliminate contamination of the electrode with interfering substances, which worsens its analytical characteristics?

Thus, having considered various ways of modifying carbon-containing electrodes, we come to the following conclusions:

Chemical modification makes it possible to expand the analytical capabilities and scope of voltammetric analysis methods for the determination of various substances of inorganic and organic origin and to limit the use of mercury-containing electrodes. In the near future, the main task of electrochemical analysis methods is to improve the analytical parameters of electrodes with modification of their surface and the possibility of a catalytic response.

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