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Vacek, J.
2014

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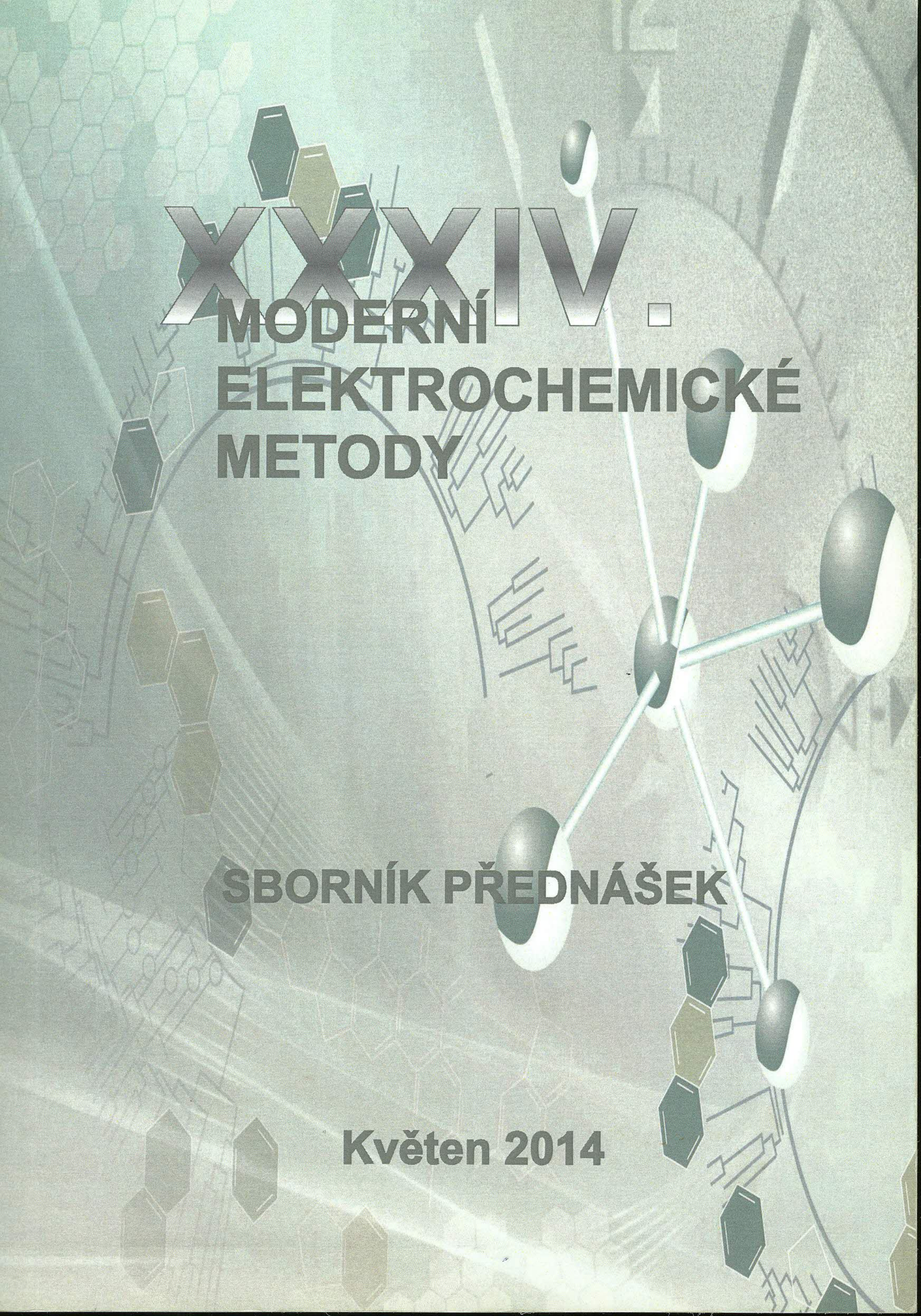

XXXIV. MODERNÍ ELEKTROCHEMICKÉ METODY

SBORNÍK PŘEDNÁŠEK

Květen 2014

Best servis Ústí nad Labem

Ústav fyzikální chemie J. Heyrovského AV ČR, v. v. i., Praha

Biofyzikální ústav AV ČR, v. v. i., Brno

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mezinárodní odborné konference

XXXIV.
Moderní Elektrochemické Metody

Jetřichovice 19. – 23. května 2014

Uspořádali:

Navrátil Tomáš, Fojta Miroslav a Karolina Pecková

ISBN 978-80-905221-2-1

Application of Cyclopentenediones for Preparation of Permselective Layers (Využití cyklopentendionů pro přípravu permselektivních vrstev)

Jan Vacek [a], Jan Hrbac [b], Pavel Matejka [c], and Jan Storch [d]
[a] Department of Medical Chemistry and Biochemistry, Faculty of Medicine and Dentistry, Palacky University, Hnevotinska 3, 775 15 Olomouc, Czech Republic,
[b] Department of Physical Chemistry, Palacky University, tr. Svobody 26, 771 46 Olomouc, Czech Republic
[c] Department of Physical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
[d] Institute of Chemical Process Fundamentals of the AS CR, v.v.i., Praha 6,165 02, Czech Republic, E-mail: jan.vacek@upol.cz

Abstract

In this contribution, we report that electrooxidation of PCD, phenolic cyclopentenedione, 2,2′-bis[4,5-bis(4-hydroxybenzyl)-2-(4-hydroxyphenyl)-cyclopent-4-ene-1,3-dione] results in the formation of stable films with permselective properties on metal and carbon surfaces. The electropolymerization process proceeds in neutral and alkaline aqueous medium at potentials higher than +0.6 V (vs. Ag/AgCl/3M KCl). The PCD polymer prepared was characterized by electrochemical methods, quartz crystal microbalance and optical spectroscopy techniques. The PCD film can be used for electrode coating and preparation of an anti-interference barrier. Thus, we performed SAR study which could open the door to developing novel functional films and electrochemical tools for bioactive compounds sensing.

Key words: Cyclopent-4-ene-1,3-dione, Structure-activity Relationship, Bioactives sensing.

Introduction

Functional barriers and development of permselective layers (films) are important goals for many applications in chemistry today, e.g. analytical chemistry, energy conversion, biochemistry and industrial chemistry in general. Compact permselective layers, directly fabricated onto the electrode surface are used to suppress the access of the interfering species. The selectivity is mainly provided on the basis of molecular weight, charge and hydrophobicity or hydrophilicity differences among the analyte and several interfering molecules which pass or do not pass through the layer. To prepare anti-interference barriers two experimental approaches can be used, the first one being "solvent casting" and the second approach is electrosynthesis.

In the view of analytical chemistry, electrodes equipped with permselective films are used for the electrochemical analysis of biologically active compounds. The elimination of interferences during the determination of basal metabolites and selected bioactives is one of the most noteworthy applications of permselective layers. Owing to the broad spectrum of applications of these compact layers, new compounds for their preparation are being designed.

Here, we focus on preparation of novel phenolic cyclopentenedione (PCD) based polymeric permselective layer using carbon, gold and platinum as solid supports. This study was aimed at **(a)** developing a procedure for the preparation of PCD layer by electropolymerization, **(b)** characterization of PCD layer prepared, **(c)** evaluating of the stability and applying of PCD permselective layer for bioactives (e.g. dopamine) amperometric sensing, and **(d)** performing the SAR study for finding of CPD compounds useful for electropolymerization process and novel functional films preparation.

Experimental

The PCD used in this study (2,2′-bis[4,5-bis(4-hydroxybenzyl)-2-(4-hydroxyphenyl)-cyclopent-4-ene-1,3-dione]), also known as nostotrebin 6 (Fig. 1A), was isolated and purified according to previously published protocol [1].

Ascorbic acid (AA) and paracetamol (PA) were purchased from Sigma Aldrich (USA). Sodium nitrite was obtained from Lachema (Czech Republic). Dopamine (DA) and uric acid (UA) were purchased from Fluka (Germany). PBS solution (0.05 M NaCl and 0.05 M Na_2HPO_4 and NaH_2PO_4) at pH 7.4 was used as supporting electrolyte.

Voltammetric analysis was performed using the CH-Instruments Model 660C electrochemical workstation in three-electrode configuration. Ag/AgCl/3M KCl was used as a reference electrode, and Pt-wire served as an auxiliary electrode. The range of working electrodes used in this study included CHI101 gold, CHI102 platinum and CHI104 glassy carbon electrode. A custom-made carbon fiber microelectrode (CFE) was prepared as described in ref. [2].

EQCM measurements were performed on CH-Instruments 440C apparatus using gold coated quartz crystals. The signal is expressed as $\Delta f = f - f(\mathrm{ref})$, i.e. frequency change relative to reference crystal.

Fourier transform Raman spectra were acquired using Equinox 55/S (Bruker, Germany) spectrometer equipped with FRA 106/S Raman module (Bruker). Samples were irradiated by the Nd-YAG laser beam (1064 nm, 50 mW, Coherent, USA). The spectra were collected and processed using the OPUS 4.0 (Bruker) software. The electrodeposition was performed on electrochemically gold coated platinum electrodes (7 mm side, 0.3 mm thickness of Pt, thickness of Au layer ca. 2 μm).

Fourier transform infrared (FTIR) spectra were collected using Nicolet 6700 (Thermo Scientific) spectrometer equipped with single-bounce attenuated total reflection (ATR) accessory MIRacle based on ZnSe crystal. The spectra were processed using the Omnic 8.2 (Thermo Scientific) software. The electrodeposition was performed on gold foils (thickness 0.1 mm).

Relative standard deviation (RSD) for the preparation of PCD permselective layer was evaluated with six PCD-modifications of one gold electrode prepared independently and tested to 50 μM DA in the presence of 10 mM AA. For intra-day reproducibility measurement, DA was analyzed after 1 h periods in a mixture of various concentrations of AA (1–10 mM). In case of inter-day reproducibility, DA was measured in the presence of AA for 14 consecutive days.

Results and Discussion

Cyclic voltammograms of PCD (for chemical structure see Fig. 1A), obtained on glassy carbon electrode (GCE) in PBS at $v = 100\ \mathrm{mV\ s^{-1}}$, are characterized by a broad peak around + 0.6 V (Fig. 1B, line 1). The complex irreversible anodic reaction probably proceeds via hydroxyl groups and this is in agreement with previously published results on structurally similar substances [3]. In the second and subsequent scans, the current of the oxidation peak sharply decreased, indicating the polymerization process and the film formation (Fig. 1B).

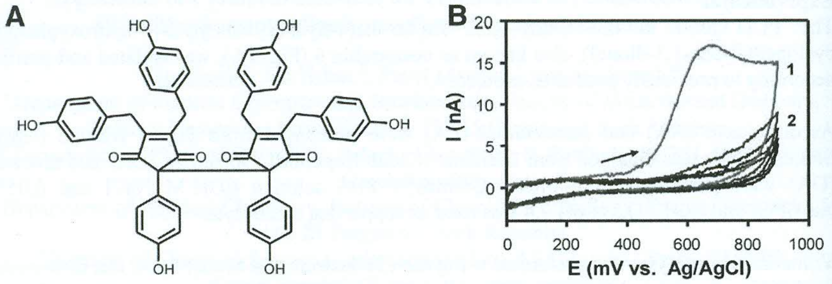

Fig. 1. Structure of the PCD unit used in the study, formerly called nostotrebin 6 **(A)**. Cyclic voltammograms of 0.1 mM PCD in PBS at glassy carbon electrode **(B)**.

In addition to GCE, similar behavior was observed for gold and also platinum electrodes. For all experiments in the study, PCD film was prepared onto electrode surfaces after bare-electrode immersion into PBS containing 0.1 mM PCD and potential cycling from 0 to + 0.9 V at v = 1000 mV s^{-1} for 60 s. Then the electrode was washed by distilled water and used for other experiments. The 0.1 mM PCD was used corresponding to fully saturated solution under the conditions used. At higher concentrations, limited solubility of the PCD monomer was observed. The formation of PCD layer can be found only in aqueous environment.

The formation of PCD layer was studied by electrochemical quartz crystal microbalance (EQCM), Fourier transform Raman spectroscopy and reflection infrared (FTIR) spectroscopy. The EQCM experiment was based on the frequency decrease occurring when the mass of the oscillating gold coated quartz crystal is increased. The observed decrease in frequency of the quartz crystal in PBS electrolyte containing PCD, at potentials higher than +0.6 V, confirmed the formation of the film. Similar polymerization phenomena occurring for (poly)hydroxylated compounds has been confirmed by several authors, ref. [3].

Raman spectra of solid monomeric form of PCD and also PCD layer after electropolymerization on gold surface were compared to corresponding FTIR data. The spectral data indicate that for the polymeric form of PCD: **(i)** the enhancement of characteristic bands of CH_2 groups is evident, **(ii)** aromatic ring vibrations exhibit only negligible shifts and **(iii)** cyclopentenedione ring modes are changed markedly.

The spectral changes in cyclopentenedione skeleton observed after electropolymerization indicate initial adsorption onto gold electrode surface via the electron-rich carbonyl groups. Subsequently, anodic reaction of the most sterically accessible phenolic moieties gives rise to oxidative coupling (C–C) and hence polymer formation. The formation of *p*-substituted oxo groups instead of a certain fraction of hydroxyl groups, additional hydroxylation processes and C-O oxidative coupling cannot be fully neglected. The structure will be further elucidated also with respect to the participation of cyclopentenedione rings in the polymerization process probably occurring at higher potentials of oxidation, which is manifested as CH_2 bands enhancement in Raman and FTIR spectra after PCD polymerization [4].

During the investigation of PCD electrochemical behavior and characterization of PCD polymeric film by the above approaches, we also focused on the functionality evaluation of the PCD film. It was found that the PCD polymeric layer formed onto carbon surface gives unique permselectivity for dopamine (DA). Given that DA is a target molecule in neuroscience, the PCD layer was prepared onto cylindrical carbon fiber microelectrodes (CFEs) which were prepared and pretreated according published protocol [2]. In contrast to cationic DA, the PCD layer deposited on the CFE prevents oxidation of anionic and neutral interfering species and such as ascorbate (AA), uric acid (UA), paracetamol (PA) and nitrite. DA can therefore be determined amperometrically in significant excess of easily oxidizable species.

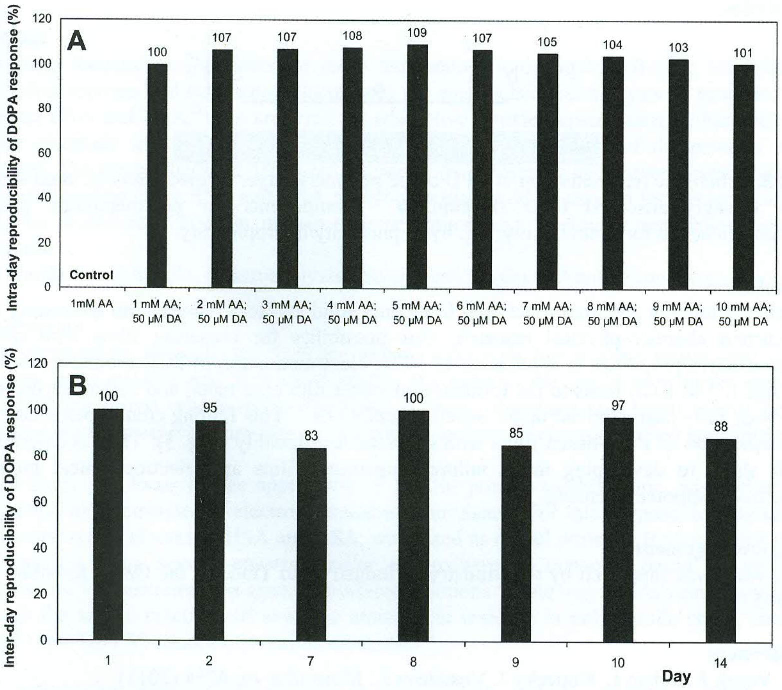

Fig. 2. **(A)** Intra- and **(B)** inter-day reproducibility measurement for 50 µM dopamine (DOPA) in presence AA (10 mM if not stated otherwise) by using DPV at PCD-modified gold electrode (*n*=3 for each measurement; average values are presented).

For amperometry at CFE, PBS (pH 7.4) was used as supporting electrolyte and a constant potential of + 0.4 V was applied. The detection limit was estimated to be 50 nM for S/N = 3 and the current response of DA was linear ($R^2 = 0.999$, $Y = 0.63X - 0.13$ (nA dm^3/µmol)) from 50 nM to 30 µM. The permselective properties of PCD layer were also studied on gold electrode by differential pulse voltammetry (DPV). The dependence of peak height vs. concentration of DA was linear in the concentration range from 50 nM to 5 µM ($R^2 = 0.993$, $Y = 6.4 \times 10^{-3}X + 1.5 \times 10^{-2}$ (A dm^3/mol)).

The permselectivity is most probably driven by a charge exclusion mechanism for DA because the addition of high concentration of NaCl leads to lack of selectivity for DA in the presence of AA excess. This effect is highly probably connected to elimination (unmasking) of charge exclusion properties of formed PCD film (deposit). The key contribution of the other exclusion mechanism is improbable because of quite similar molecular weight and the hydrophilic nature of tested analytes.

Finally, the stability of PCD film was tested as a function of permselectivity for DA in the presence of interfering AA using gold electrode and DPV. RSD for the preparation of PCD permselective layer was ± 1.3% ($n = 6$). Intra-day reproducibility was 105% with RSD ± 2.9%. For inter-day measurements, a reproducibility of 93% with RSD ± 6.5% was found (Fig. 2). A very similar stability and reproducibility can also be found for carbon electrodes.

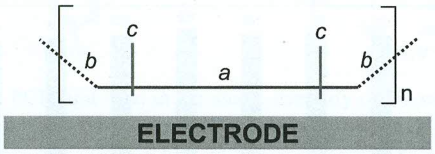

Fig. 3. Schematic representation of CPD based polymeric layer formed onto electrode surface. ***a*** – strongly adsorbed CPD skeleton, ***b*** – components for polymerization process, ***c*** – modifications for functionality, e.g. hydrophobicity/hydrophilicity.

Conclusion

Electrochemically prepared functional films onto solid surfaces represent an interesting topic in current chemico-physical research. One possibility for preparing films with specific permselective properties is application of PCD. Electrooxidation of PCD around + 0.6 V (vs. Ag/AgCl, 3 M KCl) leads to the formation of stable film onto metal and carbon surfaces that has been fully characterized under aqueous conditions [4]. This finding could open a new area in preparation of PCD-based films with different functionality (Fig. 3). Thus, we performed SAR study to developing novel tailored functional films and electrochemical tools for bioactive compounds sensing.

Acknowledgements

This work was supported by the Ministry of Industry and Trade of the Czech Republic (FR-TI4/457).

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