Non-traditional Metal Electrode Materials in Electrochemical Environmental Analysis of Biologically Active Compounds

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Abstract: - Solid, paste and composite amalgam electrodes, developed in our laboratory were tested for study and determination of different inorganic as well as organic compounds. Hydrogen overvoltage on amalgam electrodes remains high and therefore such electrodes can be used for measurement of compounds, reducible in range of high negative potentials. Amalgam electrodes including metal more active than mercury (e.g., Cu, Bi, Cd) can be applied for specific purposes when an analyte interacts just with this metal. Mercury meniscus or mercury film modified silver solid amalgam electrode is the best for analytical purposes. Liquid mercury free polished silver solid amalgam electrode can be used in applications where work with liquid mercury is prohibited or undesirable. Working electrode from amalgam paste connect advantages of paste and metal electrodes. In most cases, amalgam electrodes allow substitute mercury ones and moreover, a work on these electrodes in flowing systems or in mobile laboratories is more reliable and comfortable. All of tested amalgam electrodes can be easily prepared in any laboratory.

Key-Words: - Voltammetry, Solid Amalgam Electrodes, Paste Amalgam Electrodes, Environmental Analysis

1 Introduction

Biological active compounds, such as some heavy metals, agrochemicals, medicaments, industry dyes and many other pollutants contaminating the environment, are often electrochemically active too and therefore voltammetric methods can be used for their study and determination. Apart from being highly sensitive, voltammetric techniques allow simultaneous determinations of several elements and they are also capable of discriminations between mobile forms (i.e., free metal ions and small labile complexes) and strong complex or colloidal metal forms. Working electrode (WE) in voltammetry is the soul source of signal which is processed and evaluated during measurements. Mercury electrodes have been used for voltammetric determinations most frequently. The new types of non-toxic electrode materials, such as different types of amalgams [1-3], are looked for because using of metallic mercury is limited by European Union´s legislative [4].

2 Substitution of liquid mercury electrodes

Legislative restrictions concerning working with liquid mercury on one side and exaggerated fear of metal mercury toxicity on the other side are motivation for electrochemists to search for new materials, perspective in mercury electrode substitution.

Substitution of conventional mercury electrode with electrodes from other materials is very often connected with lowering of hydrogen overvoltage and decline of measurement reproducibility. The first from above mentioned parameters depends mainly on the electrode material nature, whereas for the second, status of the working electrode surface before each measurement is important. The regeneration of surface and properties of WE can be performed by different ways or their combination, e.g. electrochemically, chemically or mechanically with complete renovation of part of the electrode material. For disposable electrodes, the replacement of whole electrode or set of electrodes is carried out.

3 Amalgam electrodes

Different types of amalgams shoved as a suitable electrode material. In the dependence on the mercury to metal ratio, liquid or solid amalgam is formed. From the solid amalgams can be prepared electrodes (MeSAE – metal solid amalgam electrode, where Me is Ag, Au, Ir, Cu, Bi and other), which can not only substitute mercury working electrodes, but also exhibit new qualities. There is rather narrow range of metal content within mercury, where mixture exhibits long-time paste consistence. For classic paste electrodes, mixture of carbon powder and suitable pasting liquid is used, which presence is manifested as a retarded surface reaction kinetics on carbon paste surfaces [5]. Paste amalgam based electrodes do not need any binder and

Table 1. Range of working potentials (in V) of different electrodes in some supporting electrolytes

Experimental results obtained by direct current voltammetry; saturated calomel reference electrode; scan rate 0.02 V s^{-1}; the potential limits correspond to 1 μA current level for the electrodes diameter of witch is less than 1 mm and 20 μA - for the larger electrodes; air oxygen was removed by nitrogen.

Electrode (disc diameter, mm)	Potential range, V					
	0.1M $HClO_4$	0.1M HCl	0.2M acetate buffer, pH 4.8	0.05M Na_2EDTA, 0.2M acetate buffer, pH 4.8	0.05M $Na_2B_4O_7$, pH 9.2	0.1M NaOH
HMDE	-1.19 … +0.44	-1.27 … +0.11	-1.70 … +0.31	-1.55 … +0.09	-1.98 … +0.15	-1.97 … -0.07
PtE (0.40)	-0.32 … +1.37	-0.30 … +1.11	-0.51 … +1.28	-0.51 … +1.05	-0.77 … +1.16	-0.96 … +0.85
AuE (0.40)	-0.54 … +1.69	-0.55 … +0.93	-0.91 … +1.49	-0.84 … +0.75	-1.39 … +1.15	-1.62 … +0.81
AgE (0.40)	-0.64 … +0.39	-0.81 … +0.08	-0.99 … +0.36	-0.99 … +0.35	-1.20 … +0.38	-1.41 … +0.19
CuE (0.60)	-0.95 … +0.02	-0.80 … -0.12	-0.99 … -0.01	-0.97 … -0.04	-1.17 … +0.97	-1.34 … -0.19
p-AgSAE (0.70)	-1.12 … +0.45	-1.12 … +0.11	-1.51 … +0.31	-1.45 … +0.11	-1.88 … +0.16	-1.96 … -0.06
m-AgSAE (0.54)	-1.11 … +0.44	-1.12 … +0.12	-1.39 … +0.30	-1.39 … +0.10	-1.92 … +0.15	-1.99 … -0.06
m-AuSAE (0.40)	-1.12 … +0.45	-1.11 … +0.12	-1.47 … +0.31	-1.45 … +0.11	-1.90 … +0.16	-1.91 … -0.05
m-IrSAE (0.67)	-1.01 … +0.43	-1.01 … +0.12	-1.32 … +0.29	-1.34 … +0.10	-1.63 … +0.15	-1.72 … -0.06
m-CdAgSAE (0.53)	-1.07 ... -0.66	-1.06 ... -0.69	-1.29 ... -0.68	-1.29 ... -0.73	-1.93 ... -0.69	-1.93 ... -0.84
m-CuSAE (0.48)	-1.17 … +0.06	-1.18 … -0.07	-1.44 … -0.03	-1.43 … -0.13	-1.75 … +0.95	-1.86 … -0.24
m-BiAgSAE (0.70)	-0.97 … -0.02	-0.96 … -0.09	-1.25 … -0.18	-1.29 … -0.17	-1.84 … -0.29	-1.82 … -0.48
AgSA-CE (2.9)	-1.09 ... +0.45	-1.07 ... +0.15	-1.34 ... +0.45	-1.33 ... +0.45	-1.63 .... +0.52	-1.85 ... +0.17
AgSA-PE (3.0)	-1.04 … +0.36	-0.90 ... +0.21	-1.15 … +0.38	-1.09 … +0.36	-1.50 … +0.24	-1.45 … +0.30
AgA-PE (2.0)	-1.24 ... +0.48	-1.24 ... +0.15	-1.47 ... +0.36	-1.46 ... +0.15	-1.90 ...+0.21	-1.83 ... +0.01

Table 2. The use of solid and paste amalgam electrodes for the determination of biologically active substances. L_Q – limit of quantitation; DPV – differential pulse voltammetry; DCV – direct current voltammetry; ASV – anodic stripping voltammetry; CSV – cathodic stripping voltammetry; AdSV – adsorptive stripping voltammetry; FIA-ED – flow injection analysis with electrochemical detection; catalyt. – catalytic evolution of hydrogen; BR – Britton-Robinson; MeOH – methanol; DNA-Os,bipy – DNA marked with the complex of osmium tetroxide with 2,2'-bipyridine.

Substance	Electrode/technique	Supporting electrolyte	L_Q	Ref.
Cu^{2+}	m-AgSAE/ASV	0.4M acetate buffer (pH 4.8)	3×10^{-4} mg L^{-1}	[9]
Pb^{2+}	m-AgSAE/ASV	0.4M acetate buffer (pH 4.8)	7×10^{-4} mg L^{-1}	[9]
Pb^{2+}	m-CuSAE/ASV	0.2M acetate buffer (pH 4.8)	2×10^{-3} mg L^{-1}	[19]
Cd^{2+}	m-AgSAE/ASV	0.4M acetate buffer (pH 4.8)	1×10^{-3} mg L^{-1}	[9]
Cd^{2+}	m-CuSAE/ASV	0.2M acetate buffer (pH 4.8)	2×10^{-3} mg L^{-1}	[19]
Zn^{2+}	m-AgSAE/ASV	0.4M acetate buffer (pH 4.8)	9×10^{-4} mg L^{-1}	[9]
Tl^{+}	m-AgSAE/ASV	0.4M acetate buffer (pH 4.8)	4×10^{-4} mg L^{-1}	[9]
Ni^{2+}	m-AgSAE/AdSV	0.1M [$NH_4Cl + NH_3$], 0.001 % dimethylglyoxime, (pH 9.8)	9×10^{-4} mg L^{-1}	[10]
Fe^{3+}	m-AgSAE/DPV	0.35M NaOH, 3 % triethanolamine, 0.01M EDTA	0.20 mg L^{-1}	[10]
Mn^{2+}	m-CuSAE/CSV	0.05M $Na_2B_4O_7$ (pH 9.2)	0.03 mg L^{-1}	[19]
IO_3^-	m-AgSAE/DPV	0.1M NaOH	0.14 mg L^{-1}	[11]
IO_3^-	p-AgSAE/DPV	0.1M NaOH	0.34 mg L^{-1}	[11]
IO_3^-	AgA-PE/DPV	0.1M NaOH	0.03 mg L^{-1}	[8]
NO_3^-	m-AgSAE/DPV	0.02M $CeCl_3$	1.2 mg L^{-1}	[10]
1,3-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10) – MeOH, 1:1	2×10^{-6} mol L^{-1}	[12]
1,5-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10) – MeOH, 1:1	1×10^{-6} mol L^{-1}	[12]
1,8-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10) – MeOH, 1:1	5×10^{-7} mol L^{-1}	[12]
3-Nitrofluoranthen	m-AgSAE/DPV	0.01M NaOH – MeOH, 1:9	4×10^{-7} mol L^{-1}	[13]
3-Nitrofluoranthen	m-AgSAE/AdSV	0.01M NaOH – MeOH, 1:1	3×10^{-8} mol L^{-1}	[13]
Nitrobenzene	m-AgSAE/DPV	0.1M acetate buffer (pH 4.8)	6×10^{-7} mol L^{-1}	[10]
1,3-Dinitrobenzene	m-AgSAE/DPV	0.1M acetate buffer (pH 4.8)	3×10^{-7} mol L^{-1}	[10]
2-Nitrophenol	m-AgSAE/DPV	BR buffer (pH 8)	1×10^{-6} mol L^{-1}	[6]
2-Nitrophenol	p-AgSAE/DPV	BR buffer (pH 5)	1×10^{-6} mol L^{-1}	[6]
4-Nitrophenol	m-AgSAE/DPV	BR buffer (pH 6)	1×10^{-6} mol L^{-1}	[6]
4-Nitrophenol	p-AgSAE/DPV	BR buffer (pH 6)	3×10^{-6} mol L^{-1}	[6]
4-Nitrophenol	m-AgSAE/FIA+ED	BR buffer (pH 6)	3×10^{-6} mol L^{-1}	[14]
4-Nitrophenol	AgA-PE/DPV	0.1M acetate buffer (pH 4.8)	0.03 mg L^{-1}	[8]
2,4-Dinitrophenol	m-AgSAE/DPV	BR buffer (pH 4)	2×10^{-6} mol L^{-1}	[6]
2,4-Dinitrophenol	p-AgSAE/DPV	BR buffer (pH 5)	3×10^{-6} mol L^{-1}	[6]
2-Methyl-4,6-dinitrophenol	m-AgSAE/DPV	BR buffer (pH 4)	2×10^{-7} mol L^{-1}	[15]
Pendimethalin	m-AgSAE/DPV	BR buffer (pH 7) – MeOH, 1:1	3×10^{-7} mol L^{-1}	[13]
N,N-dimethyl-4-amino-2'-carboxyazobenzene	m-AgSAE/DPV	BR buffer (pH 5)	4×10^{-7} mol L^{-1}	[16]
Ostazine orange	m-AgSAE/AdSV	0.01M NaOH	2×10^{-7} mol L^{-1}	[17]
Cysteine	m-AgSAE/CSV	0.05M $Na_2B_4O_7$	3×10^{-9} mol L^{-1}	[18]
Cysteine	m-CuSAE/CSV	0.05M $Na_2B_4O_7$	1×10^{-8} mol L^{-1}	[18]
Phytochelatin (PC2)	m-CuSAE/CSV	0.05M $Na_2B_4O_7$ (pH 8.1)	3×10^{-9} mol L^{-1}	[21]
Phytochelatin (PC3)	m-CuSAE/CSV	0.05M $Na_2B_4O_7$ (pH 8.1)	2×10^{-9} mol L^{-1}	[21]
Adenine	m-CuSAE/CSV	0.05M $Na_2B_4O_7$	6×10^{-9} mol L^{-1}	[10]
Adenine	p-AgSAE/CSV	0.005M NaOH, 0.4 mg L^{-1} Cu^{2+}	3×10^{-9} mol L^{-1}	[23]
Guanine	p-AgSAE/CSV	0.005M NaOH, 0.4 mg L^{-1} Cu^{2+}	7×10^{-9} mol L^{-1}	[23]
DNA (plasmid)	p-AgSAE/CSV	0.005M NaOH, 0.4 mg L^{-1} Cu^{2+}	7×10^{-9} mol L^{-1}	[23]
DNA (acid-treated)	p-AgSAE/CSV	0.005M NaOH, 0.4 mg L^{-1} Cu^{2+}	6×10^{-9} mol L^{-1}	[23]
DNA (acid-treated)	m-CuSAE/CSV	0.005M NaOH	4×10^{-9} mol L^{-1}	[23]
DNA-Os,bipy	m-AgSAE/catalyt.	0.1M acetate buffer (pH 4.7)	2×10^{-4} mg L^{-1}	[10]

behave as metal ones. Paste amalgam working electrodes therefore combine advantage of paste electrodes (simple mechanical exchange of working surface) and metal electrodes (high rate of electrode processes).

According to the way of preparation and active surface status, solid and paste amalgam electrodes can be dividend on:

- **polished** – liquid mercury free solid amalgam electrode (p-MeSAE)
- **film** – polished MeSAE covered by mercury film (MF-MeSAE)
- **meniscus** – polished MeSAE covered by mercury meniscus (m-MeSAE)
- **composite** – electrode based on a fine solid amalgam powder and a solid polymer (MeSA-CE)
- **paste** – electrode based on a paste amalgam (MeA-PE).

Solid or paste amalgam electrodes as environmentally friendly alternatives to mercury electrodes are suitable both for batch analysis and for HPLC with electrochemical detection or flow injection analysis with electrochemical detection of electrochemically active substances with limit of quantification down to 10^{-7} mol L^{-1}. They can be easily prepared in any laboratory and their simple electrochemical pretreatment in many cases eliminates problems with their somewhat worse reproducibility.

One of basic characteristic of working electrode is the range of working potentials, which determine the spectrum of compounds, possible to study on the electrode concerned. Table 1 presents working potential ranges for different amalgam electrodes and for comparison, also those for traditionally used metal electrodes. As can be seen, hydrogen overvoltage on amalgam electrodes remains high and therefore such electrodes can be used for measurement of compounds, reducible in range of high negative potentials. For such type of measurement, majority of other electrodes is useless. Solid, paste and composite amalgam electrodes, developed in our laboratory were tested for study and determination of different inorganic as well as organic compounds. Table 2 summarizes conditions and sensitivity for determination of majority of compounds studied. Both the selectivity and the sensitivity of many of the above mentioned determinations can be increased by the combination of voltammetry on amalgam electrodes with preliminary separation and preconcentration using liquid-liquid extraction or solid phase extraction [6] which enables determination of nanomolar concentrations of tested substances. At present, paste and composite working electrodes based on solid amalgams are being tested with promising results in the field of environmental analysis [7,8].

From environmental point of view studies of DNA and corresponding nucleic acid bases on amalgam electrodes are of interest because they can result in techniques detecting substances damaging DNA. m-CuSAE, m-AgSAE and p-AgSAE were used for determination of adenine, guanine, their mixtures, and acid-treated DNA [22,23], m-CuSAE can be used for determination of chromosomal DNA at the ppb level [20] in several microliter volumes and thus serve for a label-free DNA detection in DNA hybridization sensor. m-AgSAE modified with supercoiled DNA can be utilized as a sensor for DNA nicking substances [24]. p-AgSAE and MF-AgSAE were applied for the measurements of redox and tensammetric voltammetric signals of single- and double-stranded, linear or supercoiled DNA, synthetic polynucleotides and free adenine [25]. m-AgSAEs was used as a detection electrode in DNA hybridization experiments offering highly specific discrimination between complementary and nonspecific DNA, as well as determination of the length of a repetitive DNA sequence [26].

4 Conclusions

The above discussed solid, paste and composite amalgam electrodes can play a very useful role in environmental electroanalysis. Portability and non-toxicity of amalgam electrodes make them convenient substitute of mercury electrodes for on spot electroanalytical monitoring of electrochemically active substances and their mechanical properties makes them compatible with measurements in flowing systems.

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