APPLICATION OF PRUSSIAN BLUE IN THE DEVELOPMENT OF ENZYMATIC BIOSENSORS

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Prussian blue (PB) is an inorganic pigment widely applied in formation of sensors and biosensors. The application of PB in biosensors is based on PB's sensitivity to various parameters of the medium, which are changing during enzymatic reactions, e.g. change in H_2O_2 concentration [1, 2, 3], change in NH_4^+ ion concentration [4] or pH [3, 5]. The sensitivity of PB to hydrogen peroxide is based on chemical reaction between reduced form of PB, which is called Prussian white (PW), and H_2O_2 (1):

$$K_2Fe^{II}[Fe^{II}(CN)_6]\,(PW) + K^+ + H_2O_2 \rightarrow KFe^{III}[Fe^{II}(CN)_6]\,(PB) + H_2O \qquad (1)$$

Hydrogen peroxide-caused oxidation of PW can be monitored optically, since PW changes its color from transparent to deep blue when it is oxidized by H_2O_2 [1, 3]. Therefore, optical biosensors which involves PW sensitivity to glucose have been successfully used to detect glucose. Moreover, when potential value around 0 V vs Ag|AgCl|$KCl_{(sat.)}$ is applied to PB layer, PB exhibits electrocatalytic activity in reduction of hydrogen peroxide [2]. Special attention should be paid to very low potential (0 V vs Ag|AgCl|$KCl_{(sat.)}$) at which PB acts as a catalyst in H_2O_2 reduction – at low values of potential interferences of the most electrochemical active species presented in clinical sample is avoided [6], therefore, the usage of PB allows to create electrochemical glucose biosensors which exhibit high reliability.

The sensitivity of PB to NH_4^+, K^+, Cs^+ and Rb^+ ions is based on unique role of this ions in reduction of PB. When PB is being reduced to PW, these ions (NH_4^+, K^+, Cs^+ and Rb^+) are intercalating into the crystal lattice of PB to maintain charge neutrality of newly-formed PW [4]. Moreover, concentration of NH_4^+, K^+, Cs^+ and Rb^+ affects reduction potential of PB, thus, PB can be used as signal transducer for electrochemical or electrochromic biosensors which involve urease [4].

PB exhibits two types of sensitivity to pH: (i) when PB is formed in so-called "insoluble" form, Prussian blue undergoes reversible hydrolysis in alkaline conditions [2], therefore, PB can be used to monitor changes in pH which occurs during enzymatic reactions; (ii) PB also exhibits dependency of charge transfer resistance on pH – when PB is being reduced to PW or PW is being oxidized to PB, hydrogen ions are considered to participate in electron-hopping conduction mechanism through the PB layer [5], therefore, pH of solution affects intensity of charge transport through the layer of PB.

The aim of this work is to analyze the performance of PB as a signal transducer in enzymatic biosensors, to highlight the common problems which occurs during PB-based sensing and to discuss possible ways to improve reliability and overall performance of PB-based biosensors. The applicability of structural analogues of PB (PBsa) in biosensors and comparison between analytical performance of PB and PBsa are also discussed in this work.

References

1. P. Virbickas, et al. J. Electrochem. Soc. **166** (2019) B927-B932.
2. A.A. Karyakin. Electroanal. **13** (2001) 813-819.
3. R. Koncki et al. Analyst **126** (2001) 1080-1085.
4. A. Valiūnienė et al. Electroanal. **32** (2020) 503-509.
5. J.J. Garcia-Jareno et al. Electrochim. Acta **44** (1998) 395-405.
6. A. Valiūnienė et al. J. Electrochem. Soc. **164** (2017) B781-B784.