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Effect of the modification of mercuric oxide on the properties of mercury films at HgO-modified carbon paste electrodes

Received: 06 December 1999 / Accepted: 16 March 2000

Abstract The influence of modifications of the mercuric oxide on the voltammetric properties of mercury film carbon paste electrodes was studied. The mercury film was formed electrochemically from the bulk red or yellow mercuric oxide-modified carbon paste electrodes. Differential pulse anodic stripping voltammetry and optical microscopy in polarised light were used to characterise the properties of the mercury films. The results were compared with those obtained using the conventional preparation of mercury-plated carbon paste electrodes when the mercury film is deposited on the surface of the electrode by reduction of Hg(II) ions in solution utilising a sufficient negative potential. It was shown that the mercury film formed from the yellow modification of the mercuric oxide provides better voltammetric characteristics than the red one owing to the high distribution of its small particles, i.e. the mercury droplets after electrochemical treatment. Such a mercury film has similar properties to those of a mercury film generated from solution.

Key words Mercuric oxide · Mercury film · Modified carbon paste electrode · Anodic stripping voltammetry · Optical microscopy

Introduction

For the determination of heavy metals, mercury film electrodes (MFEs) have been widely used combined with anodic stripping voltammetry (ASV). Applying the MFEs provides a lower detection limit for amalgam-forming metals in comparison with mercury drop electrodes and allows minimising the handling of elemental mercury. However, the interferences arising from intermetallic compounds are more pronounced, and the change of electrolyte composition and the presence of surfactants also affect the behaviour of MFEs [1]. Different carbon substrates have been employed as a support for the deposition of the mercury. The most common are glassy carbon [2–7], epoxy carbon [8, 9], thick-film graphite [10–12] and carbon paste [13, 14]. Many other carbon materials such as pyrolytic carbon, sprayed graphite layers [1] and carbon fibres [1, 15] have also been utilised for this purpose.

Generation of mercury film on carbon electrodes is mostly performed *in situ* by reduction of Hg(II) ions added to the supporting electrolyte during the accumulation step of the ASV analysis. The preplating of the mercury film in pure Hg(II) solution before analysis, sometimes protected with a membrane, is also used [5, 16]. The deposited mercury film comprises a thin layer of microdroplets of mercury on the carbon supports [2–4] and its properties depend upon the quality of the support substrate, the concentration of Hg(II) ions in the solution and the deposition potential [3].

Another way of preparation of the mercury film is utilising the carbon materials either modified on the surface or bulk modified by a selected mercury compound and its electrochemical reduction during the conditioning or accumulation step. Brainina et al. [11] reviewed the properties of thick-film graphite electrodes modified with mercury(I) chloride, mercury(II) nitrate, mercury(II) diethyldithiocarbamate and mercury(II) pyrrolidinedithiocarbamate and their use in the determination of heavy metals by the ASV technique. The

Presented at the international conference “Modern Electroanalytical Methods”, 19th to 23rd September, 1999, in Seč, Czech Republic

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performance of the electrodes prepared in such a way was very good, but some types of electrodes were not stable enough for routine use. Nafion film improved their stability, prolonged the storage time and lowered the contamination of the test samples by mercury. Incorporation of mercury(II) acetate into a Nafion membrane on a glassy carbon electrode [17] was used successfully for the determination of lead and copper in waste water samples by means of flow-injection analysis. Guo and Khoo [18] prepared a carbon paste electrode which was bulk modified with mercury(II) diethyldithiocarbamate. Seo et al. [19] applied the mercury(II) oxide-modified composite electrode for fast-scan ASV determination of copper, lead and cadmium with the deoxygenation step omitted. Recently, Zakharchuk et al. [12] have published a comprehensive comparison of electroanalytical properties of thick-film graphite electrodes with the mercury film deposited in situ and the surface modified with mercury(II) dithiocarbamate. Special attention was given to the surface morphology of the deposited mercury films.

Carbon paste represents one of the promising carbon substrates for the deposition of the mercury film. As the electrode is a composition of carbon powder and pasting liquid, the behaviour of the corresponding paste is affected by numerous parameters, such as the particle size, uniformity and porosity of the powder and the physical and chemical properties of the pasting liquid. The modification of the carbon paste by a chemical compound (chemically modified electrodes, CMEs) has also great influence on the behaviour of the electrodes [14, 20]. This work focused on the effect of the red and yellow mercuric oxide used for the formation of the mercury film at the surface of a mercuric oxide-modified carbon paste electrode (MO-CPE). According to literature data [21, 22], modifications of mercury(II) oxide differ in the grain size only, as the crystal structure seems to be the same. Differences in the physical and chemical properties are then attributed to the fineness of the oxides. The behaviour of the MO-CPE was studied by means of differential pulse ASV (DPASV) and by optical microscopy in situ and ex situ.

Experimental

Preparation of electrodes

Bulk modified CPEs were prepared by thorough mixing 0.5 g of RW-B graphite powder (Ringsdorff Werke, Germany) with 0.1 g of red or yellow mercuric oxide (Merck, Germany) and 150 μ l of Uvasol paraffin oil (Fluka, Germany). Particles of mercury(II) oxide were not ground before mixing. Pastes were then packed into piston-like electrode holders and left unused for 5 days to homogenise the content under internal pressure. An unmodified CPE used as support for the mercury film generated in situ was prepared by mixing the above-mentioned quantities of carbon powder and paraffin oil only. The hole diameter of the electrodes (active surface of the paste) was 2 mm. A saturated calomel reference electrode and a platinum auxiliary electrode complemented the three-electrode arrangement.

Instrumentation

An EA9 electrochemical analyser (Zakład Elektroniki MTM, Kraków, Poland) together with a home-made electrode stand were used for voltammetric measurements. An ordinary computer with a Pentium processor was utilised for acquiring the voltammetric data and their evaluation by EAGRAPH software. The solutions were stirred by means of a Teflon-coated magnetic bar. A Neophot-2 (Carl-Zeiss Jena, Germany) microscope was used for microscopic observations of the electrode surfaces. All observations were carried out using polarised light for better distinction between mercuric oxide particles and the carbon surface. In ex situ observations, after the electrochemical treatment the surface of the electrodes was dipped in ethanol and left to dry out to remove the solvent from the electrode surface.

Procedures

To evaluate the electrochemical behaviour of the formed mercury film, the DPASV technique was applied throughout the study. Lead and cadmium were accumulated for 60 s at the selected potentials. Then, after an equilibration time of 15 s, the voltammograms were recorded within the potential range from -1000 mV to $+160$ mV by means of a DPV ramp with a scan rate of 25 mV/s and a pulse height of 50 mV. Peak heights were calculated as the average of at least five measurements. Before each experiment, the surface of the CPEs was wiped with wet filter paper and the solution was deaerated by purging with argon for 10 min. Standard solutions of lead, cadmium and mercury (Merck, Germany) were used, as well as hydrochloric acid and calcium chloride of analytical grade (POCh, Poland), together with double-distilled water to prepare the supporting electrolytes.

Results and discussion

Optical microscopy

The surface of a MO-CPE containing the yellow modification is shown in Fig. 1a. Particles of the yellow mercuric oxide are widely spread in the carbon paste, showing yellow dots clearly visible on colour photographs, of size about 2 μ m. The roughness of the surface of the carbon paste made focusing of the image quite different. Figure 1b presents the surface after applying a deposition potential of -1200 mV for 2 min in a solution containing lead and cadmium, as an illustration of the accumulation of heavy metals at the electrode surface using ASV. The size of the mercury droplets generated and visible on the surface is roughly the same as the size of the particles of the oxide, about 10 μ m, in the presence of clusters of mercuric oxide grains.

In the case of red mercuric oxide, the particles in the paste are much bigger, about 20 μ m, and they exhibit a shiny brick-red colour in polarised light (Fig. 2a). Microscopic observations of the surface of the red MO-CPE in situ showed formation of small mercury droplets on the oxide particles during the accumulation step, which then combined during the potential scan. The resulting mercury droplets had a diameter of about 15 μ m (Fig. 2b). Unmodified carbon paste (Fig. 3a) was used as a support for the preparation of the MFE by formation of a mercury film during electroreduction of

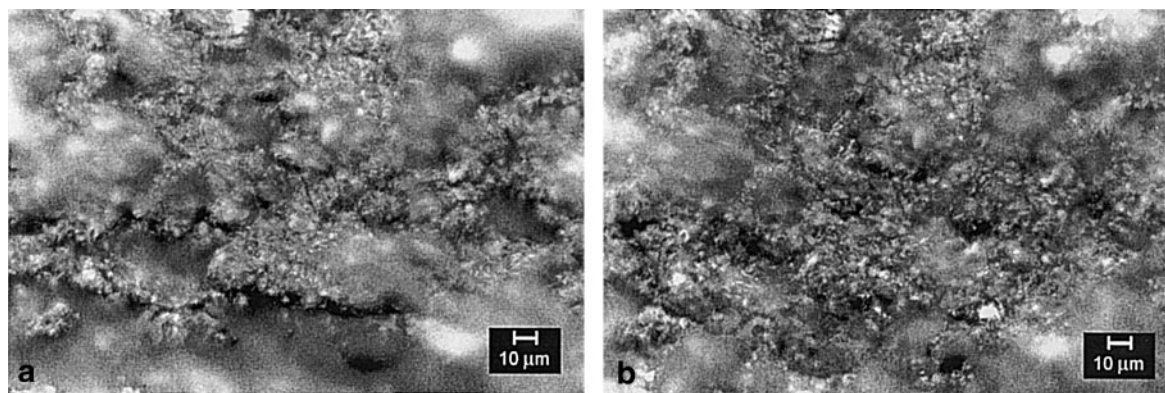


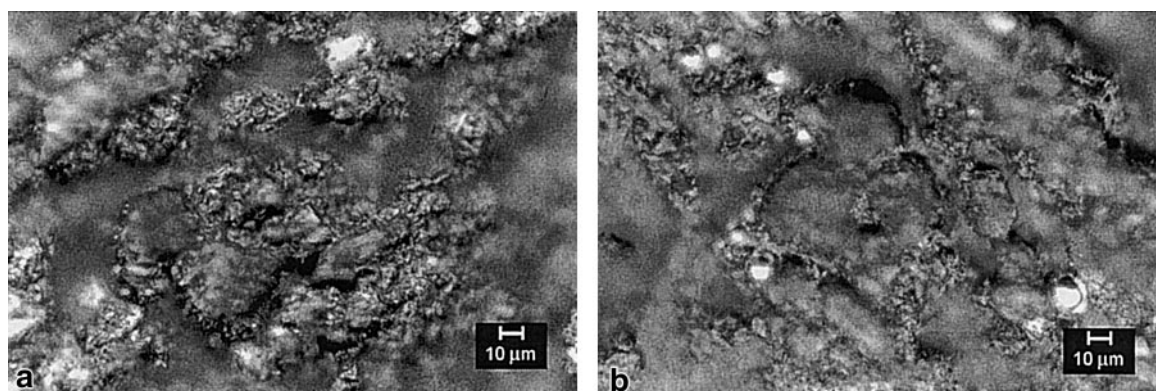
Fig. 1 Surface of yellow MO-CPE ($400\times$ magnification, polarised light): **a** before and **b** after treatment. $E_{\text{acc}} = -1200$ mV, $t_{\text{acc}} = 2$ min, 0.01 M HCl + 0.1 M KCl + 1×10^{-6} M Pb(II) and Cd(II)

Hg(II) ions added to the supporting electrolyte. Figure 3b shows the surface of the CPE after the above-mentioned treatment. The deposited mercury droplets are very small and have diameters less than $2 \mu\text{m}$.

Differential pulse anodic stripping voltammetry

As the formation of the mercury film on carbon substrates is strongly influenced by the deposition potential and the pH of the supporting electrolyte [23], the dependencies of the heights of the stripping peaks of lead and cadmium on those factors were evaluated for all the prepared CPEs. Figure 4 depicts the relationship between the peak heights of the metals, the deposition potential and the pH value of the supporting electrolyte for yellow MO-CPE. Generation of the mercury is affected by the acidity of the solution, giving the highest peak currents at a potential of -1400 mV. Repetitive measurements on the same surface of the yellow MO-CPE showed a decrease of the stripping peak of mercury, probably due to the low pH-accelerated chemical dissolution of elemental mercury at the surface of the

Fig. 2 Surface of red MO-CPE ($400\times$ magnification, polarised light): **a** before and **b** after treatment. $E_{\text{acc}} = -1200$ mV, $t_{\text{acc}} = 2$ min, 0.01 M HCl + 0.1 M KCl + 1×10^{-6} M Pb(II) and Cd(II)



carbon paste in a solution containing chlorides. This phenomenon did not occur when performing the same procedure in a solution at pH 4, thus enabling the possibility to make experiments several times on the same surface of the electrode.

Figure 5 displays how the chosen experimental parameters influence the peak currents during measurements with red MO-CPE. Here, on the contrary, the dependence of the peak heights on the deposition potential in the electrolyte at pH 4 is more pronounced. However, there is no possibility to evaluate the peak currents owing to high noisy current spikes and oscillations at less negative potentials. These interferences did not occur when using the deposition potentials from -1100 mV to -1300 mV but they appeared again at -1400 mV. An example of such a voltammogram recorded with red MO-CPE is shown in Fig. 7 below. It is believed that such an erratic behaviour of the current is closely connected with the structural changes in the mercury film. As was observed elsewhere on glassy carbon substrate [4, 23], the size of the mercury droplets strongly depends on the applied potential, being larger at less and smaller at more negative potentials. The uniformity of the droplets also increases with the applied potential. Yellow MO-CPE exhibited only small symptoms of such behaviour at less negative potentials owing to its one order of magnitude smaller particles of mercuric oxide, i.e. the mercury droplets after electrochemical treatment. The current spikes at -1400 mV are caused by simultaneous evolution of hydrogen during the accumulation step, changing the properties of the

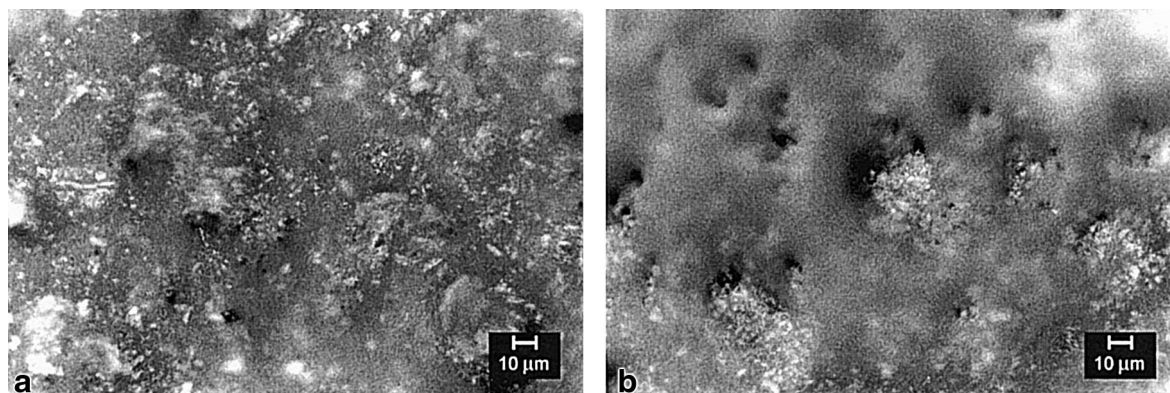


Fig. 3 Surface of unmodified CPE ($400\times$ magnification, polarised light): **a** before and **b** after treatment. $E_{\text{acc}} = -1200$ mV, $t_{\text{acc}} = 2$ min, 0.01 M HCl + 0.1 M KCl + 5×10^{-5} M Hg(II) + 1×10^{-6} M Pb(II) and Cd(II)

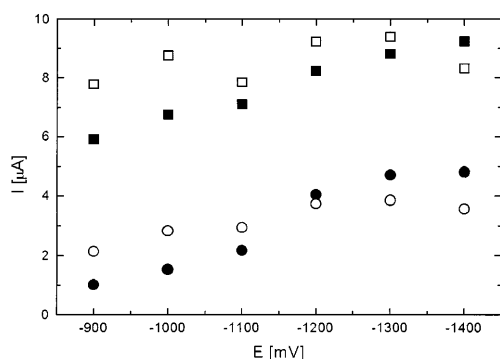


Fig. 4 Dependence of peak currents on deposition potential used for yellow MO-CPE. DPASV, $t_{\text{acc}} = 1$ min, $t_r = 15$ s, scan rate = 25 mV/s, pulse height = 50 mV; *solid symbols* 0.1 M HCl (pH 1), *open symbols* 1×10^4 M HCl + 0.1 M KCl (pH 4); *square symbols* 1×10^{-6} M Pb(II), *circle symbols* 1×10^{-6} M Cd(II)

carbon paste surface for the deposition of the mercury. Nevertheless, a significant reduction of hydrogen at carbon paste containing paraffin oil as a binder can be

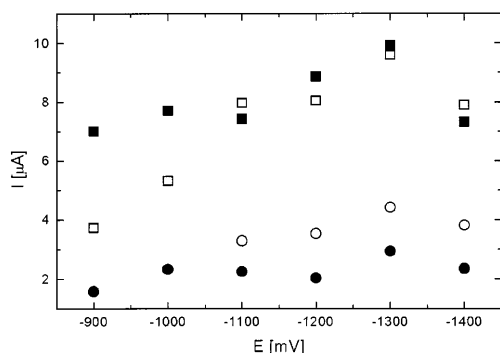


Fig. 5 Dependence of peak currents on deposition potential used for red MO-CPE. DPASV, $t_{\text{acc}} = 1$ min, $t_r = 15$ s, scan rate = 25 mV/s, pulse height = 50 mV; *solid symbols* 0.1 M HCl (pH 1), *open symbols* 1×10^4 M HCl + 0.1 M KCl (pH 4); *square symbols* 1×10^{-6} M Pb(II), *circle symbols* 1×10^{-6} M Cd(II)

suppressed by extending the cathodic polarisation limit using another pasting liquid up to -2 V [14].

In our experiments, an unmodified CPE with the mercury film formed in situ gave the best results (Fig. 6). Peak currents depend, especially for cadmium, nearly linearly on the deposition potential in the supporting electrolyte at pH 4, giving the highest values even at -1400 mV, where the MO-CPEs were not able to follow. A lower pH reduced the growing trend in dependence of the peak currents on the deposition potential. Certain influences may come from forming the mercury compounds with ions of the supporting electrolyte [12] during the deposition of mercury. However, the resulting voltammetric curves are smooth, without visible interferences (Fig. 7).

Conclusion

Optical microscopy in polarised light and DPASV were used for studying the properties of mercury film formed from MO-CPE and in situ by reducing the Hg(II) ions added to the solution. After electrochemical treatment, the yellow MO-CPE exhibited similar electroanalytical properties as the mercury film deposited on an

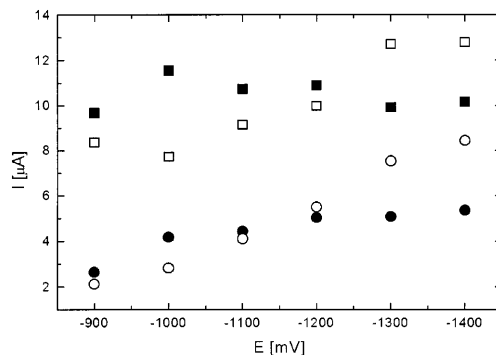


Fig. 6 Dependence of peak currents on deposition potential used for unmodified CPE. DPASV, $t_{\text{acc}} = 1$ min, $t_r = 15$ s, scan rate = 25 mV/s, pulse height = 50 mV, addition of the 5×10^{-5} M Hg(II) to the supporting electrolyte; *solid symbols* 0.1 M HCl (pH 1), *open symbols* 1×10^4 M HCl + 0.1 M KCl (pH 4); *square symbols* 1×10^{-6} M Pb(II), *circle symbols* 1×10^{-6} M Cd(II)

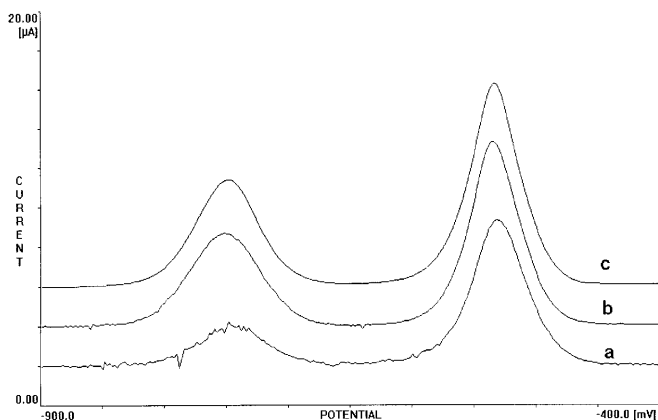


Fig. 7 Voltammograms of Cd(II) and Pb(II) using MO-CPEs. $E_{\text{acc}} = -1400$ mV, $t_{\text{acc}} = 1$ min, scan rate = 25 mV/s, pulse height = 50 mV, 0.1 M HCl + 1×10^{-6} M Pb(II) and Cd(II); *a* red MO-CPE, *b* yellow MO-CPE, *c* unmodified CPE, addition of the 5×10^{-5} M Hg(II) to the supporting electrolyte

unmodified CPE. The resulting droplets had a diameter at least one order of magnitude smaller in comparison with the red MO-CPE. Hence, the voltammetric response is not so affected by surface perturbations and coalescences of the mercury droplets. In this preliminary study, the overall analytical performance of the MO-CPE was not thoroughly tested; nevertheless, the yellow mercuric oxide seems to be one of the promising modifiers of carbon substrates for producing portable field sensors for the electroanalysis of heavy metals. All advantages of using mercury film electrodes can be achieved without the need of handling elemental mercury or mercury solutions.

Acknowledgements The authors would like to thank Dr. Jan Piekarczyk (Department of Special Ceramics, University of Mining and Metallurgy, Kraków, Poland) for technical assistance with the microscopic experiments and Dr. Ivan Švancara (Department of Analytical Chemistry, University of Pardubice, Czech Republic) for helpful comments on voltammetry with carbon paste electrodes.

Financial support of the Grant Agency of the Czech Republic (project no. 203/99/0044) as well as from the CEEPUS program (project PL-24/9899) are gratefully acknowledged.

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