

## Full Paper

# Electrochemical Properties of Lanthanum Hexacyanoferrate Particles Immobilized onto Electrode Surface by Au-Codeposition Method

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## Abstract

Lanthanum hexacyanoferrate (LaHCF) was immobilized onto a substrate surface as an electroactive material by Au-codeposition method. The LaHCF particles were attached to the electrode surface as the result of occlusion within the gold film deposited. This deposition method was first introduced for the preparation of hexacyanoferrate-based modified electrodes. It was demonstrated that this deposition method provides a higher stability of the electroactive film in comparison with available methods for the mechanical attachment of electroactive films. On the other hand, electrochemical properties of the LaHCF film modified electrode were studied for the first time. The results showed that LaHCF film has excellent electrochemical activity as well as other analogues of Prussian blue. The modified electrode was successfully used as an electrocatalyst for the oxidation of ascorbic acid.

**Keywords:** LaHCF, Modified electrode, Electroactive film, Gold-codeposition, Electrochemical stability, Electrocatalysis

## 1. Introduction

During the past three decades, Prussian blue (PB) and its analogues have been widely used as electroactive films in solid-state electrochemistry [1–4]. They have been successfully used for the modification of electrode surfaces to prepare chemically modified electrodes (CMEs). This area of research has been given considerable attention due to various applications of CMEs.

Several methods have been proposed for the deposition of transition metal hexacyanoferrate films onto a variety of substrates [6–15]. Due to the various applications of CMEs, it is very important to deposit highly stable films on electrode surfaces. The film stability is mainly related to two different factors i) stability of the compound itself, and ii) strength of the material attachment to the substrate surface. Several approaches have been suggested to enhance the stability of hexacyanoferrate films by incorporation of some anions [16–18]. This kind of stability is due to the insolubility of the electroactive material in an electrolyte medium. More recently, we have paid considerable attention to the second reason affecting the stability of electroactive films. Direct modification of metallic electrodes with hexacyanoferrates has been used as a simple method for the fabrication of CMEs with highly stable films deposited [19–21]. Using aluminum substrate for the deposition of hexacyanoferrate films [22–24] and other electroactive films has also been described [25–27] for the preparation of highly stable films. Silicon has been introduced as an excellent substrate electrode for the

deposition of highly stable transition metal hexacyanoferrate films [28].

It is well known that small particles can be attached onto a substrate surface during a codeposition process as the result of occlusion within the depositing material. Different materials such as conducting polymers have been used for this purpose; however, a comprehensive citation of such investigations seems to be too long to be referenced here. Gold is an excellent material for the codeposition process as well as its excellent properties as a substrate electrode. This method has been successfully used for the deposition of  $\text{LiMn}_2\text{O}_4$  for the fabrication lithium battery cathodes [29, 30]. In the present research, we would like to employ the Au-codeposition method for the deposition of lanthanum hexacyanoferrate (LaHCF) onto an electrode surface.

Since the first report of the deposition of a thin film of PB onto an electrode surface [31], numerous researches have been devoted to the studies of different PB analogues from a solid-state electrochemistry point of view. During the past decades, different hexacyanoferrate salts of transition metals have been introduced as electroactive materials displaying reversible redox systems. Liu et al. have recently introduced two new PB analogues namely zirconium hexacyanoferrate [32] and lanthanum hexacyanoferrate [33] to solid-state electrochemistry. During preliminary studies, they just investigated spectroelectrochemical properties of such films, though, they have later attempted electrochemical studies of ZrHCF for a specified application [34]. However, there is no report on the electrochemical properties of LaHCF. On the other hand, they have reported

[33] that due to small channels of LaHCF lattice, it is unable to accommodate alkali metal cations.

## 2. Experimental

LaHCF was synthesized by mixing 0.3 M  $\text{K}_3\text{Fe}(\text{CN})_6$  aqueous solution and 0.2 M  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  aqueous solution and heating the mixture to ca.  $90^\circ\text{C}$ . As the hexacyanoferrate salt was prepared according to the available methods, spectroscopy characterizations were completely similar to those reported in the literature [35].

The deposition of LaHCF was carried out during codeposition of gold on an Au substrate electrode. In this case, the electroactive material would be attached onto the substrate surface as the result of occlusion between the gold particles deposited. This is an appropriate deposition method for the preparation of LaHCF modified electrode, as gold does not provide any electrochemical reaction in the potential range of our experiments. This process was performed using a solution containing 15 g/L potassium gold cyanide, 80 g/L monopotassium phosphate, 70 g/L potassium citrate and 1.5 g/L cobalt chloride with near-neutral pH was prepared as the deposition electrolyte. A small amount of LaHCF was also added to this solution. The electrolyte solution was stirred for a few minutes before the deposition process to reach a well-conditioned suspension. The deposition process was carried out by applying a cathodic current of 4.0 mA in a warm bath ( $50^\circ\text{C}$ ). Finally, the electrode was washed thoroughly with water.

The electrochemical experiments were carried out using a conventional three-electrode cell containing the working electrode at room temperature. A platinum rod and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The electrochemical measurements were performed using a homemade potentiostat connected to a computer running CorrView software.

## 3. Results and Discussion

According to [33], LaHCF does not show an active electrochemical behavior in the supporting electrolytes of alkali metal ions; thus, it cannot be used for the usual applications of hexacyanoferrate-based CMEs. We also found that insertion of alkali metal ions (particularly those with large radii) into the LaHCF lattice is difficult. It is due to small channels of the LaHCF lattice, which accept only small inserting ions. In the face-centered cell of PB,  $\text{Fe}^{3+}$  and  $\text{Fe}^{\text{II}}$  bridged by a CN group appear alternatively at the sites of small cubes [36]. The body centers of these cubes are occupied by  $\text{H}_2\text{O}$  and cations of  $\text{K}^+$  (water soluble PB) or  $\text{Fe}^{3+}$  (water-insoluble PB) to maintain electroneutrality. The cell is quite spacious with a parameter of 1.02 nm. A maximum channel of 0.599 nm was estimated for counter ions. These channels are sufficiently large to easily accept different alkali metal ions. However, depending on the

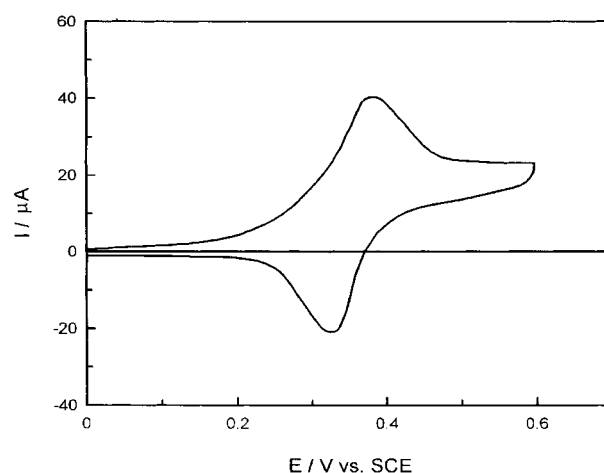
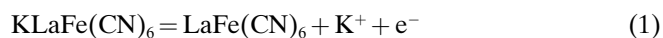


Fig. 1. Typical Cyclic voltammogram of the LaHCF modified electrode in 1.0 M KCl supporting electrolyte. Scan rate  $100 \text{ mV s}^{-1}$ .

difference of the ion radii and the channel size, electrochemical behavior of the PB film varies.

Although, LaHCF is a PB analogue and has a similar structure, the large size of  $\text{La}^{3+}$  made it a little different from PB with a different electrochemical behavior. However, the size of the channels on LaHCF is still large enough to accept small counter ion like  $\text{K}^+$  (but not larger ones). Another parameter affecting the counter ion insertion is permeability of the electroactive film deposited. Due to higher permeability of LaHCF prepared chemically in comparison with that prepared electrochemically [33], we found that the electrode fabricated in this research has an acceptable electrochemical activity in the potassium-supporting electrolyte.

Figure 1 shows a typical cycling voltammetric behavior of the LaHCF modified electrode in the supporting electrolyte of 1.0 M KCl. Similar to other PB analogues, it is accompanied by a redox couple due to the oxidation/reduction of the surface-confined iron centers. The formal potential of the redox system was evaluated by averaging the anodic and cathodic peak potentials. The redox couple reaction is corresponding to the following reaction:



It should also be taken into account that several factors may be involved in changing the ideal voltammetric behavior of the modified electrode under consideration. Since, the electroactive particles are included within the gold film, some parts of their surfaces have been covered by the deposited gold, and cannot participate in the electrochemical process from its surface side through an interfacial process. Instead, the most interconversion processes are performed via solid-state processes within the electroactive material. This process is different from that occurred in common porous modified electrodes. In addition, the electrochemical activity of gold at high potential also have a significant influence on the shape of the CV.

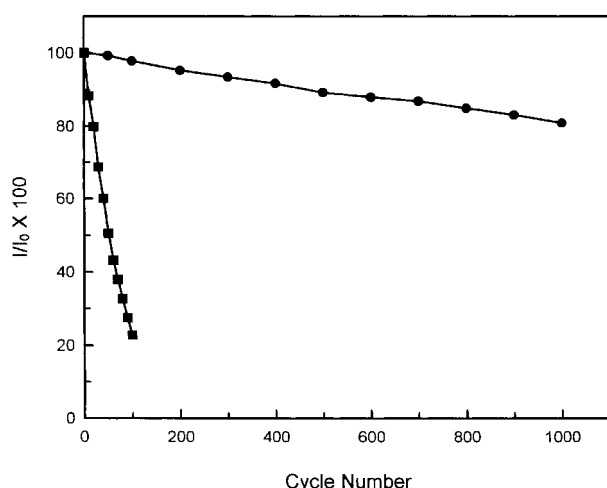


Fig. 2. Electrochemical stability of the LaHCF modified electrodes prepared by Au-codeposition method (●) and PIGE (■) during potential cycling. The data were obtained from the repetitive cyclic voltammetric measurements at the experimental conditions of Figure 1.  $I_0$  is the peak current recorded at the first scan.

Although, the cyclic voltammetric of the LaHCF modified electrode is well characterized, we need to investigate its stability under electrochemical condition during potential cycling. Figure 1 only shows the first scan, whereas, it is well known that electrochemical activity of an electroactive film attached to substrate surfaces decreases during potential cycling. This is an important problem in hindering its practical performances. It has been described that the main drawback for hexacyanometallates-based CMEs is the gradual dissolution during potential cycling [17].

To investigate this problem, we examine the film stability by repetitive cyclic voltammetric measurements. To shed light on the significance of the stability of the LaHCF film deposited by gold-codeposition method, the results were also compared with a LaHCF film modified electrode prepared by a common deposition method which was similar to the method employed here. Mechanical attachment of electroactive particles onto paraffin-impregnated graphite electrode (PIGE) has been proposed by Scholz et al. [14, 15] as an effective method for the preparation of CMEs. During the development of abrasive voltammetry, this method has been widely used for the modification of electrode surfaces and studies of electroactive materials [4]. As a successful method, we also prepared a LaHCF modified electrode by the deposition of LaHCF particles onto PIGE.

The repetitive cyclic voltammetric studies of the LaHCF modified electrode prepared by Au-codeposition method have a significant stability during potential cycling (Fig. 2a). Only a 20% decrease in the peak current is observed after 1000 potential cycles, whereas, the common hexacyanoferrate-based CMEs prepared by the deposition of transition metal hexacyanoferrates such as NiHCF and CoHCF onto conventional substrate electrodes show about 90% decrease

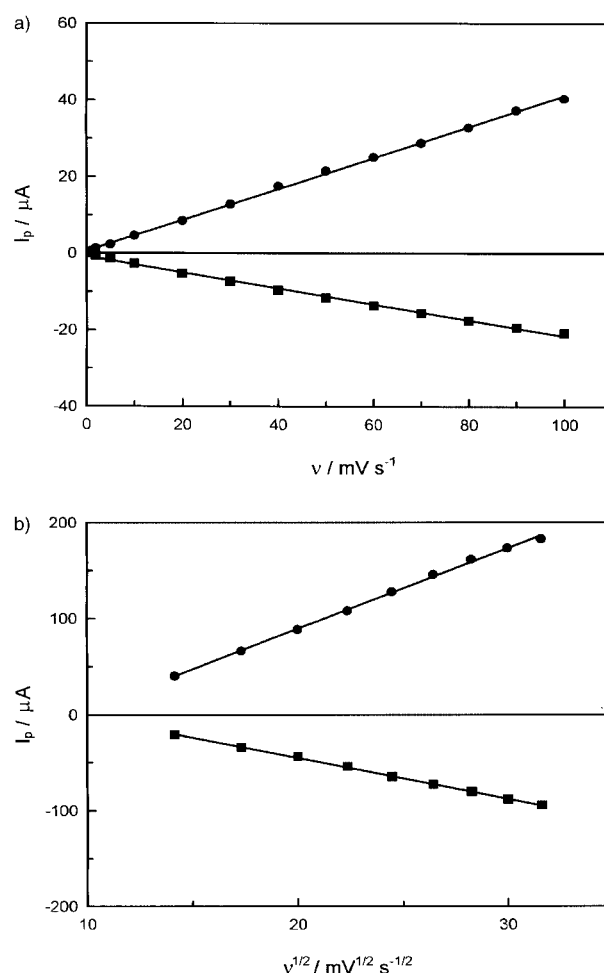


Fig. 3. Scan rate dependence of the voltammetric behavior of the LaHCF film in 1.0 M KCl solution. a) Linear dependence and b) Square root dependence.

in the peak current during the same number of cycles [17, 18]. As stated above, the film stability is also affected by the stability of the compound itself. Thus, we cannot compare stabilities of the two different hexacyanoferrates deposited onto substrate electrodes based on the deposition methods.

Figure 2 compares the results obtained from the repetitive cyclic voltammetric measurements of two similar LaHCF modified electrodes prepared by the Au-codeposition method and immobilization on PIGE. This obviously shows that Au-codeposition provides higher electrochemical stability for the LaHCF particles attached to the electrode surface.

This enhanced stability of the LaHCF film deposited by the Au-codeposition method is not restricted to electrochemical conditions and also the film has a significant chemical stability during long-term usage, as investigated by cyclic voltammetric measurements after long-term storage. The LaHCF modified electrode prepared by the Au-codeposition method loses only a 10% of its activity after 90 days storage in the supporting electrolyte (not shown).

As presented in Figure 3, both anodic and cathodic peak currents linearly increase with potential scan rate up to

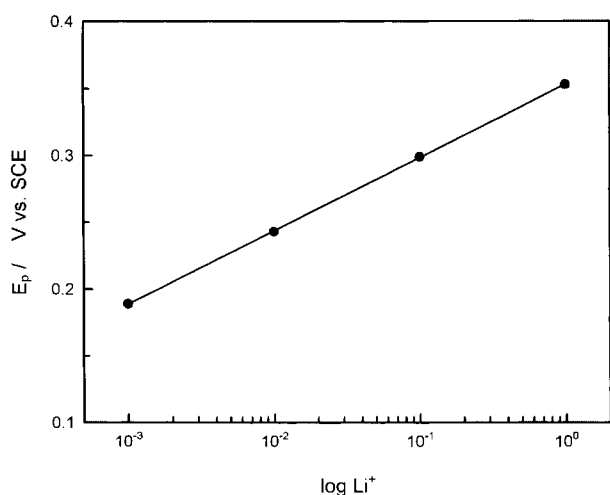


Fig. 4. Dependence of the peak potential on the ion concentration of the supporting electrolyte (KCl). The data were recorded at scan rate 100 mV s<sup>-1</sup>.

200 mV s<sup>-1</sup>, indicating a surface reaction. The deviation from the linear relationship at higher scan rates is indicative of the mass transport limitation within the electroactive film. At higher scan rates, the peak current is proportional to the square root of the scan rate, which indicates diffusional behavior in charge transport. Indeed, scan rate dependence of the LaHCF modified electrode is similar to other PB analogues.

As the main reaction of such redox systems is the insertion of the counter ion from the supporting electrolyte, the electrochemical behavior of the LaHCF modified electrode is highly dependent on the concentration of the supporting electrolyte. According to the discussion made on the thermodynamic behavior for redox system of PB and its analogues [5], the alkali metal ion of the supporting electrolyte is involved in the redox reaction of the electroactive material according to the Nernst equation. Thus:

$$E = E^0 + RT/F \ln[\text{LaHCF}][\text{K}^+]/[\text{LaKHCF}] \quad (2)$$

Figure 4 obviously displays this feature, as the slope of the curve is 54.5 mV/decade. This is very close to the theoretical Nernstian slope (59.1 V/decade). It should also be noted that the experimental generalization of the Nernst equation, better Nernstian response can be found when the activity of ions are used instead of the concentration.

It is well known that the electrochemical behavior of hexacyanoferrate film modified electrodes is affected by the type of cation of the supporting electrolyte. Different shapes of the cyclic voltammograms obtained in the presence of different cations can be explained partly by the assumption that an enthalpy term must be included in the free energy, as has been described for PB [38]. However, the main effect of the type of cations of the supporting electrolyte on the electrochemical behavior of the hexacyanoferrate film modified electrodes is the significant changes on their formal potential. This effect is also observable for the system

under investigation. However, the influence of the type of supporting electrolyte cannot be documented for the case of LaHCF, as the electrochemical behavior of the electroactive film is very weak in the presence of most alkali metals. Although, the chemical preparation method employed in the present research provided a little higher channel allowing potassium ion insertion in comparison with that reported in the literature [32], the CVs recorded with other alkali metal ion-supporting electrolytes were not well-defined or suitable for a comparative study. The investigation of the cyclic voltammetric characteristics of the LaHCF film modified electrode in different supporting electrolyte suggested the following permeability of cations:  $\text{K}^+ > \text{Li}^+ \approx \text{Na}^+ \gg \text{NH}_4^+ > \text{Cs}^+$ . In the case of  $\text{NH}_4^+$  and  $\text{Cs}^+$ , the cations cannot even be inserted completely during repetitive cycling, which is unlike the PB [36]. Indeed, the insertion process cannot be exactly explained in accordance with the hydrated ionic radii. In other words, although, the relationship of the hydrated ionic radii and the lattice channel size is of importance to understand the electrochemical behavior of the system under investigation in the presence of various supporting electrolyte, however, other factors may also be involved. This is a deviation from the ideal behavior of PB, which is more or less observed for all PB analogues.

To investigate the electrocatalytic activity of the modified electrode, electrochemical oxidation of ascorbic acid at the LaHCF modified electrode was studied. Electrochemical oxidation of ascorbic acid at conventional electrodes such as Au, Pt and glassy carbon is accompanied by high overpotentials. Figure 5a shows cyclic voltammetric characteristic of the electrocatalytic oxidation of ascorbic acid at the LaHCF modified electrode. The cyclic voltammetric behavior of the modified electrode in the absence of ascorbic acid was also presented for comparison. Bare gold electrode has no significant electrocatalytic activity in the potential range of our experiment. The electrocatalytic oxidation of ascorbic acid at the LaHCF modified electrode is evidenced from the dependence of the peak current to the concentration.

The potential of the oxidation peak suggests the combination of chemical catalysis with the redox mediation, which is probably the reason for the high catalytic activity of LaHCF towards ascorbic acid oxidation. It has been described that some of the best electrocatalysts react through an inner-sphere pathway, which are accompanied by the participation of the ligand-bridged transition states [40]. One may think that the oxidation potential of ascorbic acid is significantly higher than the formal potential of the LaHCF redox system. However, the LaHCF modified electrode has decreased the overpotential of ascorbic acid oxidation as well as other hexacyanoferrate-based modified electrodes. Such difference can be attributed to low formal potential of LaHCF.

Scan rate dependence of the oxidation peak current showed that the peak current is proportional to the square root of the scan rate (Fig. 6A), suggesting that the reaction is diffusion controlled. The shape of the current function  $i_p v^{-1/2}$  vs. scan rate plot (Fig. 6B) suggests an EC<sub>cat</sub> process.

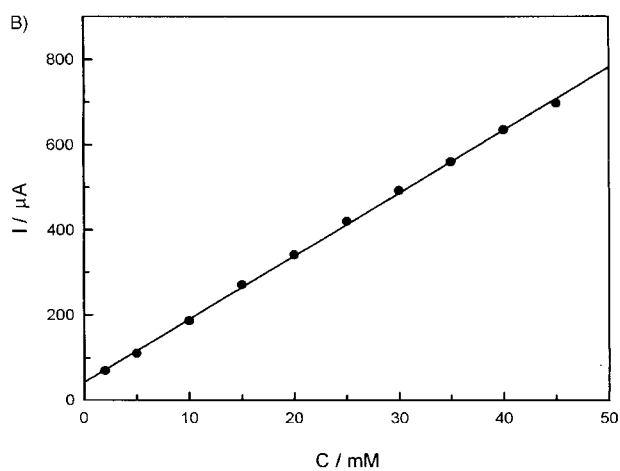
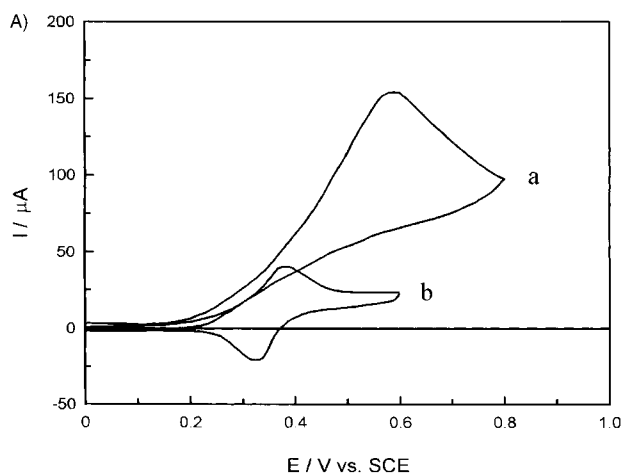
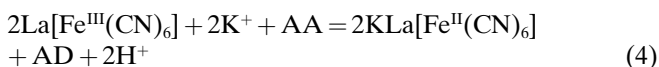


Fig. 5. A) Electrocatalytic oxidation of ascorbic acid at the presence of 10 mM AA in 1.0 M KCl with pH 7.2 (a). And similar voltammogram recorded in the absence of ascorbic acid (b). Scan rate  $100 \text{ mV s}^{-1}$ . B) The relationship of the peak current to the ascorbic acid concentration.

According to an EC catalytic mechanism, the overall reaction can be written as:



where AA and AD denote ascorbic acid and dehydroascorbic acid, respectively. The results obtained indicate an irreversible redox process with an apparent diffusion-limited step. Based on the electrocatalytic properties of the modified electrode for catalytic oxidation of ascorbic acid, the electrode can be used for amperometric detection of ascorbic acid in analytical performances. Due to the selective electrochemical redox system of LaHCF, it is thought that the LaHCF film modified electrode can be used as sensors for the determination of analytes with high

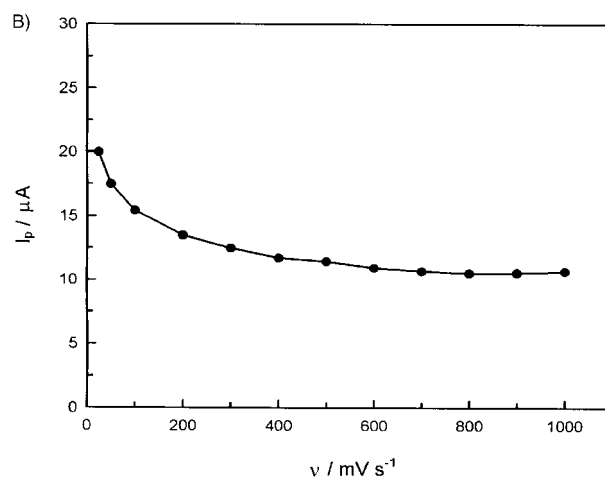
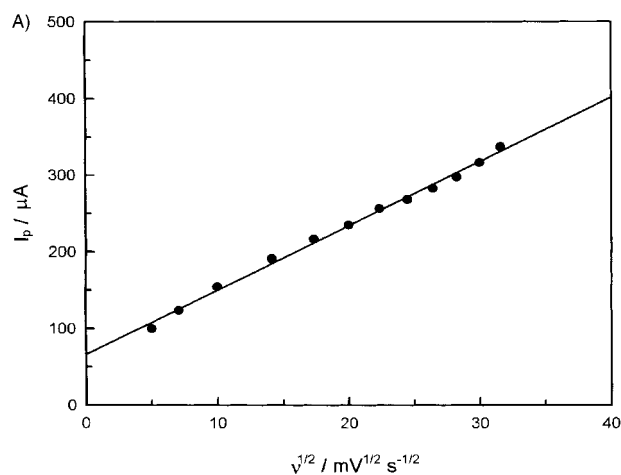


Fig. 6. Variation of the anodic peak current vs.  $v^{1/2}$  (A) and the anodic peak current function  $I_p v^{1/2}$  vs.  $v$  (B). The electrolyte solution was 10 mM ascorbic acid in 1.0 M KCl (pH 7.2).

selectivity. For example, it can be used as a potassium ion-selective electrode with negligible interference of alkali metal ions in comparison of other hexacyanoferrate-based  $\text{K}^+$  sensors.

The LaHCF film modified electrode was used as a sensor for the determination of ascorbic acid. To obtain a wide range of ascorbic acid concentration, the amperometric response of the sensor was investigated. The amperometric response of the sensor to ascorbic acid concentration is illustrated in Figure 7. The sensor exhibits a linear amperometric response to ascorbic acid over the range  $2 \times 10^{-6}$ – $5 \times 10^{-5}$  with a detection limit of  $9.1 \times 10^{-7}$ . The sensitivity of the sensor was  $0.89 \mu\text{A}/\mu\text{M}$ . As the amperometric measurements are performed under steady state condition, the amperometric sensor exhibits a wider range of concentration in comparison with non-steady state measurements made by the cyclic voltammetry technique. The detection limit of the amperometric sensor is three orders of magnitude lower than that obtained from cyclic voltammetric measurements. Indeed, the sensor prepared based on the LaHCF film

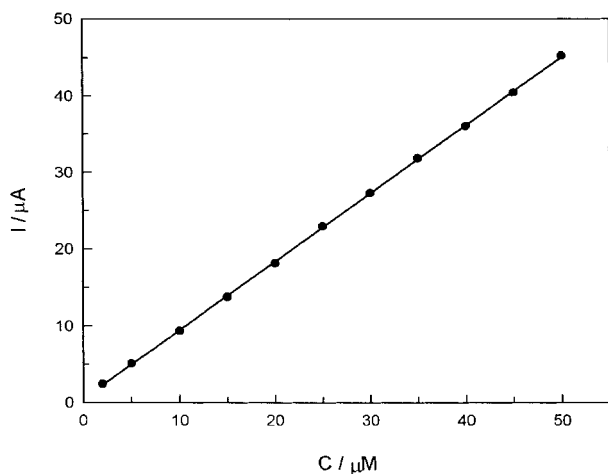


Fig. 7. Amperometric response of the modified electrode to ascorbic acid at low concentrations.

modified electrode has a good sensitivity for the determination of ascorbic acid. The calibration plot of the sensor response (Fig. 7) was accompanied by an excellent correlation coefficient of 0.9998. It can be attributed to the selectivity of the electrochemical reaction to catalysis the ascorbic acid reaction, avoiding side reactions as the sources of errors in the electrochemical signal recorded. In addition, our preliminary investigation showed that the sensor has good selectivity for this purpose and can be used for the determination of ascorbic acid in real samples such as fresh fruit and vegetable juices.

#### 4. Conclusions

It was shown that electroactive materials could be attached to electrode surfaces to fabricate CMEs as highly stable electroactive films based on the Au-codeposition method. This method was employed to prepare a LaHCF modified electrode with an enhanced stability in comparison with the modified electrode prepared based on a conventional method. On the other hand, electrochemical behavior of LaHCF was investigated for the first time. Based on the experimental results, it was shown that LaHCF could be used for the preparation of CMEs for various applications as well as other PB analogues. Indeed, the novelty of the present work is related to both methodology and case study. The approach employed for the immobilization of LaHCF can be used for the deposition of other electroactive materials.

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