

ELECTRODEPOSITION, CHARACTERIZATION AND APPLICATION OF Pt/CoHCF MODIFIED ELECTRODE

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Using repetitive cyclic voltammetry, Co(II) hexacyanoferrate film has been electrodeposited on Pt surface in order to obtain modified Pt/CoHCF modified electrode. The electrocatalytic properties of this modified electrode in electrolyte containing Na⁺ and K⁺ ions, respectively, have been determined by CV techniques. The Pt/CoHCF modified electrode exhibits electrocatalytic activity towards the oxidation of ascorbic acid in aqueous solution containing 0.1 M phosphate buffer of pH 7.0, the anodic peak being anticipated in comparison with its position on bare Pt electrode. From differential pulse voltammograms (DPV), two linear regions of the peak current versus AA concentration ranging from 2 to 67 μ M and 81 to 351 μ M, respectively, were obtained.

INTRODUCTION

In recent years, considerable interest has been directed to the investigations of polynuclear transition metal-hexacyanoferrates, also known as Prussian Blue analogous.¹⁻⁵ The main fields of interest refer to their preparation and characterization and also to their electrochemical properties: good conduction (including electron and ions transfer),^{6,7} electroanalysis and electrocatalysis.⁸⁻¹⁶

Polynuclear transition metal hexacyanoferrates can be obtained as inorganic conducting thin films deposited on a bare electrode surface by using different electrochemical techniques such as cyclic voltammetry, chronopotentiometry and so on. The inorganic conducting coating is obtained by electrodeposition of some electroactive species, which can coexist in aqueous solution in the presence of several cations that do not take part directly to their own electrode reactions but play an important role in the mechanism of electrodeposition and of operating of the resulting modified electrode during the electrochemical investigations.

In particular, the metal hexacyanoferrates films obtained on the very common electrode surface,

even if they are not enough stable for different applications,¹⁷⁻¹⁹ are easily prepared by consecutive CV and the increase in the peak currents at each repetitive scan is a valuable indication of their electrodeposition.

In electroanalysis, a challenging goal is to determine the level of ascorbic acid in a sample because its electrochemistry on usual electrodes is rather difficult to accomplish due to some drawbacks such as: the electrode reaction is irreversible, the electrode surface does not resist to fouling by the electrode reaction products, the ascorbic acid can interfere in electrochemical detection of different other biochemical electroactive species of interest.

EXPERIMENTAL

Apparatus: Electrodeposition of CoHCF was performed by using a potentiostat/galvanostat Autolab 12 (Ecochemie). A 10-mL electrochemical cell (Metrohm) was used together with a Pt disk as working electrode, Ag/AgCl in saturated KCl solution as reference electrode and a Pt disk as counter-electrode.

Chemicals: All electrolyte solutions were prepared in doubly distilled water. All other reagents, CoCl₂·6H₂O (Carlo Erba), K₃[Fe(CN)₆] (Carlo Erba), KCl (Carlo Erba), NaCl (Carlo

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Erba), ascorbic acid (Merck), as well as the components (Carlo Erba) of the phosphate buffer solution were also used without further purification and they all were of analytical reagent grade.

Preparation of Pt/CoHCF

The bare Pt electrode was polished to a mirror finish using 0.3 and 0.05 μm alumina slurry; then it was rinsed with twice distilled water, cleaned by ultrasonication in twice distilled water for 5 min and finally dried in air.

The Pt/CoHCF modified electrode was prepared by potentiodynamic procedure using the multi-cycling of the electrode potential (100 scans) by cyclic voltammetry (CV) technique, at a scan rate of 100 mV/s, in the potential range from +0.85 V to 0.00 V, in a freshly aqueous solution containing 1 mM CoCl_2 , 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 M KCl. After the deposition of CoHCF film, the modified electrode was rinsed with doubly distilled water and dried in air. Then, the obtained Pt/CoHCF modified electrode was used to study its response in a solution containing different concentrations of ascorbic acid in phosphate buffer system of pH 7.0 by using differential pulse voltammetry.

All measurements were carried out at room temperature. All solutions were deaerated by dry nitrogen stream for 5 min before every experiment and a nitrogen atmosphere was maintained above the solution during the experiment.

RESULTS AND DISCUSSION

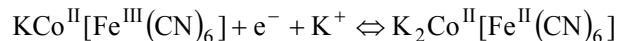
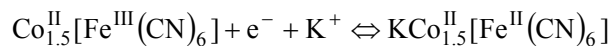
The inorganic conducting film was grown by multi-cycling (100 scans) the electrode potential between +0.85 V and 0.00 V at a scan rate of 100 mV/s. As one can see in Fig. 1, upon sequential cycles, there was a gradual increase in the current intensity (either cathodic or anodic), indicating that a film was formed on the electrode surface, that it is obtained in an electroactive form, and that its thickness grows gradually.

Fig. 1 shows the scans with number 1, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 obtained by scanning the electrode potential. Finally a limiting contour of the cyclic voltammograms is obtained (see the inset of the Fig.1; the 99th and 100th cycles are identical). There are two cathodic peaks at 672 mV and 434 mV and an anodic peak at 624 mV for (values given for the last cycle). The cathodic peak potential at more positive electrode potential is, more or less, constant, while the cathodic peak potential at less positive potential shifts negatively and the anodic peak potential (excepting the first cycle) shifts positively with increasing number of repetitive cycle, E_p for the 10th cycle is 0.600 V and for the 100th cycle is 0.624 V.

In Fig. 2 is given a comparison between the cyclic voltammograms of the following redox systems (A) 1 mM CoCl_2 , 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.5 M KCl aqueous solution and (B) 0.5 mM

$\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.5 M KCl aqueous solution. The two cyclic voltammograms show that the peaks displayed by the Pt/CoHCF modified electrode are very different from those of each individual redox system. The cyclic voltammogram of the 1 mM CoCl_2 in 0.5 M KCl aqueous solution is not shown here, but in the range between 0.00 V and 0.85 V there is no peak (anodic or cathodic) belonging to the Co^{2+} species (the cyclic voltammogram performed in the range from 0.85 V to -1.00 V shows an anodic shoulder at ca. -0.8 V and two cathodic peaks at -0.380 V and -0.78 V, respectively). It is clear that the cobalt (II) ions do not participate to an electrode process in the potential range from 0.85 V to 0.00 V (they are electroinactive in this potential range) and that the complex ion $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ has a different behaviour in this potential range due to the participation of the Co^{2+} and K^+ ions to the electrode process as counterions in the oxidation or reduction processes.

The effect is that the electrode processes involving the complex ions $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ occur at different electrode potentials. The electrode reactions describing the film formation during multi-cycling of the working electrode potential are:^{20,21}



where it was assumed the existence of two possible forms of CoHCF, namely $\text{K}_2\text{Co}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{KCo}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$. At slow scan rates there are two relatively separated cathodic peaks and two very close anodic peaks (for sweep rates of several tens of mV/s) but at large scan rates (starting with a sweep rate around 40 mV/s until several hundreds of mV/s) the two anodic peaks overlap giving rise to only one large anodic peak. The first electrode reaction is responsible for the appearance of the couple of peaks situated at less positive electrode potential due to the fact that the form $\text{KCo}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is less strongly paired (less doped) with potassium cations. Of course, the cathodic peak from more positive electrode potentials can be assigned to the second electrode reaction due to the fact that the form $\text{K}_2\text{Co}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is more strongly paired (more doped) with potassium cations and is harder to be oxidized.

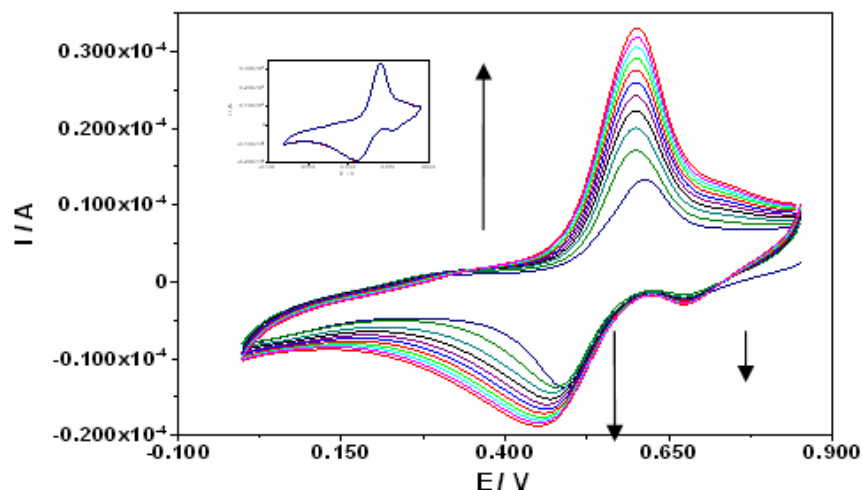


Fig. 1 – The scans with number 1, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 during the electrodeposition of CoHCF film on Pt working electrode at 100 mV/s scan rate between +0.85 V and 0.00 V. Inset: the superposition of the 99th and 100th cycles.

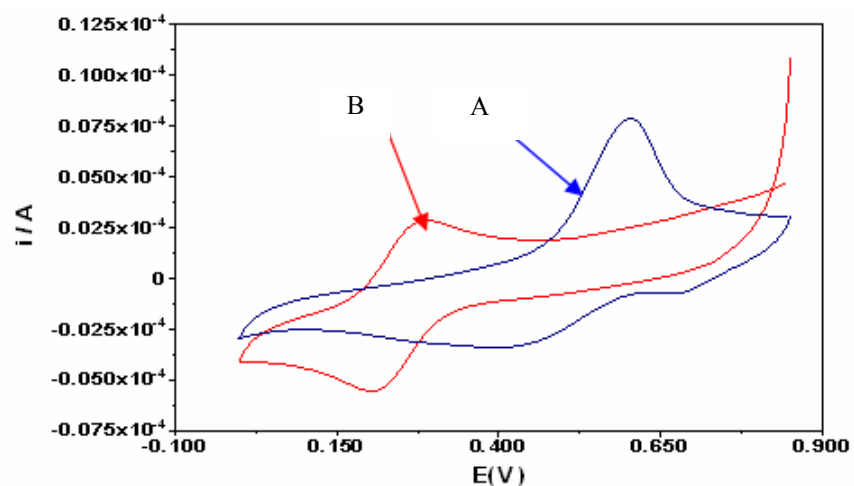


Fig. 2 – Comparison between the cyclic voltammograms (at 100 mV/s scan rate, from 0.85 V to 0.00 V) of the following redox systems: (A) 1 mM CoCl_2 , 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 M KCl; (B) 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 M KCl.

The Pt/CoHCF electrode was studied both in 1 M KCl (see Fig. 3A) and 1 M NaCl (see Fig. 3B) electrolyte solutions by cyclic voltammetry technique at different scan rates. In inset a comparison between two cyclic voltammograms at sweep rate of 500 mV/s and also between two DPV trace voltammograms at SP=10 mV and PA=25 mV, for Pt/CoHCF/KCl(1 M) and for Pt/CoHCF/NaCl(1 M), respectively, are shown. In the case of Pt/CoHCF/KCl(1 M) electrode, the doping/undoping ion is K^+ and, for a sweep rate of 500 mV/s, the peak electrode potentials are $E_p^a=743$ mV and $E_p^c=677$ mV, with a formal electrode potential $E^{o'}=E_{\text{K}^+}^{o'}=710$ mV and a peak separation $\Delta E_p=66$ mV. In the case of

Pt/CoHCF/NaCl(1 M) electrode the doping/undoping ions are Na^+ and K^+ and, for a sweep rate of 500 mV/s, the peak electrode potentials are $E_p^a=570$ mV and $E_p^c=469$ mV, with a formal electrode potential $E^{o'}=E_{\text{Na}^+}^{o'}=520$ mV and a peak separation $\Delta E_p=101$ mV. It is obvious that the electrode reactions occur easier ($\Delta E^o = E_{\text{K}^+}^{o'} - E_{\text{Na}^+}^{o'} = 190$ mV) at the Pt/CoHCF/NaCl electrode than at Pt/CoHCF/KCl electrode due to the fact that the electrochemical mobility of sodium ion is greater than that of potassium ion and the migration into and out of the film depends upon the electrochemical mobility.

One can see, in Fig. 3, that the anodic peak potentials shift anodically for both Pt/CoHCF/KCl electrode and Pt/CoHCF/NaCl electrode due to the fact that the undoping process (either cations K^+ for Pt/CoHCF/KCl electrode and respectively Na^+ for Pt/CoHCF/NaCl electrode is involved) that occurs during oxidation is diffusionally controlled. Of course, during reduction the doping process occurs using the cations from a very concentrated indifferent electrolyte solution (1 M).

The first inset in Fig. 3 also shows that the shapes of the two cyclic voltammograms are quite different: in the case of Pt/CoHCF/NaCl(1 M) the shape is more or less symmetrical around the $E^{0'}$

value. In addition, one can notice that the pair of peaks is broad. This observation regarding the behaviour of the Pt/CoHCF modified electrode in K^+ counterion and Na^+ and K^+ counterions is similar with the results found for Prussian Blue itself. The second inset in Fig. 3 also shows that the shapes of the two DPV trace voltammograms are quite different.

Plotting the peak currents against the square root of the sweep rate one obtains straight lines for both anodic and cathodic peaks and for Pt/CoHCF modified electrode both in K^+ -containing (Fig. 4 left) and Na^+ -containing (Fig. 4 right) supporting electrolyte.

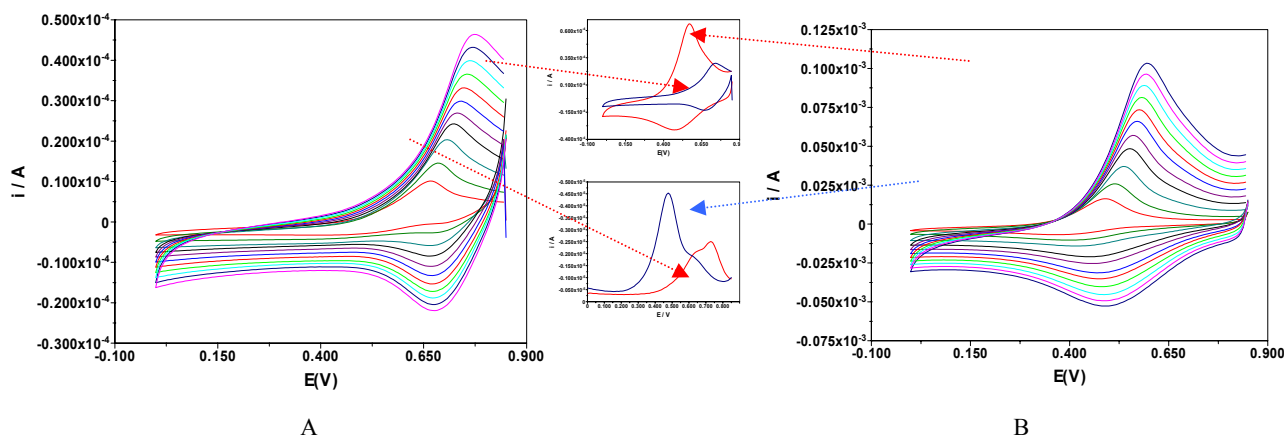


Fig. 3 – The behaviour of Pt/CoHCF/KCl(1 M) (A) and Pt/CoHCF/NaCl(1 M) (B) with the increasing sweep rate: 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV/s. Inset: cyclic voltammograms for Pt/CoHCF/KCl(1 M) and for Pt/CoHCF/NaCl(1 M) at sweep rate of 500 mV/s (upper inset figure) and DPV trace voltammograms for Pt/CoHCF/KCl(1 M) and for Pt/CoHCF/NaCl(1 M) with SP=10 mV and PA=25 mV (lower inset figure).

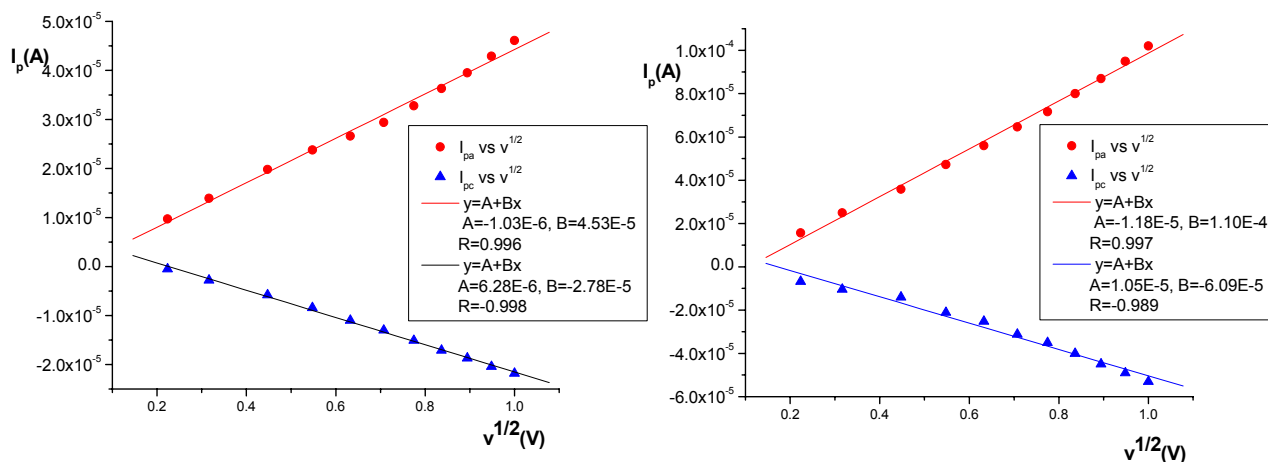


Fig. 4 – The linear dependence of the anodic and cathodic peak currents upon the square root of the sweep rate for the Pt/CoHCF modified electrode in 1 M KCl (left) and 1 M NaCl (right) aqueous solution.

This behaviour is consistent with a diffusion limiting process and probably can be explained by considering that the nature itself of the counteraction, which moves inside the electrolyte solution in a hydrated state, could be forced to lose, at least partially, solvent molecules from the hydration shell to be able, having appropriate size, to enter to the crystal lattice.²² The electrocatalytic activity of the modified Pt/CoHCF electrode was tested towards oxidation of ascorbic acid by DPV technique at different concentrations of the

electroactive species in phosphate buffer solution (pH 7.0). The DPV trace voltammograms are presented in Fig. 5. As can be seen from Fig. 5, the anodic peak potentials corresponding to the ascorbic acid oxidation shifts negatively with increasing ascorbic acid concentration, it can be localized in the range from 0.215 V to 0.180 V. On Pt bare electrode the DPV-anodic peak for the oxidation of ascorbic acid is several tens mV higher, around 0.270 V.

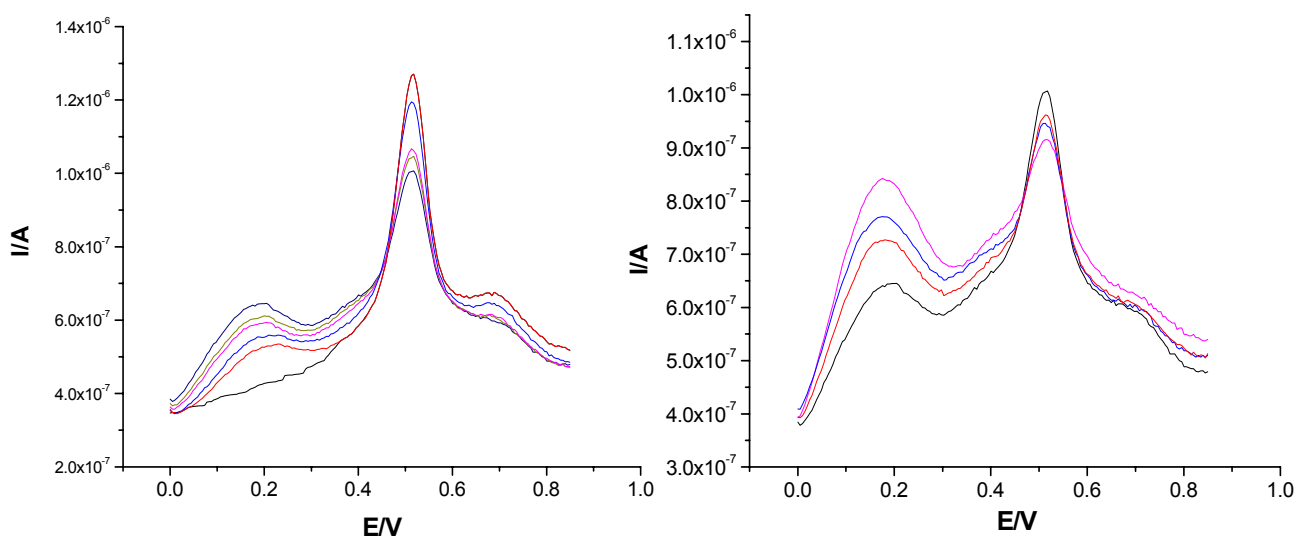


Fig. 5 – The DPV-voltammograms of the chemically modified Pt/CoHCF electrode at different ascorbic acid concentrations (from 2 μM to 81 μM (left) and from 81 μM to 351 μM (right)) in phosphate buffer solution of pH=7.0. The DPV parameters are: SP=10 mV, AP=25 mV.

On the other hand, it is obvious that the anodic peak at ca. 0.5 V, corresponding to the superposition of the two anodic electrode reactions corresponding to both $\text{Co}_{1.5}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]/\text{KCo}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{KCo}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]/\text{K}_2\text{Co}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ redox systems, decreases while the anodic peak corresponding to the oxidation of the ascorbic acid increases with increasing concentration of the electroactive species. This is due to the electrocatalytic effect of the electrodeposited film on the oxidation of the ascorbic acid, occurring after a general mechanism of electrocatalysis.⁴ Both the peak current and the peak potential of the anodic electrode reaction of the ascorbic acid are affected by the electrocatalytic properties of the inorganic film; the peak current is higher and the peak potential is anticipated with respect to the case of a Pt bare electrode.

Plotting the DPV-anodic peak current against the ascorbic acid concentration one gets the linear dependences from Fig. 6 showing the existence of two different regions of linearity. For low ascorbic acid concentrations, in the range from 2 μM to 81 μM (left) there is a linear behaviour, with a correlation coefficient of 0.998. For high ascorbic acid concentrations, in the range from 81 μM to 351 μM (right), the linear dependence has a correlation coefficient of 0.996.

The precision of peak current determinations was situated within the interval 5.00% (for 2 μM ascorbic acid) and 2.20% (for 81 μM ascorbic acid) and 1.18% (for 351 μM ascorbic acid) expressed as the relative standard deviation.

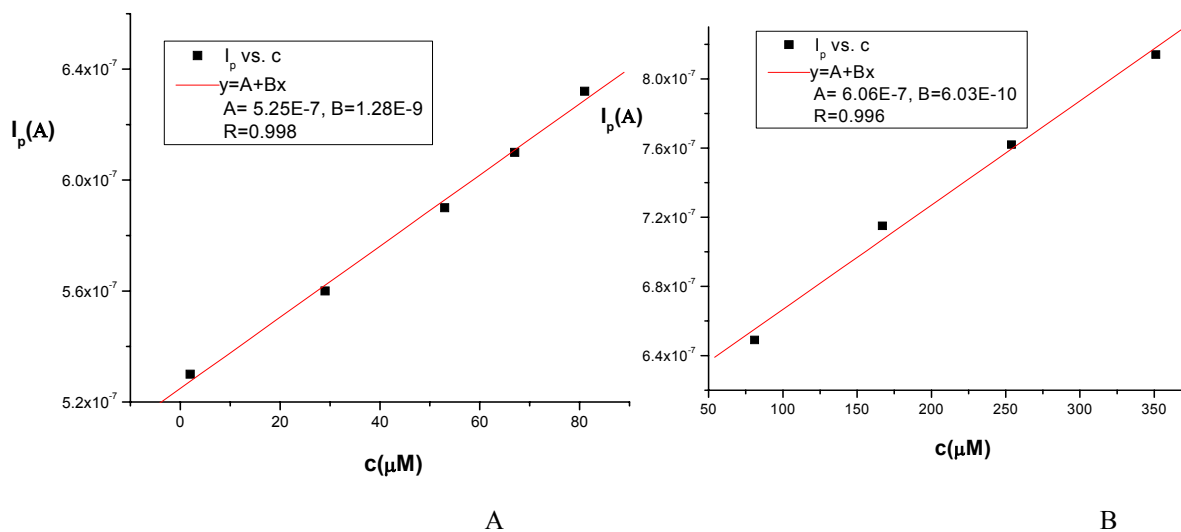


Fig. 6 – The plot of the DPV anodic peak currents versus ascorbic acid concentrations (A): 2 μM to 81 μM and, respectively, (B): from 81 μM to 351 μM for the DPV trace voltammograms in Fig. 5.

CONCLUSION

Using consecutive cyclic voltammetry technique, cobalt(II)-hexacyanoferrate film was electrodeposited onto Pt electrode surface in K^+ -containing solution and also characterized in K^+ -containing and Na^+ -containing solution. The formal electrode potentials of the inorganic film were determined in both electrolyte solutions. The cobalt(II)-hexacyanoferrate film exhibits electrocatalytic activity towards the oxidation of ascorbic acid, the anodic oxidation peak being anticipated in comparison with the bare Pt electrode. The DPV-anodic peak current depends linearly upon the concentration of ascorbic acid.

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