

## Preparation and characterization of carbon paste electrode modified with tin and hexacyanoferrate ions

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**Abstract:** A carbon paste electrode was modified chemically using Sn(II) or Sn(IV) chlorides and hexacyanoferrate(II) or hexacyanoferrate(III). The electrochemical behavior of such SnHCF carbon paste electrodes was studied by cyclic voltammetry. The study revealed that Sn(IV) and hexacyanoferrate(II) yield the best results. This electrode showed one pair of peaks: the anodic and cathodic peak at the potentials of 0.195 and 0.154 V vs. SCE, respectively, at a scan rate of 20 mV s<sup>-1</sup> in a 0.5 M phosphate buffer as the supporting electrolyte. The SnHCF modified electrodes were very stable under potential scanning. The effects of pH and alkali metal cations of the supporting electrolyte on the electrochemical characteristics of the modified electrode were studied. The results showed that cations have a considerable effect on the electrochemical behavior of the modified electrode. The diffusion coefficients of hydrated K<sup>+</sup> and Na<sup>+</sup> in the film, the transfer coefficient and the electron transfer rate constant were determined.

**Keywords:** carbon paste electrode, modified electrode, tin, hexacyanoferrate.

### INTRODUCTION

To date various inorganic materials,<sup>1</sup> organometals<sup>2</sup> and polynuclear cyanometalate<sup>3–44</sup> have been used to make modified electrodes (MEs). Among the various mediators used for electrode modification, solid metal hexacyanoferrates have attracted the attention of electrochemists as excellent electron transfer mediators. Ever since the work of Neff *et al.* on Prussian blue (PB) modified electrode (ME),<sup>45,46</sup> there have been many papers published over the years on the preparation and characterization of metal hexacyanoferrates as electroactive materials.<sup>3–44</sup> Various transition metal cations have been used with hexacyanoferrate to fabricate metal hexacyanoferrate (MHCF) modified electrodes, in which M can be: cadmium,<sup>3</sup> chromium,<sup>4,5</sup> cobalt,<sup>6–9</sup> copper,<sup>10–12</sup> dysprosium,<sup>13</sup> gallium,<sup>14</sup> indium,<sup>15–17</sup> iron HCF (PB),<sup>18–20</sup> lanthanum,<sup>21</sup> manganese,<sup>22,23</sup> molybdenum,<sup>24</sup> nickel,<sup>25–28</sup> osmium,<sup>29</sup> palladium,<sup>30,31</sup> platinum,<sup>32</sup> ruthenium,<sup>33</sup> samarium(III),<sup>34</sup> silver,<sup>35,36</sup> mixed-valent titanium,<sup>37</sup> vanadium,<sup>38–40</sup> zinc,<sup>41</sup> zirconium,<sup>42,43</sup> and Ket–HCF (ketotifen-hexacyanoferrate).<sup>44</sup>

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The aim of the present study was to propose and examine the preparation of SnHCF MEs as a carbon paste electrode and study of the electrochemical behavior of the electrode in detail.

## EXPERIMENTAL

### *Chemicals and instrumentation*

$K_3[Fe(CN)_6]$  (HCF(III)),  $K_4[Fe(CN)_6]$  (HCF(II)),  $KNO_3$ ,  $SnCl_2$ ,  $SnCl_4$  and other chemicals were of analytical grade and were obtained from Merck and used without further purification. A solution of 0.5 M phosphate buffer solution was used as supporting electrolyte. The buffer was prepared using phosphoric acid and pH adjusted with KOH. The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP-2063 electrochemical analysis system, Behpa-joo, Iran). A conventional three-electrode cell was used at 25 °C (room temperature). A saturated calomel electrode and platinum wire (from Azar electrode Co., Iran) were used as reference and auxiliary electrodes, respectively.

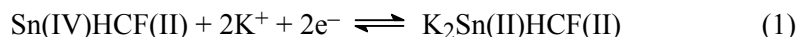
### *Electrode preparation*

The SnHCF carbon paste electrode was prepared using tin(IV) chloride. For the preparation of SnHCF, 50 ml of 0.1 M tin(IV) chloride solution containing 0.1 M  $KNO_3$  was slowly added to 50 ml of 0.1 M HCF(II) with agitation. The formed SnHCF precipitate was filtered, washed, and dried. Then 0.05 g of the obtained precipitate was mixed with 0.5 g graphite (1:10) and a few drops of paraffin oil were added to the mixture. The mixture was housed in a polyethylene tube (inner diameter 2.4 mm) and polished on a smooth paper layer. An electric contact was made by a copper wire through the back of the electrode. The obtained SnHCF precipitate was a light green powder which was stable in aqueous solutions.

## RESULTS AND DISCUSSION

### *Electrochemical behavior of the modified electrode*

The SnHCF ME was prepared using Sn(II) and Sn(IV) chlorides with HCF(II) and HCF(III). The experimental results revealed that Sn(IV) chloride and HCF(II) after about 20 cycles at a scan rate  $100 \text{ mV s}^{-1}$  yielded a stable cyclic voltammogram with symmetric peaks with a small peak separation. To maintain the electroneutrality of the metal hexacyanoferrate modified electrode, it is important to equilibrate the compounds with the electrolyte by repeated oxidation and reduction because the starting compounds may contain metal ions in their channels from the synthesis, which must be excluded from lattice to the solution by potential scanning. The modified electrodes prepared with these two salts were characterized by cyclic voltammetry. MEs were also prepared from Sn(IV) with HCF(III), but no peaks were observed, and from Sn(II) with HCF(II) and HCF(III), but the ME had large peak separations. The cyclic voltammograms of SnHCF with Sn(II) and Sn(IV) salts are shown in Fig. 1. It seems that when Sn(IV) was used for the preparation of the ME, the following electrochemical reaction can occur:



However, when Sn(II) and HCF(II) were used for the preparation of the ME, a large peak separation was observed. This character of the ME may be due to the migration of  $K^+$  from the lattice to the solution.

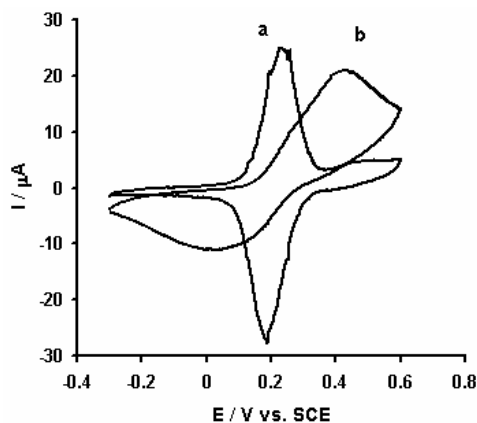
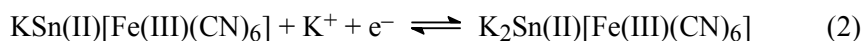


Fig. 1. Cyclic voltammograms of a) the Sn(IV)HCF(II) electrode and b) the Sn(II)HCF(II) electrode, both in a 0.5 M phosphate buffer solution pH 7 (with  $\text{K}^+$  cations) at a scan rate of  $60 \text{ mV s}^{-1}$ .

The cyclic voltammograms of SnHCF in the presence of 0.5 M phosphate buffer, containing no deliberately added electroactive material, were recorded between  $-0.25$  and  $0.6 \text{ V vs. SCE}$  at various scan rates  $10\text{--}350 \text{ mV s}^{-1}$  (Fig. 2A). As can be seen, a single and well-defined redox couple was observed. The anodic and cathodic peak potential were  $0.195$  and  $0.154 \text{ V vs. SCE}$ , respectively, at a scan rate of  $20 \text{ mV s}^{-1}$ . The formal potential, taken as the average of the anodic and cathodic peak potential,  $E_0 = (E_{\text{pa}} + E_{\text{pc}})/2$ , was about  $174 \text{ mV}$  and was almost independent of the potential scan rate for sweep rates ranging from  $20$  to  $1000 \text{ mV s}^{-1}$ . The formal potential for SnHCF was in order of that of PB. The formal potential for all hexacyanoferrate ME are compared in Table I. The  $I_{\text{pa}}/I_{\text{pc}}$  ratio remained almost unity and the peak separation,  $\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$ , was  $41 \text{ mV}$  at a scan rate of  $20 \text{ mV s}^{-1}$ ; at higher scan rates, the peak separation increased ( $327 \text{ mV}$  for  $1 \text{ V s}^{-1}$ ) indicating a limitation arising from the charge transfer kinetics. The peak currents of the voltammogram were linearly proportional to the scan rate up to  $350 \text{ mV s}^{-1}$ , which is expected for a surface confined redox process (Fig. 2B). For scan rates higher than  $350 \text{ mV s}^{-1}$ , the anodic and cathodic peak currents were proportional to the square root of the scan rate, which is expected for a diffusion-controlled electrode process. The electrode reaction was similar to those reported for other hexacyanoferrates. The redox couple was observed at relatively lower potential. The redox couple, corresponding to the surface-confined iron centers (Fe(III)/Fe(II)), has a formal potential of  $E_0 = 0.174 \text{ V vs. SCE}$ . The electrochemical reaction process can be expressed as follows:



As indicated in Table I, the formal potential of most transition metals are higher than  $0.5 \text{ V vs. SCE}$ , but the formal potential for SnHCF is low and in the order of that of PB. Therefore, it can be used for the electrocatalysis of some substrates which can not be catalyzed by other MHCF.

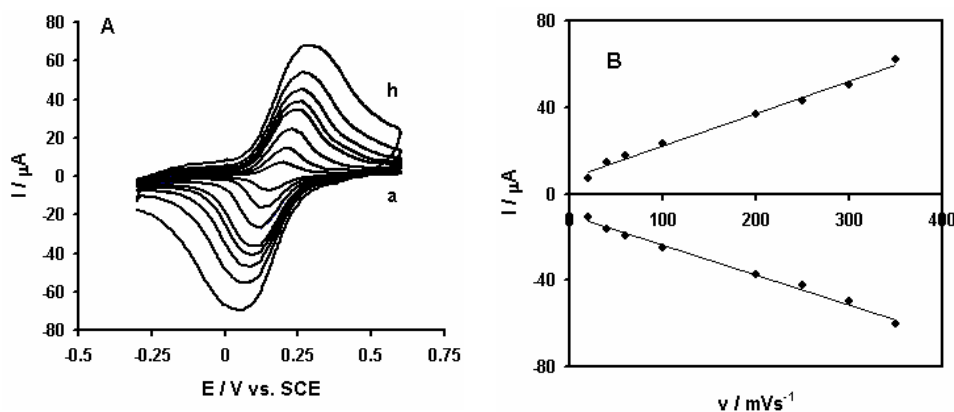


Fig. 2. A) Cyclic voltammograms of the SnHCF electrode in 0.5 M phosphate buffer solution, pH 7; potential scan rates: a) 20, b) 40, c) 60, d) 100, e) 200, f) 250, g) 300 and h) 350 mV s<sup>-1</sup> and B) plot of the anodic and cathodic peak currents vs. potential scan rate. Electrode diameter was 2 mm.

TABLE I. Formal potential of MHCf modified electrodes that have been reported until now

Modifier	Substrate	Electrolyte	Formal potential V vs. SCE or Ag/AgCl <sup>a</sup>	Ref.
PB: FeHCF	Pt	1.0 M KCl	0.2	18
Ag <sub>3</sub> HCF	Pt, Au	1.0 M KNO <sub>3</sub>	0.739	35
CdHCF	Pt	1.0 M KNO <sub>3</sub>	0.58	3
CrHCF	GC <sup>b</sup>	1.0 M KCl	0.62	4
CoHCF	GC	1.0 M NaCl	0.38	6
CuHCF	GC	1 M KCl	0.70	10
DyHCF	GC	0.2 M KCl	0.21, 0.362	13
GaHCF	Ga	1.0 M KCl	0.931 V	14
InHCF	GC	0.5 M KCl	0.74 <sup>a</sup>	15
LaHCF	Pt	1 M KCl	0.32	21
MnHCF	Sol-gel	0.1 M KCl	0.545 <sup>a</sup>	22
MoHCF	Pt	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.15 <sup>a</sup>	24
NiHCF	Al	0.5 M NaNO <sub>3</sub>	0.44	27
OsHCF	GC	0.1 M KCl	0.44 <sup>a</sup>	29
PdHCF	Al	0.5 M KNO <sub>3</sub>	0.697	31
PtHCF	GC	1 M KCl	0.76	32
RuHCF	GC	0.1 M KCl	0.31 <sup>a</sup> , 0.96 <sup>a</sup>	33
SmHCF	GE <sup>c</sup>	0.2 M NaCl	0.18	34
SnHCF	CPE <sup>d</sup>	0.5 M Phosp. buffer (K)	0.174	This Article
TiHCF	GC	1 M HCl	-0.01	37
VHCF	Pt	5 M H <sub>2</sub> SO <sub>4</sub>	0.9 <sup>a</sup> , 1.06 <sup>a</sup>	38
ZnHCF	WIGE <sup>e</sup>	0.5 M KCl	0.63	41
ZrHCF	Au	1 M KCl	0.23	42
Ket-HCF <sup>f</sup>	CPE	0.1 M Phosp. buffer (K)	0.64	44

<sup>b</sup>Glassy carbon; <sup>c</sup>graphite electrode; <sup>d</sup>carbon paste electrode; <sup>e</sup>wax impregnated graphite electrode; <sup>f</sup>ketothio-phenyl-hexacyanoferrate

The surface coverage of the SnHCF modified electrode,  $\Gamma$ , represent the moles of SnHCF redox site per unit area of the electrode surface. The amount of charge,  $Q$ , consumed for the anodic peak recorded at  $50 \text{ mV s}^{-1}$ , was measured with respect to the base line and used to calculate  $\Gamma$  from the following equation:

$$\Gamma = Q/nFA \quad (3)$$

where  $n$ , and  $F$  are the number of electrons transferred in the surface redox reaction and the Faraday constant, respectively. It should be pointed out that the calculated surface coverage is an efficiency characteristic (per cross section of the electrode) and does not reflect the actual amount of SnHCF per area of carbon paste electrode. Increasing the scan rate in the range from  $20$  to  $5000 \text{ mV s}^{-1}$  causes a continual decrease of the apparent coverage from  $5.0 \times 10^{-7}$  to  $5.0 \times 10^{-8} \text{ mol cm}^{-2}$ . The decrease of the apparent coverage with increasing scan rate is probably related to the decrease of the time window and charge transfers through the modified electrode layer, which become rate limiting at higher scan rates.

#### *Effect of pH*

Cyclic voltammetry was also used to study the effect of pH of phosphate buffers on the peak currents. The results are illustrated in Fig. 3, from which it can be seen that the peak currents increase with increasing pH up to 10. A  $0.5 \text{ M}$  phosphate buffer solution (pH 8) was selected and used as the pH for the further studies. Most MHCFs are stable in neutral or weakly acidic solutions, but this modified electrode shows a larger peak current and stability in basic solutions. This can be related to the stability of SnHCF in basic solutions, whereas other metal hexacyanoferrates hydrolyze at higher pH values and are gradually dissolved.

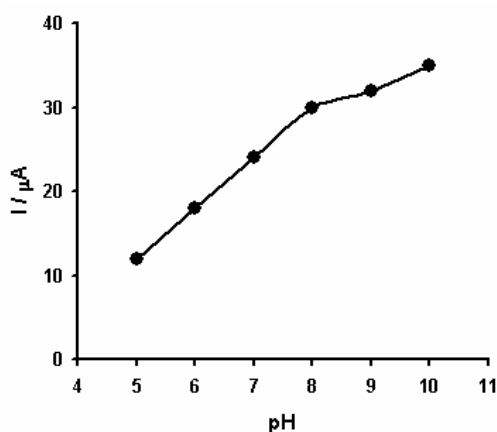


Fig. 3. Effect of pH on the peak currents of SnHCF in  $0.5 \text{ M}$  phosphate buffer solution.

#### *Stability of modified electrode*

The stability of the SnHCF modified electrode was examined by repetitive scans in the  $0.5 \text{ M}$  phosphate buffer solution. During the first few scans, the peak

current increased with continuous scanning. Subsequently, negligible variation in the height and separation of the cyclic voltammetric peaks was observed. The SnHCF modified electrode was stable under repeated CV scanning. The response of modified electrode had decreased by 5 % after 100 cycles. Furthermore, there was no loss of redox activity after storing the modified electrode in air for a month.

#### *Ion effect on electrochemical behavior of SnHCF*

In order to maintain the electroneutrality of the SnHCF film, motion of counter cations always accompanies electron transfer during the redox process. Thus, cations can have a considerable effect on the electrochemical behavior of SnHCF films. In this study, the cations  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  at the same concentration (0.5 M) were examined (Fig. 4). The obtained results showed that the peak currents were higher and the peak separation larger in the presence of  $\text{Na}^+$  cations than in the presence of  $\text{K}^+$  cations, while the peaks are completely depressed in the presence of  $\text{Li}^+$ . It is feasible that hydrated  $\text{Li}^+$  ions enter the channels of the SnHCF lattice where they become trapped, thus blocking access to all channels into the lattice. Therefore, even by changing the counter ion of the bulk electrolyte, no redox signal was observed. Therefore, it can be concluded that the SnHCF modified electrode exhibits a preference for alkali metal cations in order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$  in aqueous solution. The results also lead to the conclusion that sodium and potassium cations can freely penetrate into the SnHCF crystal lattice. The results of the study also showed that the voltammetric characteristic of the SnHCF electrode was strongly affected by the nature of anions present in the solution. Therefore, the effect of various anions, such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and phosphate was studied. The obtained results showed well-defined and reproducible cyclic voltammograms in 0.5 M phosphate buffer solution.

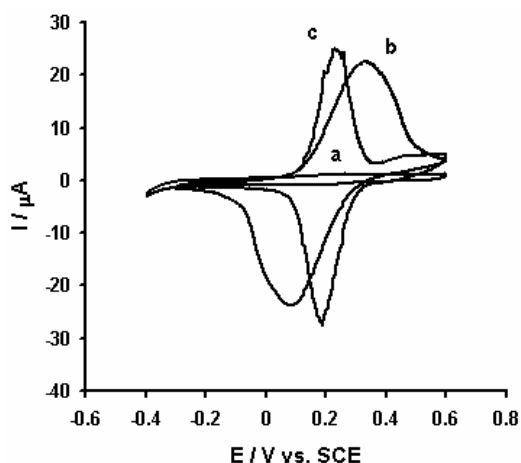


Fig. 4. Cyclic voltammograms of the SnHCF electrode in the presence of 0.5 M alkali metal cations (a)  $\text{LiCl}$ , (b) phosphate buffer solution containing  $\text{Na}^+$  cations (c) phosphate buffer solution containing  $\text{K}^+$  cations; scan rate:  $60 \text{ mV s}^{-1}$ .

### Charge transfer rate in the film

Laviron derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electro-active species.<sup>47</sup> From these expressions, it is possible to determine the transfer coefficient ( $\alpha$ ) by measuring the variation of the peak potentials with scan rate,  $\nu$ , as well as the apparent charge transfer rate constant ( $k_s$ ) for electron transfer between the electrode and a surface deposited layer. According to Laviron's expressions, a plot of  $E_p - E_0 = f(\log \nu)$  yields two straight lines with a slope equal to  $2.3RT/\alpha nF$  for the cathodic peak and  $2.3RT/(1-\alpha)nF$  for the anodic peak. An example of this plot for the SnHCF film in 0.5 M phosphate buffer is shown in Fig. 5. Using such a plot and the following equation:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log \frac{RT}{nF\nu} - \alpha nF(1-\alpha) \frac{\Delta E_p}{2.3RT} \quad (4)$$

the values of  $\alpha$  and  $k_s$  were found to be 0.6 and  $2.1 \pm 0.2 \text{ s}^{-1}$ , respectively. Notice that the surface coverage,  $\Gamma$ , evaluated from the relation  $\Gamma = Q_H/nFA$  was about  $5.0 \times 10^{-8} \text{ mol cm}^{-2}$  at a scan rate of  $20 \text{ mV s}^{-1}$ . Further experiments showed that the values obtained for  $\alpha$  and  $k_s$  remained almost constant for  $\Gamma$  values in the range  $10^{-7}$ – $10^{-8} \text{ mol cm}^{-2}$ . The peak separation will be close to zero when the electron transfer rate is fast relative to the scan rate and will increase when the electron transfer rate is slow.

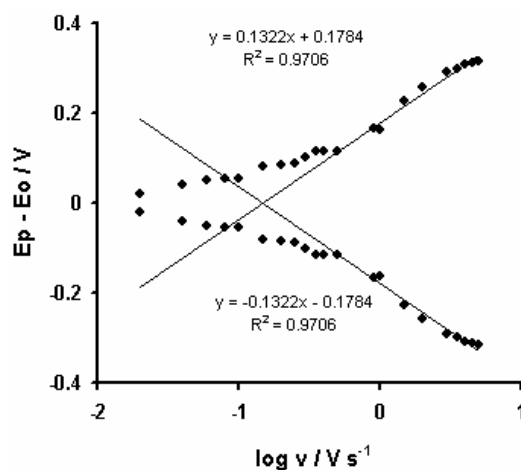


Fig. 5. Plot of  $E_p - E_0$  vs.  $\log \nu$  for cyclic voltammograms recorded for the SnHCF electrode in 0.5 M phosphate buffer solution at scan rates between  $0.01$ – $1 \text{ V s}^{-1}$  for the anodic and cathodic peaks.

### Diffusion coefficient of $K^+$ and $Na^+$ in the film

The height of the cyclic voltammogram peaks obtained at scan rates  $> 350 \text{ mV s}^{-1}$  is an important criterion, which can be related to the facility of cation diffusion in a modified film.<sup>34</sup> The peak current of cyclic voltammograms obtained at scan rates higher than  $350 \text{ mV s}^{-1}$ , in the presence of potassium cations was proporti-

onal to the square root of the scan rate,  $v^{1/2}$ , indicating its diffusion nature. According to the experimental results, the diffusion coefficient of the cations in the modifier film could be calculated using the equation:<sup>48</sup>

$$I_p = 2.99 \times 10^5 n^{3/2} \alpha^{1/2} A D^{1/2} c v^{1/2} \quad (5)$$

where  $D$  is the diffusion coefficient of the cations in the film ( $\text{cm}^2 \text{s}^{-1}$ ),  $A$  the electrode area ( $0.045 \text{ cm}^2$ ),  $v$  potential scan rate ( $\text{V s}^{-1}$ ) and  $I_p$  the peak current (A). Since at high scan rates, not all redox sites, including mixed valence iron, in the film are electroactive due to an insufficient amount of counter ions in the film, in Eq. (5),  $c$  represents the concentration of alkali metal cations in the film ( $\text{mol cm}^{-3}$ ). The value of  $c$ , which varies with the scan rate, was calculated by means of the total moles of cations in the film, obtained from  $Q_H$  (the area under cyclic voltammograms recorded at scan rates higher than  $350 \text{ mV s}^{-1}$ ) and the total volume of the film obtained from  $Q_L$  (the area under the cyclic voltammogram recorded at a scan rate of  $20 \text{ mV s}^{-1}$ ). Using a plot of  $I_p$  vs.  $cv^{1/2}$ , the diffusion coefficient for  $\text{Na}^+$  and  $\text{K}^+$  was calculated to be  $(2.45 \pm 0.23) \times 10^{-10}$  and  $(4.83 \pm 0.34) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , respectively. A typical example of these plots is shown in Fig. 6 for the cyclic voltammogram peaks recorded in the presence of  $\text{K}^+$ .

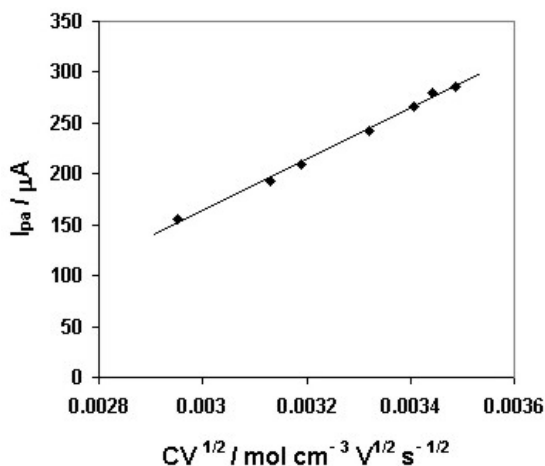


Fig.6. Plot of  $I_{pa}$  vs.  $cv^{1/2}$  for cyclic voltammograms recorded for the SnHCF electrode ( $A = 0.0314 \text{ cm}^2$ ) in 0.5 M phosphate buffer solution with  $\text{Na}^+$  cations at scan rates between 0.3 and  $5 \text{ V s}^{-1}$  for anodic peak currents.

#### CONCLUSIONS

The preparation of a SnHCF modified electrode using tin chloride and hexacyanoferrate was reported. The preparation of the modified electrode is easy, fast, and reproducible. This modified electrode showed good stability toward potential recycling. Both the pH of the solution and the alkali metal cations and anions of the supporting electrolyte have a considerable effect on the electrochemical behavior of the film.  $\text{K}^+$  and  $\text{Na}^+$  ions can freely enter the SnHCF crystal lattice, while hydrated  $\text{Li}^+$  are probably trapped in the SnHCF lattice. The prepared modified electrode is stable for several weeks in air, as well as in 0.5 M phosphate buffer solution.



## ИЗВОД

ПРИПРЕМА И КАРАКТЕРИЗАЦИЈА ЕЛЕКТРОДЕ НА БАЗИ КАРБОНСКЕ ПАСТЕ  
МОДИФИКОВАНЕ ЈОНИМА КАЛАЈА И ХЕКСАЦИЈАНОФЕРАТА

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Електроде на бази карбонске пасте су хемијски модификоване калај(II) или калај(IV) хлоридом и хексацијаноферат(II) или хексацијаноферат(III) јоном. Њихово електрохемијско понашање је испитивано цикличном волтаметријом. Показано је да Sn(IV) и хексацијаноферат(II) дају најбоље резултате. Циклични волтамограм такве SnHCF електроде је окарактерисан једним паром пикова: анодним на 0,195 V и катодним на 0,154 V (према ЗКЕ) при брзини линеарне промене потенцијала  $20 \text{ mV s}^{-1}$  и у 0.5 M фосфатном пуферу као основном електролиту. Током циклизирања потенцијала електрода се показала као веома стабилна. Испитиван је ефекат pH основног електролита и присутних катјона алкалних метала на електрохемијске карактеристике SnHCF електроде. Утврђено је да катјони имају значајан ефекат. Одређени су коефицијенти дифузије хидратисаних јона  $\text{K}^+$  and  $\text{Na}^+$  у филму, коефицијент прелаза и константа брзине прелаза електрона.

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