

References

- [1] Y. D. Kim, S. L. Cooper, M. V. Klein, B. T. Jonker: *Appl. Phys. Lett.* **62** (1993) 2387
- [2] R. Dahmani, L. Salamanca-Riba, N. V. Nguyen, D. Chandler-Horowitz, B. T. Jonker: *J. Appl. Phys.* **76** (1994) 514
- [3] C. C. Kim, S. Sivanathan: *Phys. Rev. B* **53** (1996) 1475
- [4] M. S. Koo, T. J. Kim, M. S. Lee, M. S. Oh, Y. D. Kim, S. D. Yoo, D. E. Aspnes, B. T. Jonker: *Appl. Phys. Lett.* **77** (2000) 3364
- [5] Y. D. Kim, S. G. Choi, M. V. Klein, S. D. Yoo, D. E. Aspnes, S. H. Xin, J. K. Furdyna: *Appl. Phys. Lett.* **70** (1997) 610
- [6] D. Franta, I. Ohlídal, P. Klapetek, A. Montaigne-Ramil, A. Bonanni, D. Stifter, H. Sitter: *J. Appl. Phys.* **92** (2002) 1873
- [7] D. Franta, I. Ohlídal, P. Klapetek, A. Montaigne-Ramil, A. Bonanni, D. Stifter, H. Sitter: submitted for publication
- [8] C. M. Herzinger, B. Johs, W. A. McGahan, J. A. Woollam, W. Paulson: *J. Appl. Phys.* **83** (1998) 3323
- [9] D. Franta, I. Ohlídal: *Acta Phys. Slov.* **50** (2000) 411
- [10] D. Franta, L. Zajčková, I. Ohlídal, J. Janča: *Vacuum* **61** (2001) 279
- [11] D. Franta, L. Zajčková, I. Ohlídal, J. Janča, K. Veltruská: *Diamond Relat. Mater.* **11** (2002) 105
- [12] I. Ohlídal, K. Navrátil, F. Lukeš: *J. Opt. Soc. Amer.* **61** (1971) 1630
- [13] D. E. Aspnes, G. P. Schwartz, G. J. Gualtieri, A. A. Studna, B. Schwartz, *J. Electrochem. Soc.* **128** (1981) 590
- [14] I. Ohlídal, D. Franta: in *Progress in Optics XLI* edited by E. Wolf, North-Holland, Amsterdam (2000), pp 181-282
- [15] Ohlídal I., D. Franta: *Acta Phys. Slov.* **50** (2000) 489
- [16] S. O. Rice: *Commun. Pure. Appl. Math.* **4** (1951) 351
- [17] D. Franta, I. Ohlídal: *J. Mod. Opt.* **45** (1989) 903
- [18] D. Franta, I. Ohlídal: in *Proc. 12th Czech-Slovak-Polish Optical Conference on Wave and Quantum Aspects of Contemporary Optics 2001*, SPIE Vol. 4356, p. 207
- [19] J. B. Theteeen, D. E. Aspnes, R. P. H. Chang: *J. Appl. Phys.* **49** (1978) 6079

SENSITIVITY ENHANCEMENT OF THE CARBON FIBRE MICROELECTRODE
MODIFIED BY LB LAYERS OF POLYTHIOPHENE TO TRACE METALS IN
AQUEOUS SOLUTIONS. *

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The detection of trace metals in aqueous solutions is of great importance in relation to the environmental protection. A significant sensitivity enhancement in the double-step voltacoulometry was reached by using a chemically modified carbon fibre microelectrode. The sensitivity to the method used for cleaning of the microelectrode surface before being coated by the Langmuir-Blodgett polythiophene film was demonstrated. The changes in kinetics of redox reactions, taking place on the microelectrode surface, were described.

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1 Introduction

The voltammetry, as an alternative to the polarography introduced in the year 1922 [1], is a technique widely used for the analytical detection of electrically active species in solutions. In order to improve the sensitivity of voltammetric methods a variety of the chemically and physically modified electrodes was developed in the past 20 years [2–4]. In [5] we have reported the possibility to prepare a polythiophene coated carbon fibre microelectrode with the help of the Langmuir-Blodgett method [6] which enables us to deposit thin films in the layer-by-layer manner [7]. The characteristics of the electrodes modified by polythiophene thin film are detailed, with respect to its sensitivity to trace metals, in the presented study.

2 Experimental

The basic principles of the kinetics-sensitive double-step voltacoulometry (DSVCM), used in the presented experiments, were described in our previous work [8]. The main innovation of this method resides in the new sampling scheme – the transient charge response $Q(t)$ of the electrochemical system to the excitation pulse is measured at three different sampling events ($t_1, 5t_1, 9t_1$) and obtained data are combined according to the formula

$$\Delta Q(E) = Q(t_1) - 2Q(5t_1) + Q(9t_1). \quad (1)$$

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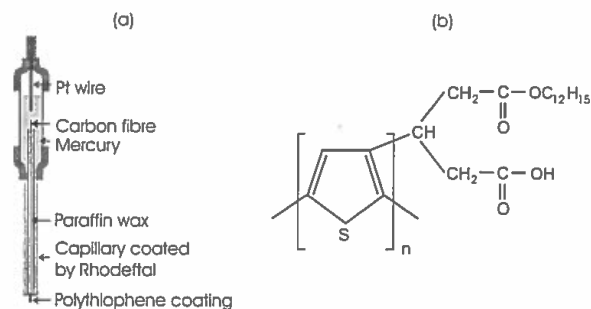


Fig. 1. (a) Construction of the carbon-fibre microelectrode, (b) Structural formula of polythiophene

As was argued in [8], better discrimination in the kinetics of observed redox processes is reached by that means. Furthermore, each measuring period is preceded by the measurement of the steady-state current with the excitation pulse being switched off. In such a manner both the DSVC signal and steady-state voltammetric wave, respectively, are obtained during the same potential scan. Such simultaneous application of two electrochemical methods (one of them sensitive to kinetics) can be useful in the better understanding of the studied redox processes.

In the course of all the measurements the electrochemical cell was kept at room temperature, equipped with a carbon fiber microelectrode as the working electrode and an Ag/AgCl structure as the reference electrode. The working electrode consisted of a silica glass capillary (the inner diameter being approximately 500 μm with up to three carbon fibers (diameter of each fiber being approximately 7 μm). The capillary was filled with paraffin wax to prevent liquid seeping inside around the carbon fibers. To avoid a possible mechanical damage during the low frequency sound treatment it was covered by a thin layer of the polymer Rhodofal 311 (Rhône-Poulenc Chimie Fine, Paris). Contact with a connecting wire was established by means of a Hg-Pt bridge (Fig 1).

Before the coating of the carbon fibre by the LB-layer several kinds of the microelectrode pretreatment were used:

- E The electrochemical pretreatment in the 0.15 M solution of NaCl resided in the following procedure. At first, the cathodic potential of -0.8 V was applied for 40 s (against Pt electrode), followed by a triangular waveform from 0 to +3 V for 10 s and finally an anodic potential of +1.5 V was applied for 10 s.
- S The low-frequency sound pretreatment was exerted by the use of the broad-band loud-speaker, to which the microelectrode was directly mounted. Subsequently the microelectrode was submerged into the 0.15 M solution of NaCl and during 5 min exposed to the low frequency sound of the frequency 100 Hz and of the effect 10 mW [10, 11].
- A The argon pretreatment consisted in the procedure, when the microelectrode was for 20 minutes bubbled (2 l/min) with pure argon in the 0.15 M solution of NaCl (prepared in the

redistilled water) to prevent possible contamination of the electrode surface by adsorbed gaseous species.

The following combinations of microelectrode pretreatment were tested:

- The electrochemical pretreatment (E)
- The low-frequency sound pretreatment followed by the electrochemical pretreatment (S+E)
- The argon pretreatment, followed by the low-frequency sound pretreatment, as well as by the electrochemical pretreatment. Moreover the microelectrode was kept (approximately for an hour) under Ar atmosphere until the coating by the polythiophene LB-layer (A+S+E)

Subsequently the LB layer was formed on the carbon fibre tip. At first, the monolayer of the ion-exchange polymer polythiophene (see Fig. 1b) was formed at the air-water interface. Thereafter it was transferred onto the carbon fibre tip to produce a layer of thickness of several nanometers [7].

Let us proceed to the short description of the mathematical formalism used in our work. To describe the deviations from the ideal Cottrell behaviour the kinetics parameter β , that enters the non-ideal time dependence of the diffusion-limited part of the charge in the form $\Delta q_D \sim t^\beta$ (instead of $\Delta q_D \sim t^{1/2}$), was introduced in [8]. The above mentioned power function can be regarded as a Cottrell term, multiplied by series of polynomial terms. Similar corrections were made to correct the Cottrell equation for the conditions valid on a finite disc electrode e. g. in [9]. If the first sampling event chosen for the measurement of the transient charge response is marked as t_1 , the potential of the working electrode as E , the potential step on the working electrode as ΔE , the standard (formal) potential of the reaction as $E^{O'}$, the diffusion coefficients of the oxidized and reduced species as D_O and D_R , respectively, the concentration of the oxidized species in the solution as c_O^* , the Faraday constant as F , the gas constant as R , the number of electrons entering the reaction as n , the area of the working electrode as S , the temperature of the analyte as T , and the parameter introduced to keep the correct dimensions of the transient charge as t_0 , then after running the single potential scan are by using the DSVC method obtained two data sets, which can be mathematically described by the following formulas

$$\Delta q_D = \frac{2nFS D_O^{1/2} c_O^*}{\pi^{1/2} t_0^\beta} \frac{P_A (1 - \sigma^2)}{(\sigma + P_A)(1 + P_A \sigma)} \left[t_1^\beta - 2(5t_1)^\beta + (9t_1)^\beta \right], \quad (2)$$

where

$$\sigma = \exp\left(\frac{nF \Delta E}{RT} \frac{1}{2}\right), \quad (3)$$

and

$$P_A = \sigma \exp\left[\frac{nF}{RT} \left(E + \frac{\Delta E}{2} - E^{O'}\right)\right], \quad (4)$$

for the correlated differential charge coming from the diffusion current contribution to the measured signal - according [8, 12], and

$$I_{lim} = nF \sqrt{2\pi S D_O c_O^*}, \quad (5)$$

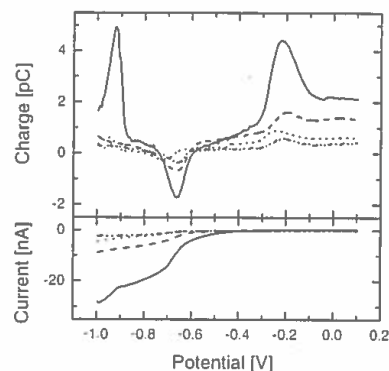


Fig. 2. Double-step voltacoulometry protocol of 2mM HCl p. a. Solid line – coated electrode, A + S + E; dashed line – coated electrode, S + E; dot line – coated, E; dash-dot line – bare electrode, E. Upper part – voltacoulometric signal; lower part – steady-state voltammetric wave.

for the steady-state voltammetric wave.

The experimental results, shown on Fig. 2, were obtained on 2mM aqueous solution of the hydrochloric acid p. a. The measurements correspond to the potential step $\Delta E = -0.085\text{mV}$ and to the sampling time $t_1 = 15.98\text{ms}$.

According to the information given by the producer the content of trace metals (Fe, Pb...) in the prepared analyte was several ng/ml or lower (e. g. for iron less than 7ng/ml). The peak 2 in the measured signal can be ascribed to hydrogen ion. Its typical negative sign is caused by the anomalous superlinear kinetics of protons redox reaction in unsupported acids [14]. The peak 3 was identified as redox reaction of Fe^{3+} . The activation (formal) potential was the same, as was measured on the iron standard. The peak 1 could be, according to the producer's information, ascribed to Pb^{2+} redox reaction, but its position on the potential axis does not accurately match the position of the peak measured on the lead standard. The inaccuracy in the respective activation potential may be caused by the fact, that we did not use the saturated reference electrode. Nevertheless, on the basis of the experiment made on cadmium standard, we cannot exclude the possibility, that we are dealing with the redox reaction of Cd^{2+} .

The parameter β was evaluated with the help of Eqn. (2) by the procedure detailed in [13] (for $t_1 = 15.98\text{ms}$ and $t_1 = 11.52\text{ms}$). In [14] we have introduced the ratio $R_\beta = \Delta Q_{\text{max}}/I_{\text{lim}}t_1$ (ΔQ_{max} stands for the maximum of the peak height), as an effective tool for estimating the deviations of parameter β from the ideal value. Both the above mentioned parameters, obtained from measured data for all the three observed redox processes, are summarized in Tab. 1. The

blank cell indicates, that the relevant parameter should not be obtained from the measured data either due to the experimental inaccuracy, or due to some changes in the kinetics during the experiment.

Tab. 1. Kinetics parameters of redox reactions taking place in 2 mM aqueous solution of HCl p. a.

	Peak 1		Peak 2		Peak 3	
	R_β	β	R_β	β	R_β	β
Bare, E	–	–	-0.012	~1.00	>0.12	0.30
Coated, E	0.010	–	-0.013	1.01	>0.25	0.33
Coated, E+S	–	–	-0.011	1.08	>0.30	–
Coated, E+S+A	0.027	–	-0.008	2.52	>1.75	–

As is apparent from Tab. 1, the highest enhancement in the sensitivity of the DSVCM method, compared to the steady-state voltammetry, is reached for the Fe^{3+} redox reaction on the microelectrode coated by polythiophene LB-layer after the E+S+A pretreatment ($R_\beta > 1.75$). The parameter β was different from the ideal Cottrell value for all the observed redox reactions.

3 Conclusions

It was found, that the electrochemical pretreatment of the carbon fibre microelectrode in the Ar-bubbled 0.15 M solution of NaCl, combined with the cleaning of the microelectrode by the low-frequency sound before being coated by the LB layer, can significantly improve their properties with respect to the ability to detect trace metals. Nevertheless, the most questionable point of our work consists in the low reproducibility of the measurements, which are of the best kinetics parameters with respect to the highest reached sensitivity. The probable origin of the above mentioned problem can be ascribed to the fouling of the microelectrode by some adsorbed species resulting in a change of the properties of the electrical double-layer formed on the interface electrode surface/liquid analyte. As already confirmed in [10, 11], this problem could be solved by using the low-frequency sound during the entire experiment. Unfortunately, the elasticity of the prepared microelectrode causes an expressive increasing of the measured noise level when the sound of the effect of several mW was used during the experiment performed in Faraday cage. Apart from the above mentioned fact the modification of the carbon fibre microelectrode by the polythiophene LB layer seems to have a potential to be a powerful tool in the enhancement of sensitivity to trace metals.

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References

- [1] J. Heyrovský: *Chem. Listy* **16** (1922) 256
- [2] D. Petridis: in *Multifunctional Mesoporous Inorganic Solids*, (Eds. C.A.C Sequeira and M. J. Hudson) Kluwer Academic Publisher, Netherlands, 1984, 433
- [3] J. L. Anderson, L. A. Coury Jr., J. Leddy: *Anal. Chem.* **70** (1988) 519
- [4] E. Barendrecht: *J. Appl. Electrochem.* **205** (1990) 173
- [5] D. Barančok, J. Cirák, P. Tomčík, K. Gmucová: *Bioelectrochemistry* **55** (2002) 153
- [6] K. B. Blodgett: *J. Am. Chem. Soc.* **57** (1935) 1007
- [7] J. Cirák, D. Barančok: *acta phys. slov.* **45** (1995) 479
- [8] I. Thurzo, K. Gmucová, J. Orlický, and J. Pavlásek: *Rev. Scient. Instr.* **70** (1999) 3723
- [9] K. Aoki: *J. Electroanal. Chem.* **122** (1981) 19
- [10] Ø. Mikkelsen, K. H. Schrøder: *Electroanalysis* **11** (1999) 401
- [11] Ø. Mikkelsen, K. H. Schrøder: *Analytical Letters* **33** (2000) 1309
- [12] A. J. Bard, L. R. Faulkner: *Electrochemical Methods – Fundamentals and Applications*, Wiley, New York 1980
- [13] K. Gmucová, I. Thurzo, J. Orlický and J. Pavlásek: *Electroanalysis* **14** (2002) 943
- [14] I. Thurzo, K. Gmucová, J. Orlický, and J. Pavlásek: *J. Electroanal. Chem.* **513** (2001) 26

EXTRACTION OF OPTICAL PARAMETERS OF THIN FILMS FROM SPECTRAL MEASUREMENTS FOR DESIGN AND OPTICAL PERFORMANCE OF MULTILAYER STRUCTURES *

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Optical parameters of a-Si:H and indium tin oxide (ITO) thin films deposited on glass substrates are determined from spectral measurements of reflectance and/or transmittance. It is shown how important the exact knowledge of optical parameters as well as thicknesses of the layers for the design and the optical performance of multilayer structures is. The model of the p-i-n-based a-Si:H solar cell with ITO as transparent conductive oxide layer is used for illustrating. The modelling of the solar cell integral reflectance in the spectral region of (650–830) nm is used as a criterion to reverse engineering of a multilayer structure with suppressed reflectance losses. The reflectance of a solar cell is modelled and the simulation of the varying optical parameters of individual layers including their thicknesses is discussed. Besides this, the advantage of using an antireflective layer under ITO is discussed.

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1 Introduction

As optical properties of thin films differ markedly from those of the same bulk material and even are deposition-process-dependent, the knowledge of optical parameters of any individual thin film is central task for the design and performance of multilayer structures with thin films. Optical properties of hydrogenated amorphous silicon (a-Si:H) and indium tin oxide (ITO) that both often act in Schottky-type sensors (e.g. alignment and position sensors) and solar cells were determined from reflectance and/or transmittance spectra. Reflectance of a similar-to-real solar cell structure is modelled and discussed when varying optical parameters and antireflective coatings are used for the simulation. As light energy reflected from the entire structure is lost, from the optical point of view a solar cell should operate as a broad band-pass filter with suppressed reflectance losses.

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