

Prussian Blue and its Analogues for Design of Chemical and Biological Sensors

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We propose a review of the electrochemistry of Prussian Blue and its analogues with the special attention to transition metal hexacyanoferrates with potential analytical applications.

Prussian Blue and its analogues are considered as advanced sensing materials for **non-electroactive ions**. Electroactivity of Prussian Blue (fig. 1) includes two redox reactions, the cathodic one involves an entrapment of cations for charge compensation upon electron transfer: $Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ \longleftrightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3$. In contrast to common 'smart materials', the sensitivity and selectivity of metal hexacyanoferrates to monovalent ions, which promote the electroactivity (K^+, NH_4^+, Cs^+, Tl^+) is provided by thermodynamic background. The possibility of the development of the selective sensors for anions using Fe, Co, and Ni-hexacyanoferrates is discussed.

A particular case is the development of chemical sensors for **hydrogen peroxide**, a chemical threat agent, which presents in rain and ground waters as waste product of industry and atomic stations. In addition, H_2O_2 is used for disinfection of water pools, food and beverage packages, which makes it important to measure its residual concentration. At the other hand, hydrogen peroxide is a side product of oxidases, the enzymes, which are included as terminal ones in more than 90% of the existing enzyme-based biosensors and analytical kits. The low-potential detection of H_2O_2 was found to be the most progressive procedure for operation of the biosensors.

Transition metal hexacyanoferrates as electrocatalysts for H_2O_2 reduction/oxidation are compared and Prussian Blue was found to be the best one. Optimizing the deposition procedure for Prussian Blue, the selective electrocatalyst for H_2O_2 reduction in the presence of oxygen able to operate in a wide potential range has been synthesized. In optimal potential range for sensor and biosensor applications the current of H_2O_2 reduction was *several hundred times higher* than of O_2 reduction.

In neutral aqueous media optimal for analytical applications the *activity* of the Prussian Blue based electrocatalyst for hydrogen peroxide reduction was found to be very high and was characterized by the electrochemical rate constant exceeded 0.01 cm s^{-1} . For comparison, in similar conditions the *activity* of platinum electrodes ($k \gg 10^{-5} \text{ cm s}^{-1}$) is *thousand times lower*.

The *stability* of the modified electrode is a crucial point for its applications. Improving of the crystalline structure of the deposited Prussian Blue and due to its additional post-treatment, excellent operational stability has been achieved (100% within 8 hours under continuous flow of $0.1 \text{ mM } H_2O_2$).

A linear dependence of the peak current on H_2O_2 concentration in flow-injection mode was obtained in a wide range ($0.1 \text{ } \mu\text{M} \rightarrow 0.1 \text{ mM}$) (fig. 2). The sensitivity determined was $0.6 \text{ A M}^{-1} \text{ cm}^{-2}$.

Immobilizing different enzymes oxidases on the top of Prussian Blue modified electrodes, biosensors to glucose, alcohols, amino acids, oxalate have been developed. Prussian Blue based biosensors exhibited the improved analytical characteristics. For example, glutamate biosensor (fig. 3) showed 10 times lower detection limit (10^{-7} M) and at least 10 fold improved sensitivity ($0.2 \text{ A M}^{-1} \text{ cm}^{-2}$) compared to the reported devices.

In conclusion, we note, that Prussian Blue is the best transducer hydrogen peroxide, and in combination with the advanced immobilization approaches, it provides elaboration of the most advantageous biosensors. Prussian Blue modified electrodes are ready-to-use in analytical devices for either sampling or continuous monitoring of chemical threat agents, important food additives and key metabolites of life pathways. The particular importance of application of Prussian Blue based biosensors is expected in certain areas of clinical diagnostics, where high sensitivity and selectivity as well as the possibility for miniaturization are required, e.g. brain research and non-invasive monitoring of blood chemistry.

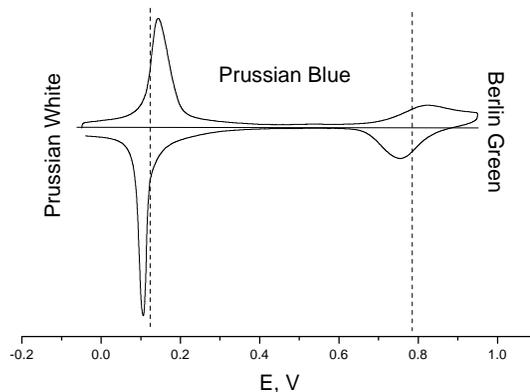


Fig. 1. Typical cyclic voltammogram of Prussian Blue modified electrode; 0.1 M KCl , 40 mV s^{-1} .

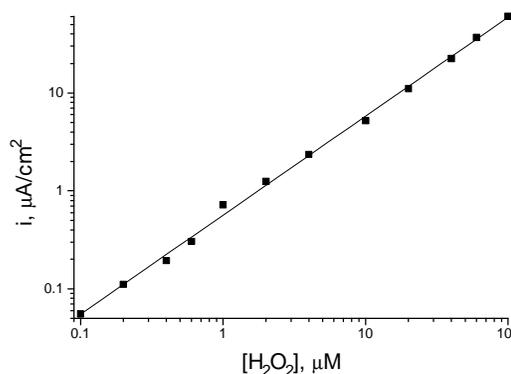


Fig. 2. Hydrogen peroxide sensor in FIA; 0.8 ml/min , 0.0 V (Ag|AgCl) , 0.05 M phosphate , $\text{pH } 6.0 + 0.1 \text{ M KCl}$.

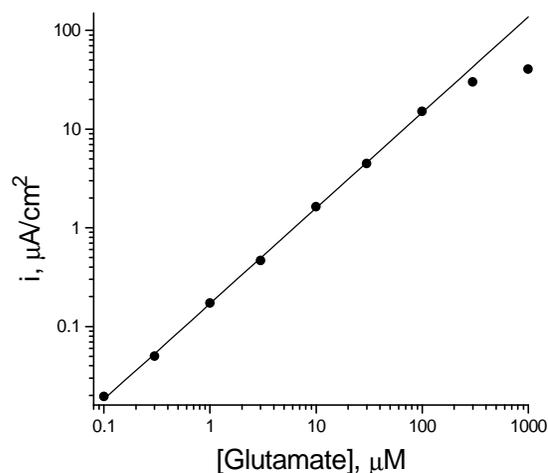


Fig.3. Glutamate biosensor in FIA ; 0.5 ml/min , 0.0 V (Ag|AgCl) , 0.05 M phosphate , $\text{pH } 6.0 + 0.1 \text{ M KCl}$.