ELSEVIER

Bioelectrochemistry 55 (2002) 153–155

Bioelectrochemistry

www.elsevier.com/locate/bioelechem

Short communication

Surface modified microelectrodes for selective electroanalysis of metal ions in environmental components

D. Barančok [a], J. Cirák [a,*], P. Tomčík [a], K. Gmucová [b]

[a]Department of Physics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19, Bratislava, Slovak Republic
[b]Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 842 28 Bratislava, Slovak Republic

Received 1 June 2001; received in revised form 11 September 2001; accepted 19 September 2001

Abstract

The surface modification of electrodes was achieved by the Langmuir–Blodgett technique. The monolayers of laponite clay and polythiophene were formed at the air–water interface and these films were then transferred onto carbon microelectrodes. The behaviour of both untreated and coated electrodes was tested by originally developed double-step voltcoulometry (DSVCM). The dependence of charge response on the concentration of Cu^{2+} species was investigated. Straight calibration curves were obtained and enhanced sensitivity of coated electrodes was documented. It is shown that the accumulation of Cu ions into laponite clay was maintained even after transferring the electrode into a pure water. The characteristic features of the "memory effect" are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemically modified electrodes; Langmuir–Blodgett technique; Double-step voltcoulometry

1. Introduction

Modified electrodes have attracted considerable interest over the past two decades in the attempt to exert more direct control over the chemical nature of an electrode [1–4]. They have found numerous important applications in, e.g. solar energy conversion and storage, selective electro-organic synthesis, molecular electronics, electrochromic display devices, corrosion protection. The ability to manipulate the molecular architecture of the bulk matrix of an electrode and its surface in particular has led to a wide range of analytical applications and created powerful opportunities for electroanalysis.

The communication deals with fabrication and investigation of modified electrodes for effective qualitative and quantitative determination of toxic ions in aqueous solutions. Smectite clays and polythiophenes as electrode modifiers were deposited by the Langmuir–Blodgett technique.

2. Experimental

Synthetic laponite used as electrode coating material was of the elemental composition: $[Mg_{5.482}Li_{0.364}\ Ti_{0.07}][Si_{7.953}Al_{0.047}]O_{20}(OH)_4$. Polymer material used in this study was poly(3-pentylmethoxythiophene), P5OMe.

The new kinetics-sensitive double-step voltcoulometry [5] was used in this study. Electrochemical experiments were carried out in a two-electrode cell. The carbon fibre working electrode was composed of two or three fibres (7 μm in diameter) protruding from a wax-filled capillary. The Ag/AgCl electrode was used as a reference. The measurements were performed at room temperature. The deposition of the coating layers was accomplished in the Langmuir–Blodgett trough supplied from NIMA Technology, UK.

3. Results and discussion

The modification of carbon fibre electrodes by LB layers results in a remarkable decrease of the activity of protons in distilled water (originated from H_2CO_3) as documented by the comparison of Figs. 1 and 2. On the other hand, the signal maximum situated at -0.25 V was considerably

---

[*] Corresponding author. Tel.: +421-2-60291459; fax: +421-2-65427427.
E-mail address: cirak@elf.stuba.sk (J. Cirák).

PII: S1567-5394(01)00153-0

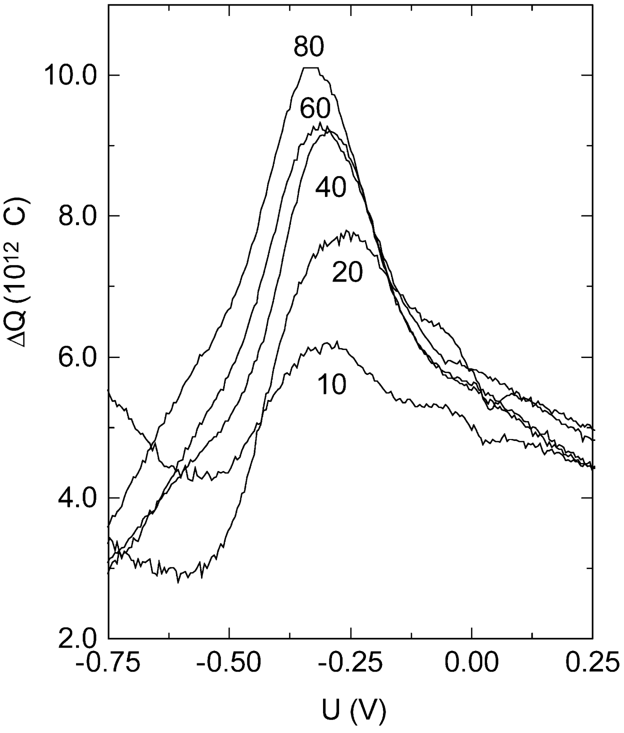

Fig. 1. Double-step voltcoulometric recording of transient charge response as a function of the potential U applied onto the uncoated working electrode with respect to the Ag/AgCl reference electrode. The numbers stand for the concentration of Cu^{2+} ions (10–80 μg/l).

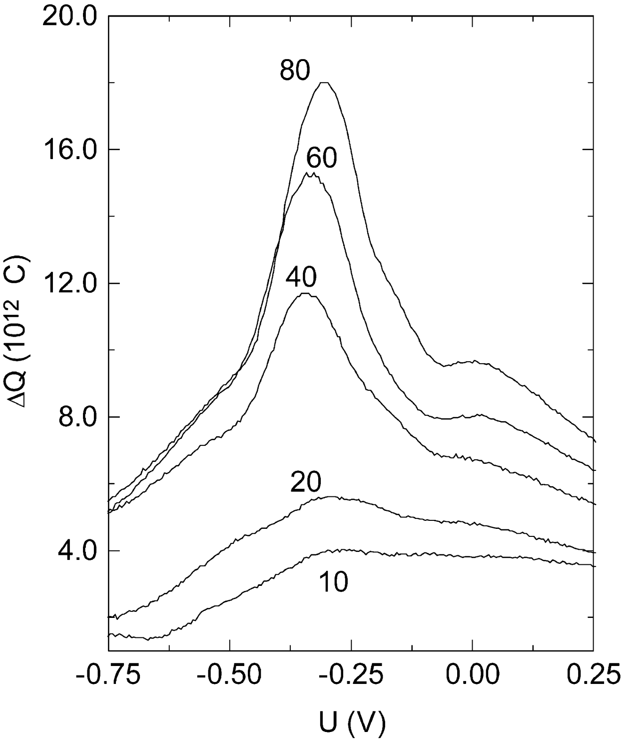

Fig. 2. DSVCM spectra for various Cu^{2+} concentrations using the working electrode coated with 20 LB layers of polythiophene (the numbers correspond to the respective ion concentrations in μg/l).

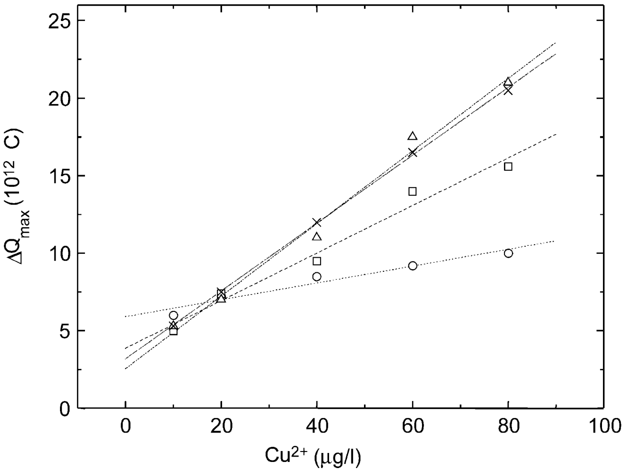

Fig. 3. Effect of the thickness of electrode coating on the calibration curves: ○—bare electrode, □—6 LB layers of polythiophene, △—10 layers, × —20 layers. The straight lines are added as a guide for the eye so as to visualise the effect of added monolayers.

raised by the formation of the electrode coating either with polythiophene or laponite clay. This tendency is presented in Fig. 3 for polythiophene. The presented potential region U is restricted to the interval which is dominated by a presence of Cu ions in the electrode redox reaction. Straight

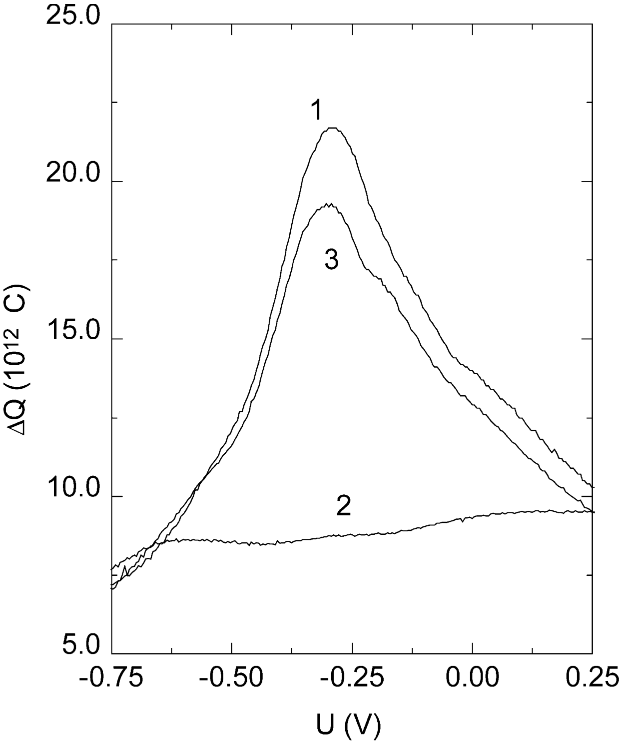

Fig. 4. DSVCM spectra obtained in successive measurements in different media: (1) 80 μg/l solution of Cu^{2+}, (2) deionized water, (3) 80 μg/l solution of Cu^{2+}. The experiment demonstrates no “memory effect” in the case of polythiophene as an electrode-coating material.

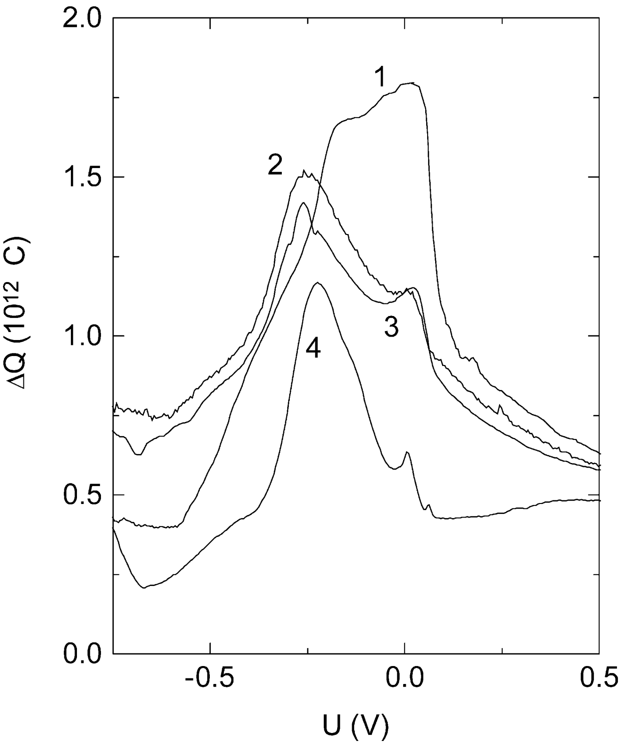

Fig. 5. DSVCM spectra obtained on carbon microelectrodes modified by 20 layers of laponite. (1) 80 μg/l solution of Cu^{2+}, (2) immediately after transferring the working electrode from Cu^{2+} solution into deionized water, (3) 1 h after measurement 2, (4) 12 h after measurement 2. Between the measurements the working electrode was withdrawn from water and kept in atmosphere. The experiment demonstrates existence of "memory effect" with laponite surface modifier.

calibration lines were observed for a concentration range between 10 and 80 μg/l. A detection limit of 5 μg/l was reached.

The interesting "memory effect" [6] was detected using the laponite coverage (Fig. 5) in contrast with results obtained with the polythiophene modifier (Fig. 4). The accumulation of Cu ions into the laponite film was maintained even after withdrawing the electrode from the solution measured. The uptake of the analyte during a prolonged exposure ceases after some time and the ultimate concentration in the thin layer of the clay is still considerably higher than that in the external medium. The "memory effect" suggests the application possibility to remove a clay-coated electrode exposed to the analyte during in situ measurements to a laboratory for detailed analysis using all necessary technique support.

4. Conclusions

Successful modification of carbon fibre ultramicroelectrodes with laponite clay and polythiophene was achieved using the Langmuir–Blodgett technique. The coating of electrodes both by laponit and polythiophene caused the increase in sensitivity by a factor of 2–3. The dependence of charge transient response in DSCVM on the number of deposited layers was studied. The laponite coating exhibits the "memory effect".

References

[1] A. Fitch, Clay-modified electrodes: a review, Clays Clay Miner. 38 (1990) 391–400.

[2] P. Labbé, B. Brahimi, G. Reverdy, Ch. Mousty, R. Blankesppor, A. Gautier, Ch. Degrand, Possible analytical application of laponite clay modified electrodes, J. Electroanal. Chem. 379 (1994) 103–110.

[3] Z. Gao, D. Yap, Y. Zhang, Voltammetric determination of dopamine in a mixture of dopamine and ascorbic acid at a deactivated polythiophene film modified electrode, Anal. Sci. 14 (1998) 1059–1063.

[4] R.W. Murray, in: A.J. Bard (Ed.), Electroanal. Chem., vol. 13, 1984, New York.

[5] I. Thurzo, K. Gmucová, J. Orlický, J. Pavlásek, Introduction to a kinetics-sensitive double-step voltcoulometry, Rev. Sci. Instrum. 70 (1999) 3723–3734.

[6] D. Baranok, J. Cirák, P. Tomík, I. Thurzo, Carbon ultramicroelectrodes modified by LB monolayers, in: H. Mohwald, L. Brehmer (Eds.), Proc. 9th Int. Conf. on Organic Molecular Films (LB9), August 28–September 1, Potsdam (Germany), vol. II, 2000, p. 147.