

# Modified carbon-containing electrodes in stripping voltammetry of metals. Part II. Composite and microelectrodes

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**Abstract** The second part of the review, which covers modified carbon-containing electrodes, describes composite and microelectrodes. Electrodes made of commercial and laboratory carbon-containing composite materials are discussed. Impregnated and thick-film electrodes and microelectrodes made of carbon fibers form a separate group. Various modifiers and methods of electrode modification are presented. Prospects for the future development of solid-state modified electrodes are considered.

**Keywords** Carbon-containing electrodes · Modified electrodes · Composite electrodes · Microelectrodes · Stripping voltammetry · Metal ions determination

## Graphitized carbon and composite electrodes

The advancement of modern engineering and the use of new principles and approaches to the synthesis of carbon materials have facilitated the development of new commercial carbon–graphite materials with assigned properties. The use of the following commercially available electrode materials is reported in the literature: pencil lead [1–3]; spectral [4, 5], pyrolytic [6], and felt [7] graphites; carbon glass ceramic [8–10]; nonwoven graphite films [11]; carbon film resistors; and switches [12–16]. In most cases, electrodes of these materials are modified by metal films (mercury, copper, and bismuth), molecularly imprinted

TiO<sub>2</sub> [17]. The occurrence in the last decade of new types of carbon materials “from carbon nanotubes to edge plane pyrolytic graphite” [18, 19] has significantly changed the scope and sensitivity of electroanalytical methods for the measurement of diverse targets from metals ions to biological markers. Investigators considered in detail electrochemical characteristics [20] and practical use [21] of the “edge” plane pyrolytic graphite, which proved to have a wider interval of working potentials and a low detection limit as compared to those of the basal pyrolytic graphite and GC. For example, in situ bismuth film modified edge plane pyrolytic graphite electrode was successfully applied to the ultra trace simultaneous determination of cadmium(II) and lead(II) with detection limit  $5.5 \cdot 10^{-10}$  and  $4 \cdot 10^{-10}$  M, respectively [22].

Synthetic diamonds (nitrogen- [23, 24] and boron-doped [25–49]) have come into use quite recently for electrochemical measurements. In particular, a gold-coated, boron-doped, diamond thin-film electrode was used for total inorganic arsenic detection in real water samples [50]. Unlike properties of other carbon materials, which are widely used in electroanalysis, properties of synthetic diamonds became the subject of comprehensive study just about 10 years ago. The research was hindered by two circumstances: shortage of the material and the absence of conduction. The situation radically changed with the advent of highly efficient methods for growing of polycrystalline diamond compounds.

A more efficient separation, accumulation, and determination of components is achieved with electrodes of composite materials made of graphite, carbon, glassy carbon, or diamond powders and binders such as paraffin, epoxy resins, methacrylate, silicon, styrene–acrylonitrile copolymer, polyester, and silica gel. The reviews [51–54] deal with properties and applications of various composite

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materials. Some original papers describe the use of unmodified electrodes made of graphite [55–62], glassy carbon [63], template carbon [64]-polymer composites, a composite based on natural and synthetic diamonds [65], nanocomposite made of carbon nanofibers [66], and a carbon-containing material prepared by a sol-gel technology [67, 68]. Much attention is given for the study of electrochemical properties and application of graphite-epoxy composite electrodes [69–72]. Specific features of the last material are its strength, chemical inertness, absence of impurities, nonswelling in water solutions, stability in organic solvents for prolonged periods, ease and simplicity of fabrication, and secure fixing of water-soluble reagents.

Table 1 gives examples of the use of modified composite electrodes in stripping voltammetry with the composite materials made under industrial and laboratory conditions using simple sol-gel, sono-gel, spin-casting, and molding technologies [73, 74–92]. The electrodes shown in the table can be divided into two groups: those made of carbon-(soot, amorphous carbon) [73–79] and those made of graphite-containing [80–92] materials. It should be noted that the detection limit of graphite-containing materials is somewhat higher than that of carbon-containing materials. Composite electrodes may be used to achieve the electrochemical response of ground solids, iron pigments, and insoluble samples [93, 94].

The bulk or surface modification of composite materials by metals or organic compounds considerably reduces the detection limit for metal cations. Silicon-carbon electrodes were proposed for determination of Cu (II), Pb (II), and Zn (II) after modification by mercury [76]; Ni (II) after modification by dimethyl glyoxime [77]; Os (IV) after modification by 9-phenyl-3-fluorone [78]; and Cu (I), Fe (II), and Ni (II) after modification by neocupferron, phenanthroline derivatives, and dimethylglyoxime, respectively [79]. A satisfactory reproducibility of responses of elements to be determined, a high selectivity, and the time stability of sol-gel electrodes can be noted.

Modified electrodes of composite materials are attractive because not only their surface but also the bulk can be easily modified at the stage of the composite formation [73–75, 77–80, 84–86, 90–92], facilitating fabrication of more reproducible electrodes. Simplicity of technologies used for production of many current-conducting composite materials with preset properties makes them promising for electroanalysis applications.

### Impregnated graphite electrodes

Impregnated graphite electrodes (IGE), which have found application in the electroanalytical practice, are basically of two types: those impregnated with a paraffin-polyethylene

mixture and those with epoxy resins. IGE are widely used by electroanalysts in Russia. Unmodified [95, 96] and modified [97–129] IGE, shown in Table 2, are used in electrochemical inorganic analysis. IGE are modified by metals (Hg, Au, Cu, Tl, Jr) [97, 98–114], polymer films fixing the modifier and capable of the ion exchange [115], and Mo (IV) oxocomplexes [116, 117]. The IGE surface has good adsorbability and, hence, is readily modified by reagents specific for determined ions [118–129]. The IGE surface is modified most frequently, but examples of the IGE bulk modification can be found too [118, 119]. In this case, porous graphite is first held in an acetone solution of 2-mercaptobenzoxazole and then impregnated with a two-component epoxy compound under exposure to ultrasound. IGE modified by this method were used to determine Ag (I) and Hg (II). They were additionally modified *in situ* by mercury and rhodamine for measurements of Bi (III) and Au (III), respectively.

IGE are widely used in abrasive stripping voltammetry developed by Scholtz et al. [130]. Abrasive stripping voltammetry is a new electroanalytical technique designed for qualitative and quantitative analysis of solid materials. The essence of this method is a recording of the voltammetric response of a set of solid microparticles of the analyte immobilized on an inert electrode (most frequently paraffin-impregnated graphite) both unmodified and modified, for example, with zeolites [131] immersed in an appropriate electrolyte. Voltammetry of microparticles is a rapidly growing field of research. This scheme was previously used to analyze metals, alloys, minerals, natural and synthetic sulfosalts, sulfides, and ceramic materials [132–138].

### Thick-film carbon-containing electrodes

So-called “screen-printed” or “thick-film” electrodes have been used on a wide scale recently. They are reproducible and inexpensive. Thanks to their good electrochemical and metrological characteristics, these electrodes can serve for environmental monitoring and foodstuff quality control [139]. Thick-film electrodes are made of carbon- [140], graphite- [141, 142], carbon-nanotube-containing [143] inks or special current-conducting, e.g., graphite-epoxy, pastes. The design and the fabrication technology of the electrodes, as described, for example, in [144], allow easy modification of their surface by immobilizing a modifier on the electrode surface or adding it to the ink before the electrode is made.

Table 3 gives examples of the use of modified thick-film electrodes for voltammetric determination of elements [145, 146–192]. Metals and their oxides are the most common modifiers [145–163]. Sometimes the film electrodes are

**Table 1** Modified composite electrodes

Electrode material/ modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Purge <sup>a</sup>	Sample	Ref.
CC/Ag <sub>3</sub> [Fe(CN) <sub>6</sub> ]	bulk	Fe (III)	7.2·10 <sup>-6</sup>	0.1 M KNO <sub>3</sub>	DP CSV	+	BGD	[73]
CC /Au	bulk	Hg (II)	1·10 <sup>-10</sup>	0.035 M H <sub>2</sub> SO <sub>4</sub> + 2 mM KCl	LS ASV	-	Waters	[74, 75]
CCSG /Hg	in situ	Cu (II), Pb (II), Zn (II)	1·10 <sup>-8</sup> (Pb)	0.1 M HNO <sub>3</sub> + 2·10 <sup>-5</sup> M Hg (II) (Pb), 0.1 M NaAc (Cu, Pb, Zn)	DP ASV	-	Fuel	[76]
CCSG/DMG	bulk	Ni (II)	2.6·10 <sup>-6</sup>	0.1 M amm.buff. (pH 8.2)	DP CSV	-	Waters	[77]
CCSG /9P3F	bulk	Os (IV)	2.4·10 <sup>-9</sup>	0.15 M NaF	DP ASV	-	Waters	[78]
CCSG/DMPT (1); DMG (2); neocuproine (3)	bulk	Fe (II) (1); Ni (II) (2); Cu (I) (3)	7·10 <sup>-9</sup> (Fe)	NaOH + 0.5 M TFAA (pH 2) (Fe), NaAc (pH 6) (Cu), TFAA (pH 9.2) (Ni)	SQW ASV	-	SS of leaves	[79]
GCSG/DAN	bulk	Se (IV)	1·10 <sup>-9</sup>	0.1 M HCl	LS CSV	-	Waters	[80]
GCSG /RNSH	ex situ	Ag (I)	4.5·10 <sup>-14</sup>	0.1 M McIlvaine buffer (pH 5)	DP ASV	-	Human hair	[82]
SGC/PMTP	ex situ, on surface	Hg (II)	7·10 <sup>-9</sup>	0.2 M B-R buff. (pH 4–8)	DP ASV	-	Waste waters	[81]
GEC /Hg.	ex situ	Cu (II), Pb (II), Cd(II)	4.4·10 <sup>-10</sup> (Cd)	0.05 M NaAc (pH 4.5)	SQW ASV	-	Waters	[83]
GEC /MBT	bulk	B <i>i</i> (III), Hg (II), Cu (II)	4.2·10 <sup>-9</sup> (Hg); 3.6·10 <sup>-9</sup> (B <i>i</i> ); 9.5·10 <sup>-8</sup> (Cu)	B-R buff. (pH 3.8) (acc.); 1 M HCl (sweep)	DP ASV	+	SS, hair	[84]
GEC /8HQ	bulk	Sn (II)	4.6·10 <sup>-10</sup>	0.1 M acetate buffer (pH 5.8) (acc.); 0.05 M HCl + 2 M CaCl <sub>2</sub> (sweep)	DP ASV	-	SS, hair, juice, sea water	[85]
GCC /Ag	bulk	Pb (II)	1·10 <sup>-8</sup>	0.1 M KCl + 0.005 M HCl	DP ASV	+	Waters	[86]
GCC /Hg	in situ	Pb (II)	9.7·10 <sup>-9</sup>	0.1 M H <sub>2</sub> SO <sub>4</sub> + 2·10 <sup>-5</sup> M Hg(NO <sub>3</sub> ) <sub>2</sub>	LS ASV	-	BGD	[87]
GCC /Hg	in situ	Cu (II)	1.6·10 <sup>-9</sup>	0.25 M H <sub>2</sub> SO <sub>4</sub> + 2·10 <sup>-4</sup> M Hg(I)	LS ASV	-	Waters	[88]
GCC /Hg (1); GCC/ DPCO (2); GCC (3)	in situ	Cu (II) (1); Pb (II) (1); Cd (II) (1); Zn (II) (1); Cr (VI) (2); Ni (II) (3); Ag (I) (3)	7.8·10 <sup>-9</sup> (Cu); 1.4·10 <sup>-9</sup> (Pb); 4.4·10 <sup>-9</sup> (Cd); 7.6·10 <sup>-8</sup> (Zn); 9.6·10 <sup>-9</sup> (Cr); 8.5·10 <sup>-8</sup> (Ni); 4.6·10 <sup>-9</sup> (Cu)	0.1 M HCl + 5·10 <sup>-5</sup> M Hg (II) (Cu, Pb, Cd); NaAc (pH 4–5) + 2·10 <sup>-4</sup> M Hg (II) + 10 <sup>-4</sup> M Ga (III) (Zn); 0.5 M HCl + 10 <sup>-6</sup> M DPCO (Cr); FB buff. (pH 5–7) (Ni); 0.05 M H <sub>2</sub> SO <sub>4</sub> (Ag)	LS ASV (1, 3) LS CSV (2)	-	Model solutions	[89]
GCC /HgO	bulk	Cu (II), Pb (II), Cd (II)	7.9·10 <sup>-10</sup> (Cu); 2.4·10 <sup>-10</sup> (Pb); 4.4·10 <sup>-10</sup> (Cd)	0.1 M KCl + 0.01 M HCl	LS ASV	-	Waters	[90]
GCC + MWN/TCC	bulk	Ag (I)	5·10 <sup>-11</sup>	0.5 M NaClO <sub>4</sub>	DP CSV	-	Waters	[91, 92]

CC carbon composite, CCSG carbon-containing silica gel, DMG dimethylglyoxime, 9P3F 9-phenyl-3-fluorone, DMPT 4,7-dimethyl-1,10-phenanthroline, GCSG graphite-containing silica gel, DAN diamonaphthalene, RNSH 5-(4-dimethyl amino benzyliden)-rhodamin, SGC sonogel-carbon, PMTP poly-3-methylthiophene, GEC graphite-epoxy composite, GCC graphite-containing composite, MBT 2-mercaptobenzothiazole, 8HQ 8-hydroxyquinoline, DPCO diphenyl carbazone, MWN multi-walled nanotubes, TCC thiocrown compound, bulk modifier introduced to electrode bulk preliminary, ex situ modifier fixed on surface preliminary, in situ formation of modifying layer during deposition of substance to be determined, NaAc sodium acetate, amm.buff. ammonium buffer, TFAA trifluoroacetic acid, B-R buff. Britton-Robinson buffer, acc. stage of electrochemical accumulation, FB buff. fluoride-borate buffer, EDTA ethylenediaminetetraacetic acid, DP differential-pulse, CSV cathodic stripping voltammetry, LS linear sweep, ASV anodic stripping voltammetry, SQW square-wave, BGD supporting electrolyte, SS standard sample a,+, after, “-” without oxygen removal

**Table 2** Modified IGE

Electrode material/ modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Purge	Sample	Ref.
IGE-P /Hg	in situ	Pt (IV)	$1.3 \cdot 10^{-7}$	1 M HCl + 13.4 mg L <sup>-1</sup> Hg (II)	LS ASV	–	Biomaterials	[97]
IGE-P /Hg	in situ	Cu (II), Pb (II)	$3.7 \cdot 10^{-8}$ (Pb); $1.2 \cdot 10^{-7}$ (Cu)	0.1 M HCl + $1 \cdot 10^{-4}$ M Hg (II) + 1.2 M NaSCN	LS ASV	–	Model solutions	[98]
IGE-P / Hg + Cu	in situ	Se (IV)	$2.5 \cdot 10^{-7}$	0.1 M HCl + $2.5 \cdot 10^{-5}$ M Hg (II) + $3 \cdot 10^{-5}$ M Cu(II)	SQW CSV	+	Foodstuffs	[99]
IGE-R	ex situ	Au (III)	$5 \cdot 10^{-9}$	0.1 M HCl	LS ASV	–	Rocks	[100]
IGE-R /Hg	ex situ	Tl (III)	$9.8 \cdot 10^{-12}$	0.05 M EDTA (pH 4.4)	DP ASV	+	Waters	[101]
IGE-R /Hg	ex situ	Cu (II), Pb (II), Cd (II)	$6.3 \cdot 10^{-9}$ (Cu); $4.8 \cdot 10^{-10}$ (Pb); $8.9 \cdot 10^{-10}$ (Cd)	0.5 M NaCl (pH 3)	LS ASV	–	Natural waters	[102]
IGE-R /Hg	ex situ	Pb (II), Cd (II), Zn (II)	$10^{-10}$	0.02 M KNO <sub>3</sub> + 1 mM HCl (pH 3)	LS ASV	–	Model solutions	[103]
IGE-P /Au	ex situ	As (III)	$2.7 \cdot 10^{-10}$	0.02–0.1 M EDTA + citrate Na (pH 4–5)	LS ASV	+	Drinking, mineral waters, strong drinks	[104]
IGE-P /Au	ex situ	As (III), Hg (II)	$1.3 \cdot 10^{-8}$ (As); $2.5 \cdot 10^{-9}$ (Hg)	0.1 M HCl	LS ASV	–	Natural waters	[105]
IGE-P /Au	ex situ	Se (IV)	$3.8 \cdot 10^{-8}$	0.3 M HClO <sub>4</sub>	LS ASV	–	Waters	[106]
IGE-P /Au	ex situ (1), in situ (2)	As (III) (1), Se (IV) (1), Hg (II) (2)	$1.0 \mu\text{g g}^{-1}$ (As); $0.6 \mu\text{g g}^{-1}$ (Se); $0.3 \mu\text{g g}^{-1}$ (Hg)	0.02–0.05 M EDTA (As); 0.1–0.3 M HClO <sub>4</sub> (Se); HClO <sub>4</sub> , HNO <sub>3</sub> , HCl + Au (III) (Hg)	LS ASV	–	Toys	[107]
IGE-P /Au	in situ	Hg (II)	$5 \cdot 10^{-10}$	0.02–0.05 M HClO <sub>4</sub> (or 0.1 M HNO <sub>3</sub> ) + $4 \cdot 10^{-6}$ M Au(III) + 5 mM Cl <sup>-</sup>	LS ASV	–	Natural waters, foodstuffs	[108, 109]
IGE-R /Au	ex situ	As (III), Cu (II)	$9.3 \cdot 10^{-8}$ (As); $1.1 \cdot 10^{-7}$ (Cu)	0.01 M H <sub>3</sub> PO <sub>4</sub> + 1 mM EDTA	LS ASV	–	Model solutions	[110]
IGE-R /Au	ex situ	Hg (II)	$5 \cdot 10^{-10}$	0.1 M HClO <sub>4</sub> + 0.03 M HCl	DP ASV	+	Sea sediment	[111]
IGE-R /Au	ex situ	Hg (II)	$8 \cdot 10^{-10}$	0.1 M HCl	LS ASV	–	Waters, foodstuffs	[112]
IGE-R /Au (1); IGE-R / Cu (2)	ex situ (1), in situ (2)	As (III)	$2.3 \cdot 10^{-7}$ (1); $6.3 \cdot 10^{-7}$ (2)	0.05 M EDTA (1); 0.1 M HCl + $5 \cdot 10^{-6}$ M Cu (II) (2)	LS ASV	–	BGD	[113]
IGE-R/Tl or In	in situ	Hg (II)	$1 \cdot 10^{-8}$	0.1 M HCl + Tl (I) or In (III) (10:1=Hg:Tl)	LS ASV	–	Model solutions	[114]
IGE-P/nafion	ex situ	Ag (I)	$2 \cdot 10^{-10}$	0.01 M HNO <sub>3</sub> + 0.03 M NaCl	LS ASV	–	Chemicals	[115]
IGE-P/Mo (VI)-OC	in situ	As (V)	$2.7 \cdot 10^{-9}$	NaCl (pH 2.5) + $1.5 \cdot 10^{-3}$ M Mo (VI)	SQW CSV	+	Waters, foodstuffs	[116]
IGE-R or IGE-P/Mo (VI)-OC	in situ	As (V)	$3 \cdot 10^{-9}$ (IGE-P); $2 \cdot 10^{-10}$ (IGE-R)	1.0 M (Na, H)Cl (pH 2.5) + $1.5 \cdot 10^{-3}$ M Mo(VI) + 30 vol. % 1,4-dioxane	DP CSV	–	Natural, sea waters, foodstuffs	[117]
IGE-R/MBO/ Rhodamine 6G	ex situ/in situ	Au (III)	$1.9 \cdot 10^{-10}$	0.1 M HCl + $1 \cdot 10^{-6}$ M Rhodamine 6G (acc.); 0.1 M HCl (sweep)	DP CVA DP CSV	–	Sea water	[118]
IGE-R/MBO (1); IGE-R/ MBO /Hg (2)	ex situ (1), ex situ/in situ (2)	Ag (I) (1), Hg (II) (1), Bi (III) (2)	$1.8 \cdot 10^{-10}$ (Ag); $1.9 \cdot 10^{-9}$ (Hg); $9.5 \cdot 10^{-9}$ (Bi)	Ag: 0.1 M NaAc (pH 4.3) (acc.); 0.07 M HCl (sweep); Hg: 0.1 M FB (pH 5.5) (acc.); 0.075 M KBr + 0.1 M HNO <sub>3</sub> (sweep); Bi: B-R buff. (pH 3.8) + $5 \cdot 10^{-6}$ M Hg (II) (acc.); 1.0 M HCl (sweep)	DP ASV	+	Sea water, urine	[119]
IGE-R/ DPCD	in situ	Cr (VI)	$1 \cdot 10^{-9}$	0.15 M H <sub>2</sub> SO <sub>4</sub> + $5 \cdot 10^{-6}$ M DPCD	LS CSV	–	Natural, sea waters, draw of soils	[120, 121]
IGE-R/ DPCO	in situ	Mn (II)	$5 \cdot 10^{-9}$	amm.buff. (pH 9.2) + $3 \cdot 10^{-5}$ M DPCO	LS CSV	–	SS of Ni- alloy, natural waters	[122]

**Table 2** (continued)

Electrode material/ modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Purge	Sample	Ref.
IGE-P/ ANTPR	in situ	Mo (VI)	$5 \cdot 10^{-10}$	0.3–2.0 M HCl + 0.05 M ANTTPR + 0.03 M SCN <sup>-</sup>	LS ASV	–	Natural waters	[123]
IGE-R / DMG	in situ	Ni (II)	$3 \cdot 10^{-9}$	0.2 M NaCl + $2.5 \cdot 10^{-4}$ M DMG + 0.03 M NaCl + pyridine (pH 8–10)	LS CSV	–	Natural, waste waters	[124]
IGE-R /CE	ex situ (1), in situ (2)	Pd (II)	$5 \cdot 10^{-9}$ (1); $1 \cdot 10^{-8}$ (2)	0.1 M HClO <sub>4</sub> (1); 0.1 M HClO <sub>4</sub> + $1 \cdot 10^{-2}$ gL <sup>-1</sup> CE (2)	LS ASV	–	BGD	[125, 126]
IGE-P/ ANTPR	in situ	W (VI)	$1 \cdot 10^{-9}$	1 M H <sub>2</sub> SO <sub>4</sub> + 0.078 M NH <sub>4</sub> SCN + 0.04 M ANTTPR	DP ASV	–	Waters	[127]
IGE-P / 9P3F	in situ	Sb (III), Sn (IV)	$1 \cdot 10^{-7}$	0.05 M H <sub>2</sub> SO <sub>4</sub> + $(2.5\text{--}3.0) \cdot 10^{-6}$ M 9P3F	LS ASV	–	Ni, Cr, SS of steels and irons	[128, 129]

For abbreviations aside from those defined here, see Table 1

*IGE-P* impregnated graphite electrode soaked with paraffin and polyethylene, *IGE-R* impregnated graphite electrode soaked with epoxy resin, *Mo (VI)-OC* Mo(VI) oxocomplex, *MBO* mercaptobenzoxazole, *DPCD* diphenyl carbazide, *ANTTPR* antipyrine, *CE* crown ether, *EDTA* ethylenediaminetetraacetic acid, *FB* phosphate buffer, *CVA* cathodic voltammetry

modified by inorganic [164–167], metalorganic [168–174], and organic substances [175–180]; self-assembled layers [181–184]; macrocyclic compounds [185–187]; polymeric films [188, 189]; and ion-exchange resins [190, 191]. Modified thick-film electrodes provide the detection limit of elements at a level of  $10^{-8}$ – $10^{-10}$  M.

Plasma, laser, temperature, and electrochemical treatments of the surface of thick-film electrodes can influence its activity, increase the rate of electron transitions, and change the electrochemical process reversibility. Preliminary anodic polarization of an electrode [192] not only extended the range of the working potentials but also improved its sensitivity. Voltammetric, microscopic, and spectroscopic studies suggested that the reason for the favorable effect of the anodic activation on the electrochemical properties of the electrode was enrichment of its surface in new functional groups, removal of unwanted inclusions from the surface, and the increase in the surface roughness.

### Carbon microelectrodes

Pioneering research into the kinetics of electrochemical reactions on microelectrodes (ME) with diameters of units to several tens of micrometers revealed that the electrodes demonstrated new properties as their diameter decreased. Specifically, capacitive currents, which are the main factor that limits fast electrochemical processes on solid electrodes, decrease to practically insignificant values, the mass transfer rate of the substance to ME increases, the

electrochemical equilibrium is established much faster than on standard electrodes, and the ohmic potential drop  $iR$  is negligibly small for ME. The unique properties of ME make it possible to analyze and use solutions with a high ohmic resistance, including pure solvents, in voltammetry and extend the range of test compounds, primarily organic substances and extracts. Growing attention is given to ME because they can serve as the basis for development of simply designed and, hence, easily realizable miniature sensors and detectors for operation in flowing liquid systems and measurement of bioactive substances in vivo. The electrochemical properties, constructions, fabrication methods, and analytical capabilities of ME are described in reviews and original papers [193–199].

Nonmetal ME are made of carbon, graphitized and glassy-carbon fibers, filaments, or carbon pastes. Carbon fibers are synthesized by thermal decomposition of fibers based on cellulose or polyacrylonitrile. They have large chemical resistance and good current conduction. Along with favorable properties of the carbon fiber, one should take into account its capacity for hydrogen and oxygen chemisorption especially at a potential of +1.4 V, which can lead to irreversible changes of the surface and the decrease in the detection limit of elements. In this connection, it is recommended [200] to realize the electrochemical accumulation of elements on carbon-fiber ME at potentials when the oxygen and the hydrogen adsorption is at a minimum. Unlike metal ME available in a variety of shapes (hemispherical, conical, cylindrical, disk, as a ring, or as a disk with a ring), carbon ME are generally shaped as a disk. When ME are made of the

**Table 3** Modified planar carbon containing electrodes

Electrode material	Modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Sample	Ref.
(C) ink	Ag	in situ	Pb (II)	$4.8 \cdot 10^{-9}$	0.1 M HNO <sub>3</sub> + 50 mM NaCl + 500 μg L <sup>-1</sup> Ag (I)	DP ASV	BGD	[145]
(C) ink	Ag <sub>nano</sub> or Au <sub>nano</sub>	ex situ	Sb (III)	$6.8 \cdot 10^{-10}$ (Ag <sub>nano</sub> ); $9.4 \cdot 10^{-10}$ (Au <sub>nano</sub> )	B-R buff. (pH 2)	DP ASV	Sea water, PP	[146, 147]
(C) ink	Au	ex situ	Hg (II), CH <sub>3</sub> Hg <sup>+</sup>	$2.5 \cdot 10^{-9}$	0.05 M HCl	SQW ASV	BGD	[148]
(C) ink	Bi	ex situ	Pb (II)	$1.4 \cdot 10^{-9}$	0.01 M NaAc (pH 4.5)	SQW ASV	Waters	[149]
(C) ink	Hg	in situ	Pb (II)	$2.9 \cdot 10^{-9}$	1.0 M NaBr + 1.2 M HCl + 50 μM Hg (II) + 100 μg L <sup>-1</sup> In (III)	SQW ASV	Blood	[150]
(C) ink	Hg	ex situ	Pb (II)	$1.4 \cdot 10^{-11}$	0.02 M NaAc (pH 4.2)	DP ASV SQW ASV	Waters, urine	[151]
(C) ink	Hg	in situ	Cu (II), Cd (II), Pb (II), Zn (II)	$1.9 \cdot 10^{-6}$ (Cu); $6.3 \cdot 10^{-7}$ (Cd); $3.1 \cdot 10^{-7}$ (Pb); $8.4 \cdot 10^{-7}$ (Zn)	0.1 M MgCl <sub>2</sub> + 10 mM KHPH + 120 μg L <sup>-1</sup> Hg (II)	DP ASV	BGD	[152]
(C) ink	Hg	ex situ	Pb (II), Cd (II)	$10^{-7}$	0.01 M HCl	SQW ASV	BGD	[153]
(C) ink	Hg	ex situ	Cu (II), Pb (II), Cd (II)	$7.9 \cdot 10^{-10}$ (Cd); $1.4 \cdot 10^{-10}$ (Pb)	0.02 M NaAc (pH 4.8)	DP ASV	Urine	[154]
(C) ink	Hg	ex situ	Cu (II), Pb (II), Cd (II), Zn (II)	$1.6 \cdot 10^{-9}$ (Cu); $8.9 \cdot 10^{-10}$ (Cd); $4.8 \cdot 10^{-10}$ (Pb); $1.5 \cdot 10^{-9}$ (Zn)	0.1 M NaAc (pH 4.0)	SQW ASV	Waters, wine	[155]
(C) ink (G-E) paste	Hg/Cu Hg	ex situ in situ	Pb (II) Cu (II), Pb (II), Cd (II)	$3.9 \cdot 10^{-9}$ $4.4 \cdot 10^{-9}$ (Cd); $1.4 \cdot 10^{-9}$ (Pb); $1.6 \cdot 10^{-8}$ (Cu);	0.02 M NaAc 0.1–0.5 M HCl + $1 \cdot 10^{-4}$ M Hg (II)	SQW ASV LS ASV, DP ASV	Waters BGD, blood	[156] [157, 158]
(C) paste	Hg	in situ	Cd (II), Cu (II), Pb (II)	$2.5 \cdot 10^{-8}$ (Cd)	0.1 M KNO <sub>3</sub> + 0.03 M HNO <sub>3</sub> + 1 mM Hg(NO <sub>3</sub> ) <sub>2</sub> + 0.1 M Fe(NO <sub>3</sub> ) <sub>3</sub>	LS ASV	Waters	[159]
Carbonized PAN	Hg	in situ	Pb (II); Cd (II)	$3.1 \cdot 10^{-9}$ (Pb); $1.8 \cdot 10^{-9}$ (Cd)	0.1 M NaAc (pH 4.2) + 10 mg L <sup>-1</sup> Hg (II)	SQW ASV	Blood	[160]
(G) ink	Hg	ex situ	Cu (II), Pb (II), Cd (II)	$1.9 \cdot 10^{-9}$ (Pb); $8.9 \cdot 10^{-9}$ (Cd); $7.9 \cdot 10^{-9}$ (Cu)	0.1 M HCl (30 mM NaAc) (pH 4.7)	SQW ASV	Waters, soil	[161, 162]
Soot + resin + PVC	HgO	bulk	Cu (II), Cd (II), Pb (II)	$1.6 \cdot 10^{-8}$ (Cu); $8.9 \cdot 10^{-9}$ (Cd); $4.8 \cdot 10^{-9}$ (Pb)	0.10 M KNO <sub>3</sub> + 0.024 M HCl	LS ASV	Waters	[163]
(G) ink	Hg <sub>2</sub> Cl <sub>2</sub>	ex situ	Cu (II), Pb (II), Cd (II), Zn (II)	$2 \cdot 10^{-9}$ (Cu); $2 \cdot 10^{-10}$ (Cd); $1 \cdot 10^{-10}$ (Pb); $8 \cdot 10^{-10}$ (Zn)	0.5 M HCl (Cu, Pb, Cd); acetic-chloride buffer (Zn)	LS ASV; SQW ASV	Waters, wines	[164, 165]
(G-E) paste	Hg <sub>2</sub> Cl <sub>2</sub> /pyrocatechin	ex situ/ in situ	Fe (III)	$3.6 \cdot 10^{-10}$	0.1 M NaAc + $5 \cdot 10^{-4}$ M pyrocatechin	LS CSV	Waters	[166]
(G) ink	BiPO <sub>4</sub>	ex situ	Pb (II), Cd (II), Zn (II)	$2 \cdot 10^{-9}$ (Pb); $4 \cdot 10^{-9}$ (Cd); $8 \cdot 10^{-9}$ (Zn)	0.1 M acetate buffer (pH 4.5)	SQW ASV	BGD	[167]
(G-E) paste	Hg (1); DPCD (2); ANTPR (3); DPCO (4); DAN (5); DMG(6)	in situ	Cu (II), Pb (II), Cd (II), Zn (II) (1); Cr (VI) (2); Mo (VI), W (VI) (3); Mn (II) (4); Se(IV) (5); Ni (II) (6)	$10^{-9}$ (Cu, Pb, Cd, Zn, Cr); $1 \cdot 10^{-9}$ (Mo); $3 \cdot 10^{-9}$ (W); $6 \cdot 10^{-9}$ (Mn); $1 \cdot 10^{-8}$ (Se); $1 \cdot 10^{-9}$ (Ni)	0.14 M NaCl + 0.04 M HCl + $1 \cdot 10^{-4}$ M Hg (II) (Cu, Pb, Cd, Zn); 0.15 M H <sub>2</sub> SO <sub>4</sub> + $5 \cdot 10^{-6}$ M DPCD (Cr); 0.5–0.9 M HCl + 0.03–0.07 M NH <sub>4</sub> SCN + 0.02–0.05 M ANTPR (Mo, W); amm.buff. + $3 \cdot 10^{-5}$ M DPCO (Mn); 0.1 M HCl + $6.3 \cdot 10^{-5}$ M DAN (Se); 0.1 M KCl + $2.5 \cdot 10^{-4}$ M DMG (Ni)	DP ASV (Cu, Pb, Cd, Zn, Mo, W); LS CSV (Cr, Mn, Se, Ni)	Waters	[168, 169]

**Table 3** (continued)

Electrode material	Modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Sample	Ref.
(G-E) paste	Hg-DDC; Hg-PDTC or HgAc + nafion (1); Au PDTC, AuCl <sub>3</sub> + nafion or HAuCl <sub>4</sub> (2)	ex situ	Cu (II), Pb (II), Cd (II), Zn (II), Sn (IV) (1); Hg (II) (2); As(III) (2)	10 <sup>-9</sup> (Cu, Pb, Cd, Zn); 8·10 <sup>-9</sup> (Sn); 2.5·10 <sup>-11</sup> (Hg); 1.4·10 <sup>-8</sup> (As)	0.1 M HCl (Cu, Pb, Cd, Zn); 4.6 g L <sup>-1</sup> NH <sub>4</sub> Cl + 9.6 g L <sup>-1</sup> (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 9.4 g L <sup>-1</sup> HCl + 10 mgL <sup>-1</sup> MB (Sn); 0.1 M H <sub>2</sub> SO <sub>4</sub> + 4 mM HCl (Hg); 2 M HCl (As)	LS ASV; DP ASV	Juices, waters	[170– 174]
(G-E) paste	NRS	in situ	Co (II)	7.3·10 <sup>-12</sup>	0.01 M citrate buffer + 5 10 <sup>-5</sup> M NRS	LS CSV	Waters	[175]
(G) ink	SF	ex situ	Cu (II), Pb (II), Cd (II), Zn (II)	8·10 <sup>-9</sup> (Cu); 3·10 <sup>-9</sup> (Pb); 2·10 <sup>-9</sup> (Cd); 8·10 <sup>-8</sup> (Zn)	0.1 M NaAc + 0.35 M NaCl + 10 <sup>-3</sup> M HCl	LS ASV	Waters	[176]
(G) ink	SF	bulk	Mn (II)	1·10 <sup>-9</sup>	0.1 M NaCl + 0.1 M amm. buff. (pH 9.2)	LS CSV	Waters	[177]
(C) ink	DMG	bulk	Ni (II)	8.5·10 <sup>-8</sup>	0.1 M amm.buff. (pH 9.2)	DP CSV	Waters	[178]
(SGG) paste	DAN	ex situ	Se (IV)	1.3·10 <sup>-9</sup>	0.1 M HCl	LS CSV	Waters	[179]
(C) ink	Alizarin	bulk	Al (III)	7.0·10 <sup>-7</sup>	0.1 M amm.buff. (pH 9)	DP ASV	Soils	[180]
(G) ink	Sol-gel film + PT	ex situ	Fe (II), Fe(III)	1·10 <sup>-6</sup>	0.1 M acetate buffer	LS ASV	Waters, wines	[181, 182]
(G) ink	Ac-Phos SAMMS	ex situ	Pb (II)	4.4·10 <sup>-9</sup>	0.3–0.5 M HCl	SQW ASV	BGD	[183]
(G) ink	Sal-SAMMS	ex situ	Eu (III)	6.6·10 <sup>-8</sup>	0.05 M acetate buffer (pH 4.6–6.5) (acc.); 0.1–0.2 M NH <sub>4</sub> Cl (sweep)	SQW ASV	BGD	[184]
(G) ink	Calix[4 or 6] arene	ex situ	Pb (II), Cd (II)	2.4·10 <sup>-8</sup> (Pb); 2.5·10 <sup>-8</sup> (Cd)	1 M amm.buff. (pH 10.5-Pb, pH 6.5-Cd) (acc.); 0.1 M HCl (sweep)	DP ASV	Waters	[185, 186]
(C) ink	CEBM	ex situ	Pb (II), Cd (II)	0.8·10 <sup>-8</sup> (Pb); 0.6·10 <sup>-8</sup> (Cd)	0.01 M KNO <sub>3</sub> (pH 2)	DP ASV	ES	[187]
(G) ink	PAN	ex situ	Pb (II)	7.2·10 <sup>-8</sup>	0.37 M amm.buff. (pH 10.5) (acc.); 0.1 M HCl (sweep)	DP ASV	Waters	[188]
(C) ink	SPE/pcPVP	ex situ	Hg (II)	1.6·10 <sup>-8</sup>	0.01 M KCl + 0.02 M H <sub>2</sub> SO <sub>4</sub>	DP ASV	CP	[189]
(C) ink	Semi chelate Q10R	bulk	Hg (II)	1.0·10 <sup>-11</sup>	0.5 M NaCl + 0.1 M NaAc (pH 4.5)	DP ASV	Waters	[190]
(G) ink	Dowex 50W-X8	bulk	Cu (II)	7.9·10 <sup>-9</sup>	5 mM FB (pH 5.7)	DP AVA	Waters	[191]

For abbreviations aside from those defined here, see Tables 1 and 2

(G) or (C) ink graphite- or carbon-containing ink, (G-E) paste graphite-epoxy paste, PAN polyacrylonitrile, PVC polyvinylchloride, (SGG) paste sol-gel graphite paste, DAN diamionaphthalene, NRS nitroso-R salt, Hg-DDC mercury diethyldithiocarbamate, Hg-PDTC mercury pyrrolidine dithiocarbamate, HgAc mercury(II) acetate, Au-PDTC aurum pyrrolidine dithiocarbamate, Ac-Phos SAMMS acetamide phosphonic acid self-assembled monolayer on mesoporous silica, SF hetaryl-substituted formazan, SPE/pcPVP 1,5-dibromopentane partially (7%) cross-linked poly(4-vinylpyridine), KHPH potassium hydrophthalate, MB methylene blue, PLH poly-L-histidine, CEBM crown-ether based membrane, AVA anodic voltammetry, PP pharmaceutical preparations, CP cosmetic productions, ES environmental samples

carbon fiber, the critical importance is attached to the technology used to cover the fiber with the insulating material because the insulation quality ultimately determines the mechanical strength and the operating stability of the electrode. A new technology by which ME are covered with a quartz film solves this problem to some extent. The film is deposited from the vapor phase

including silicon carbide, hydrogen, and oxygen [201]. The components mutually interact to form quartz gradually precipitating on carbon fibers. Coatings made by this technology have no cracks and hermetically insulate the fibers.

The problem of measuring extremely low currents at the level of nano- and picoamperes on ME is solved by the use

of up-to-date, highly sensitive electrochemical equipment or ME arrays (MEA) whose desired signal can be integrated and measured by standard electrochemical analyzers and polarographs. ME systems are made using methods of microelectronics, electron- and ion-beam technologies, X-ray and high-temperature lithography, and photolithogra-

phy. It should be noted that physical methods of producing ME systems are rather expensive and laborious.

The lower detection limit of determinable concentrations on electrodes made of a single unmodified carbon or graphite fiber is  $10^{-7}$ – $10^{-9}$  M [202–212]. Still lower detection limits of  $10^{-8}$ – $10^{-10}$  M were achieved with

**Table 4** Modified carbon micro(nano)electrodes

Electrode material/modifier	Manner	Analyte	Detection limit, M	Supporting electrolyte	Sweep mode	Purge	Sample	Ref.
GF (d= 8 μm)/Hg	in situ	Cd (II), Pb (II)	$5 \cdot 10^{-10}$	0.84 mM NaAc	SQW ASV	–	BGD	[213]
CF /Hg	in situ	Pb (II)	$4.8 \cdot 10^{-10}$	$1 \cdot 10^{-7}$ M Hg (II)	LS ASV	–	Natural waters	[214]
CF (d= 8 μm)/Hg	in situ	Zn (II)	$1 \cdot 10^{-7}$	0.15 M FB + Hg (NO <sub>3</sub> ) <sub>2</sub>	SQW ASV	–	Insulin	[215]
CF /Hg	in situ	Cu (II), Pb (II)	$2.9 \cdot 10^{-9}$ (Pb); $3.1 \cdot 10^{-8}$ (Cu)	0.1 M KNO <sub>3</sub> + 0.1 M HNO <sub>3</sub> (pH 1) + 0.01 mM Hg(NO <sub>3</sub> ) <sub>2</sub>	LS ASV	+	Natural and mineral waters	[216]
CF (d= 30 μm)/Hg	in situ	Pb (II), Cd (II), Zn (II)	$1 \cdot 10^{-10}$ (Zn)	0.01 M KCl + $1 \cdot 10^{-6}$ M Hg (II) + 0.033 M HNO <sub>3</sub>	LS ASV	+	Natural waters, rainfalls	[217]
CF (d= 6 μm)/Hg	ex situ	Cu (II), Pb (II)	$1 \cdot 10^{-7}$	0.1 M NaAc	LS ASV	+	Natural waters	[218]
GCF (d= 10 μm)/Hg,	ex situ	Zn (II)	$7.6 \cdot 10^{-7}$	10 mM KNO <sub>3</sub> + 10 mM HNO <sub>3</sub>	SQW ASV	–	BGD	[219]
GCF (d= 8 μm)/Hg	ex situ	Cu (II); Pb (II); Cd (II)	$10^{-8}$	0.01 M HCl	DP ASV, SQW ASV	+	Natural waters	[220]
CF (d= 30 μm)/Au	in situ	Hg (II)	$8.1 \cdot 10^{-11}$	0.1 M HClO <sub>4</sub> + 5 mM HCl + $5 \cdot 10^{-7}$ M Au (III)	DP ASV	–	Natural waters	[221]
CF/Bi	in situ	Tl (I), Cd (II), Zn (II), Pb (II)	$10^{-8}$ – $10^{-9}$	0.1 M NaAc (pH 4.5) + 400 μg L <sup>-1</sup> Bi (III)	SQW ASV	–	BGD	[222]
CF/Bi/cupferron	ex situ/ in situ	U (VI)	$1.3 \cdot 10^{-9}$	0.1 M NaAc (pH 4.6) + $7.5 \cdot 10^{-5}$ M cupferron	SQW ASV	–	Sea waters	[223]
CF (d= 7 μm)/Bi (1); CF/Bi/DMG (2)	ex situ (1); situ/in situ (2)	Pb (II) (1), Cd (II) (1), Co (II) (2), Ni (II) (2)	$1.2 \cdot 10^{-9}$ (Co); $1.5 \cdot 10^{-9}$ (Ni)	0.05 M NaAc (pH 4.5) (Cd, Pb); 0.01 M amm.buff. (pH 9.2) + $5 \cdot 10^{-5}$ M DMG (Co, Ni)	SQW CSV (Co, Ni), SQW ASV (Cd, Pb)	–	Model solutions	[224]
CMEA /Hg	in situ	Cd (II), Pb (II)	$1.4 \cdot 10^{-9}$ (Pb); $2.7 \cdot 10^{-9}$ (Cd)	0.1 M NaAc + $5 \cdot 10^{-5}$ M Hg(NO <sub>3</sub> ) <sub>2</sub>	SQW ASV	+	Drinking water	[225]
CMEA (d= 7 μm)/Hg	in situ	Cd (II), Pb (II)	$1 \cdot 10^{-6}$	0.1 M KNO <sub>3</sub> (pH 1.7, HNO <sub>3</sub> ) + 0.38 mM Hg (II)	LS ASV	+	Model solutions	[226]
CMEA (d= 10 μm)/Hg	in situ	Pb (II)	$1.3 \cdot 10^{-7}$	1.2 M HCl + 0.046 mM Hg (II)	SQW ASV	–	Blood	[227]
CNTA/Bi	in situ	Pb (II), Cd (II)	$2 \cdot 10^{-10}$ (Pb); $3.6 \cdot 10^{-10}$ (Cd)	0.1 M acetate buffer (pH 4.5) + $5 \cdot 10^{-4}$ μg L <sup>-1</sup> Bi(III)	SQW ASV	–	BGD	[228]

For abbreviations aside from those defined here, see Tables 1 to 3

GF graphite fiber, CF carbon fiber, GCF glassy-carbon fiber, CFA carbon fiber array, CMEA carbon microelectrode array, CNTA carbon nanotubes array



mercury-, gold-, and bismuth-modified ME, MEA and CNTA [213–227]; see Table 4.

### Future trends

Having passed the point of centuries and marched into the twenty-first century, voltammetry is advancing in the direction concisely characterized by Wang [229] as “faster, cheaper, simpler and better.” This is largely because the main line of research changed from elaboration of the theory and equipment to development and application of new electrodes, sensors, and transducers in electroanalysis. Special emphasis is on the solution/electrode interface and the selective response formed on this interface. A new generation of electrodes with chemical or physical modification of the surface is under development. A great number of studies concerned with selection of modifiers, their immobilization on the solid surface, and the use of chemically modified electrodes (ChME) provide strong evidence for sincere interest paid by researchers to this problem. A wealth of experience has been accumulated in development of ChME, some features specific to fixing of modifiers on various matrices have been established, and conditions have been formulated for the electrochemical accumulation and determination of some substances on modified electrodes. However, the phenomenological stage of the ChME development is not complete because a diversity of modifiers and variants of their immobilization on electrodes will give researchers a wide scope of work for a long time to come.

It follows from the literature survey that a very promising and hopeful line of development of electrochemical sensors is the use of nanoparticles in electroanalysis [230–232] and the creation of micro- and nanoelectrode arrays, which can uniquely measure the electrochemical response in nonconductive media and unstirred electrolytes. However, the technologies used for the production of ME ensembles are extremely complicated and unavailable for ordinary research laboratories, suggesting the need to develop new methods of their fabrication. The creation of ordered nanostructures by traditional methods is an impracticable task, and in this case, it is appropriate to use the “bottom to top” rather than the “top to bottom” strategy. A proven fact is that nanoparticles of similar dimensions, which are synthesized “from top” by dispersion and “from bottom” by construction from atoms, are sharply different. The structure of the initial sample is preserved in dispersion particles, whereas particles formed by aggregation of atoms can have another arrangement of atoms influencing the electronic structure and chemical properties. Furthermore, processes of self-organization and evolution of modified layers on graphite-containing electrodes are quite possible

because of the high surface energy of the graphite-containing matrix.

It is reasonable to expect that the next stage of development of solid-state electrodes will include comprehensive studies of the electrode surface, elaboration of physical concepts for prediction of properties and characteristics of modified electrodes, and transition from micro- to ultramicro- and nanostructures on the electrode surface that would profoundly alter its properties. At this stage of development, study, and use of electrochemical sensors, we shall have to answer a number of questions: how the surface microgeometry influences the electrochemical activity of the modifier and the response parameters, how machining of the surface influences the electrochemical activity of the modifier and the electrode process, how the surface of the modified electrode can be made reproducible and the response stable, how to avoid formation of passivating films which impair electroanalytical performance of the electrodes, and other questions. This task will require performing a comprehensive systematic study of all links in the integral chain “electrode surface–modifier–response–SV analysis.”

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