EXPERIMENTAL

Materials

Experiments were carried out with Millipore Milli-Q water. All inorganic salts ($FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $K_3[Fe(CN)_6]$) and hydrogen peroxide (30 vol %) were obtained at the highest purity from Reachim (Russia) and used as received.

Glassy carbon disk electrodes (SU-2500, 2.0 mm in diameter) pressed in Teflon were used as working electrodes. Prior to use, the working electrodes were mechanically polished in a water suspension of alumina powder with particle size of 0.3 µm and then 0.05 µm (Sigma Aldrich) up to the mirror finish observed.

Instrumentation

Electrochemical experiments were made in a three-compartment electrochemical cell with Ag|AgCl|1 M KCl reference electrode. PalmSens potentiostat/galvanostat (PalmSens Instruments BV, Netherlands) interfaced to PC was used.

The flow injection (FIA) system consisted of a Cole Parmer (Vernon Hills, IL) peristaltic pump (7519-10), homemade flow-through wall-jet cell with 0.6 mm nozzle positioned at 1-2 mm distance from the surface of disk electrode, (Ag|AgCl|1 M KCl) reference, homemade injector, and PalmSens electrochemical interface interfaced to an IBM PC. Flow rates used were in the range 0.2÷4 $mL \cdot min^{-1}$. In FIA experiments, the peak current density values were taken for data treatment, sample volume was 50 µL, and working electrode potential was 0.00-0.05 V, allowing hydrogen peroxide reduction on Prussian Blue-modified electrodes. The carrier solution in FIA experiments was 0.05 M phosphate buffer pH 6.0 containing 0.1 M KCl as the supporting electrolyte.

Concentration of hydrogen peroxide in stock solutions was controlled by optical density at 230 nm with an LKB-Ultraspec UII spectrophotometer (Broma, Sweden).

Methods

Electrodeposition of Prussian Blue was carried out in cyclic voltammetric conditions in the range from 0.4 V to 0.75 V at a sweep rate of 0.04 $V \cdot s^{-1}$ during 1÷8 cycles. The growing solution contained 2 mM $K_3[Fe(CN)_6]$ and 2 mM $FeCl_3$. A solution of 0.1 M HCl and 0.1 M KCl was used as a supporting electrolyte.

For deposition of nickel hexacyanoferrate (NiHCF) the solution containing 0.5 mM $K_3[Fe(CN)_6]$, 1 mM $NiCl_2 \cdot 6H_2O$ and 0.5 M KCl in 0.1 M HCl was used. The deposition was carried out by cycling the applied potential from 0.0 V to 0.75 V at a sweep rate of 0.1 $V \cdot s^{-1}$ during 5 ÷ 25 cycles.

Layer-by-layer deposition of Prussian Blue – Ni hexacyanoferrate composites was made in different three-compartment electrochemical cells: one was with the solution of precursors for PB electrosynthesis, another contained mixture for NiHCF electrodeposition. After the deposition of one layer, electrode was intensively rinsed with Milli-Q water and moved to another cell.

After deposition transition metals hexacyanoferrate films were electrochemically activated by cycling in the background electrolyte at a sweep rate of 40 $mV \cdot s^{-1}$ until a stable voltammogram was obtained and then annealed at 100°C during 1 h to remove weakly bounded water.

Stability measurements were carried out in a flow-through wall-jet cell under continuous flow of 1 mM H_2O_2; 0.05 M phosphate buffer pH 6.0 with 0.1 M KCl was used as supporting electrolyte.

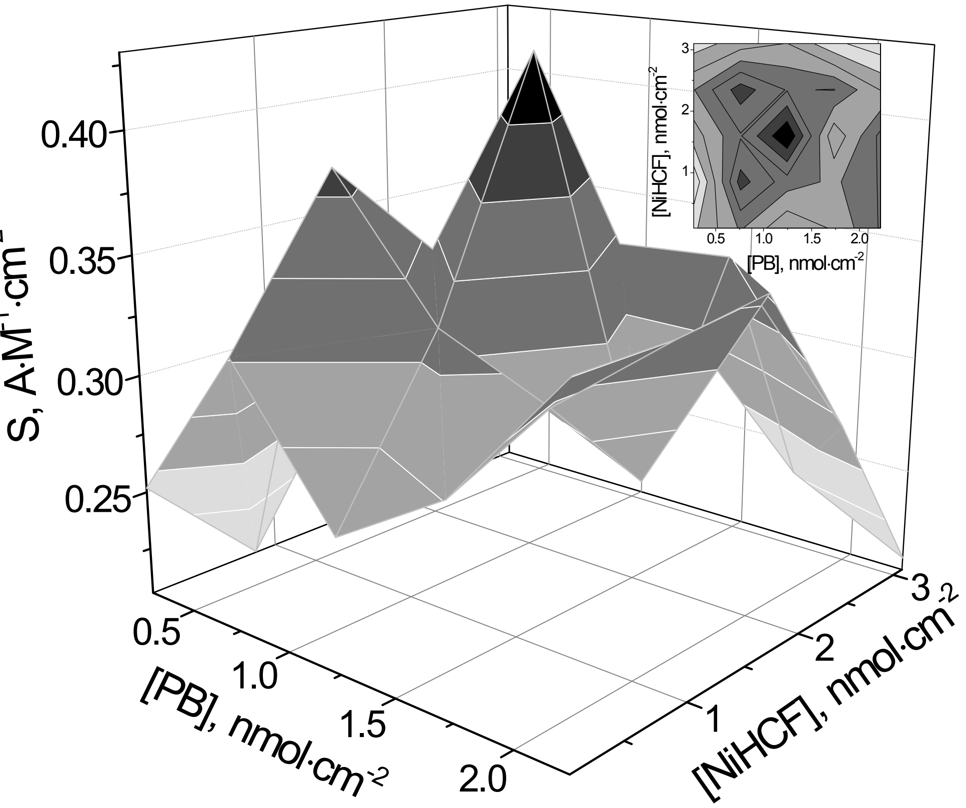

Figure 1S. Sensitivity as current response towards continuous flow of 1 mM H_2O_2 divided by its concentration (1 mM) as a function of surface coverages of iron and nickel hexacyanoferrates.

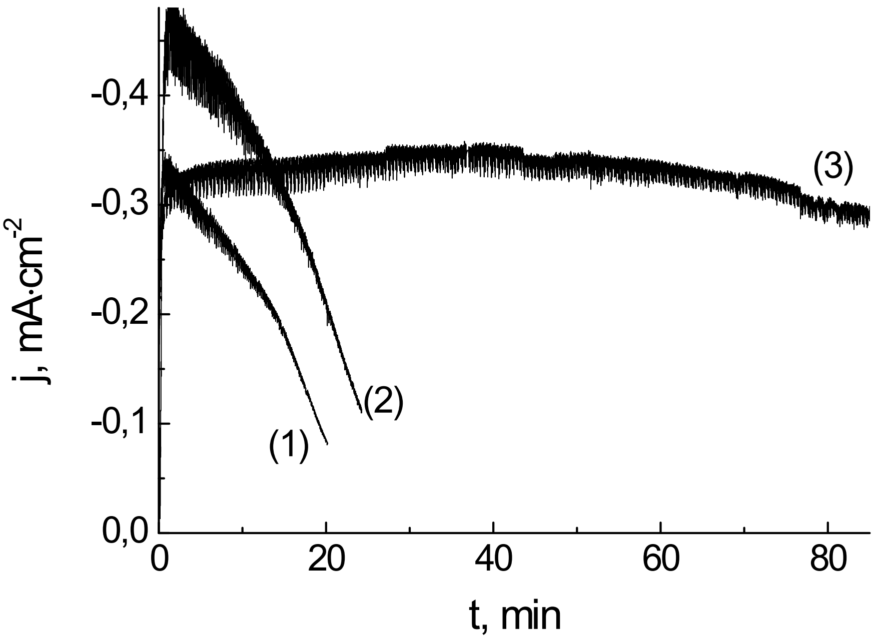

Figure 2S. Operational stability in wall-jet cell under continuous flow of 1 mM H_2O_2 of conventional Prussian Blue (1, 2): (1) – Γ_{PB} = 0.85 nmol cm^{-2}, (2) – Γ_{PB} = 1.3 nmol cm^{-2} - and hybrid Fe-Ni hexacyanoferrate (3); 0.05 M phosphate buffer pH 6.0 with 0.1 M KCl.

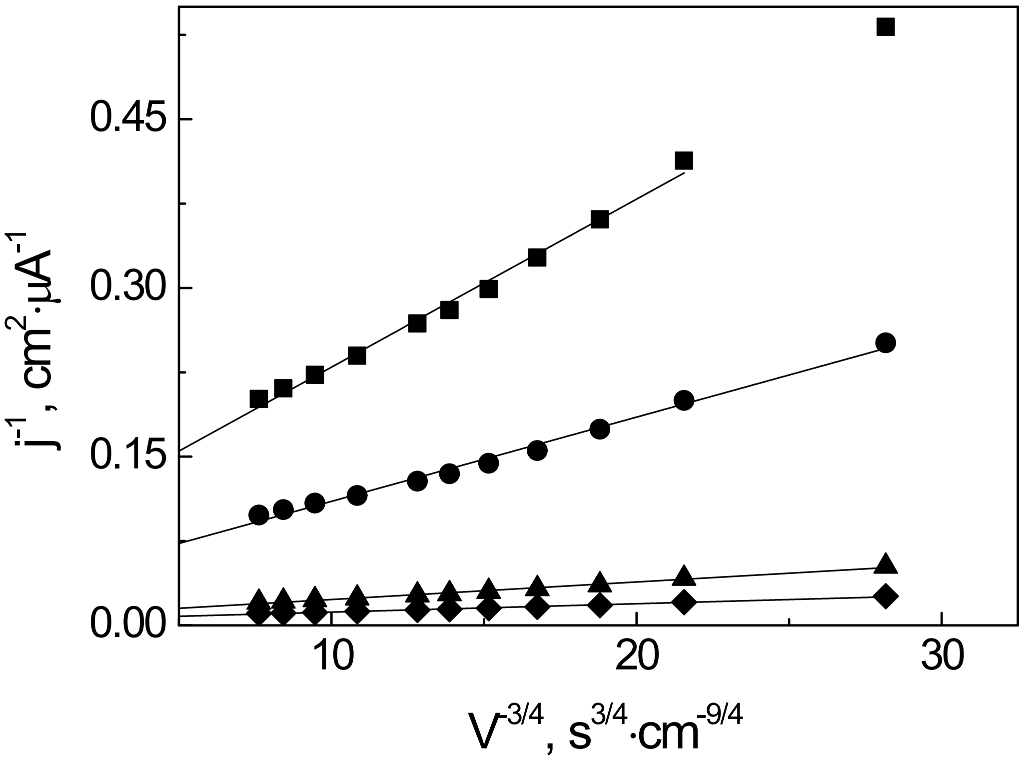

Figure 3S. Current density of hydrogen peroxide reduction as a function of the volume flow rate in a wall-jet cell: (■) $[H_2O_2]$=0.005 mM; (●) $[H_2O_2]$=0.01 mM; (▲) $[H_2O_2]$=0.05 mM, (♦) $[H_2O_2]$=0.1 mM; 50 mM phosphate, pH 6.0 with 0.1 M KCl.