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Electroless preparation and electrochemical behavior of a platinum-doped nickel hexacyanoferrate film–zinc modified electrode: catalytic ability of the electrode for electrooxidation of methanol

Abstract The use of a zinc substrate as an electrode and the modification of its surface by means of a thin film of platinum-doped nickel hexacyanoferrate (Pt-NiHCF) were developed. The modification conditions of the zinc surface including the electroless deposition of metallic nickel on the electrode surface from $NiCl_2$ solution, chemical derivatization of the deposited nickel to the NiHCF film in 0.5 M $K_3[Fe(CN)_6]$ solution, and electrochemical penetration of metallic platinum into the modified film are described. The modified zinc electrodes prepared under optimum conditions show a well-defined redox couple due to the $[Ni^{II}Fe^{III/II}(CN)_6]^{1-/2-}$ system. The effects of pH, the alkali metal cation, and the anion of the supporting electrolyte on the electrochemical characteristics of the modified electrode were studied in detail. The diffusion coefficients of hydrated alkali metal cations in the film (D), the transfer coefficient (α), and the transfer rate constant for the electron (k_s) were calculated in the presence of some alkali metal cations. The electrocatalytic activity of the modified electrode for methanol oxidation was demonstrated. The stability of the modified electrode under various experimental conditions was investigated.

Keywords Modified electrode · Zinc electrode · Nickel hexacyanoferrate film · Electroless modification · Platinum · Methanol oxidation

Introduction

Interest in the fabrication and subsequent electrochemical, spectral, and impedance characterization of many metal cyanoferrates emanates from the pioneering work carried out by Neff and coworkers. The modification of the electrode surface with metal cyanoferrate is carried out by chemical or electrochemical formation of insoluble transition metal cyanoferrate [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] or immobilizing mechanically the metal cyanoferrate as microparticles on the surface of the electrode [12, 13, 14]. Most research activities use Pt, Au or glassy carbon as matrices for the preparation of the modified electrodes in electroanalytical studies. Recently the modification of Al substrate with various transition metal cyanoferrates has been reported by Pournaghi-Azar et al. [8, 9, 15, 16, 17, 18]. The widespread use of zinc in batteries, its low cost, and the simplicity of the zinc surface modification with organic protective and conductive polymers attract our attention to this useful substrate.

As a typical example of zinc electrode modification with metal cyanoferrates, this paper deals with the preparation of a platinum-doped nickel hexacyanoferrate film|zinc (Pt-NiHCF|Zn) modified electrode via a simple dipping method and provides a detailed study of the electrochemical behavior of the electrode. It is intended to demonstrate the ability of the modified electrode for methanol oxidation.

Experimental

Chemicals and reagents

A commercial zinc bar with purity 99.9% was used as the substrate for the electrode matrix. Nickel chloride, potassium ferricyanide, phosphoric acid, sodium and potassium hydroxide, and lithium, sodium, potassium, rubidium, and cesium carbonates were of analytical grade from Merck; the chloroplatinic acid was from BDH, England. The lithium, sodium, potassium, rubidium, and cesium phosphate salts were prepared from the carbonate salts by gradual addition of H_3PO_4 solution to the carbonate solutions, then the solutions were heated to evaporate the water and carbonic acid ($H_2O + CO_2$) and crystallize the phosphate salts. All solutions were prepared with doubly distilled water.

Instrumentation

The electrochemical experiments were carried out using an EG&G PAR potentiostat/galvanostat model 273A coupled with an IBM personal computer connected to a Hewlett-Packard LaserJet 5L

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printer. A conventional three-electrode cell was used at room temperature (r.t.). A saturated calomel electrode, a platinum wire, and a zinc disk modified electrode of surface area 0.071 cm^2 were used as the reference electrode (RE), auxiliary electrode (AE), and working electrode (WE), respectively.

Electrode preparation

A cubic zinc bar was melted and filled in a cylindrical experimental glass tube, 12 mm in diameter and 90 mm in length. A cylindrical zinc bar was obtained, which was used for the preparation of the rotating-disk zinc electrode as follows.

The 30-mm-diameter cylindrical bar was diminished to 3 mm and then fitted into a Teflon rod of 12 mm diameter and 30 mm length. The zinc extremity of this bar was threaded by means of a suitable screw tap in order to connect it to an available rotating-disk system. The zinc surface fitted in the Teflon tube [8] was polished, first by a medium emery paper (320 grit) and then by a fine grade (1,500 grit) to expose a relatively mirror-like surface. The polished surface was rinsed with doubly distilled water. The Pt-NiHCF film preparation was carried out in three different steps: deposition of metallic nickel on the zinc substrate, derivatization of the nickel to a NiHCF film, and deposition of metallic Pt on the film. The electroless deposition of metallic nickel was carried out by dipping the cleaned surface in 2 M NiCl$_2$ solution (plating solution). The thickness of metallic nickel deposited on the electrode surface depends on the immersion time of the electrode in the plating solution (in this work the plating time was 1 min). The zinc electrode covered by metallic nickel was rinsed with doubly distilled water and then derivatized to NiHCF film by immersing it in freshly prepared 0.5 M K$_3$[Fe(CN)$_6$] (derivatizing solution) for about 2 h. Indeed, under these conditions, the chemical transformation of the metallic nickel to nickel hexacyanoferrate (NiHCF) film occurred via a chemical oxidation reaction of metallic nickel to Ni^{2+} and a complexation reaction between Ni^{2+} and the hexacyanoferrate anion at the electrode surface. In order to achieve morphological stabilization of the crystal lattice of the film, the freshly prepared electrode was cycled between 0.0 and 0.8 V versus a saturated calomel electrode (SCE) for about 20 cycles with a scan rate of 50 mV s^{-1}. Metallic platinum was then deposited on the film by a galvanostatic deposition procedure with a current density of 2 mA cm^{-2} using a 10^{-3} M solution of PtCl$_6^{2-}$ and 0.5 M potassium phosphate as supporting electrolyte. The surface concentration of the mediator in the film per unit surface area of the electrode (Γ) was determined from the area under the anodic part of the cyclic voltammogram peaks of the Pt-NiHCF|zinc electrode at low scan rate.

Results and discussion

Optimization of electrode modification process

We found that the simplicity and rapidity of the modified zinc electrode preparation, as well as the electrode stability and reproducibility of its electrochemical behavior, depended very much on the experimental variables such as concentration of NiCl$_2$, Fe(CN)$_6^{3-}$, and PtCl$_6^{2-}$, nickel plating time of the zinc surface, derivatization time of the nickel-coated zinc surface to NiHCF, and finally deposition time and electrochemical conditions for deposition of platinum on the NiHCF film.

Considering the surface electrochemical characteristics of the modifier layer, including peak separation $\Delta E = E_{pa} - E_{pc}$ (close to zero), peak ratio i_{pa}/i_{pc} (close to unity), thin film, lack of ZnHCF film formation, and

stability of the film, we found that the following experimental conditions for electrode modification are the most suitable:

- A 2 M solution of NiCl$_2$ as the plating solution.
- A 0.5 M freshly prepared solution of Fe(CN)$_6^{3-}$ as the derivatization solution.
- A 10^{-3} M solution of PtCl$_6^{2-}$ for Pt deposition.
- A nickel plating time of 1 min and derivatization time of 1 h, and a platinum deposition time of 5 min and electrolysis current of 2 mA cm^{-2}.

We found that cycling the freshly prepared modified electrode (about 20 cycles) in a potential range between 0.0 and 0.8 V vs. SCE increases the cyclic voltammetric current and reversibility of the redox process of the film. The physical characteristics of Pt-NiHCF film on the electrode were studied by SEM and the micrograph of the surface showed that the metallic platinum is incorporated as microparticles in the NiHCF film.

Electrochemical characterization of the modified electrode

General aspects

The Pt-NiHCF film-modified Zn electrode prepared under optimum conditions was characterized by cyclic voltammetry (CV). The representative cyclic voltammograms obtained for the Pt-NiHCF film after 100 cycles between 0.0 and 0.8 V in 0.5 M potassium phosphate solution, containing no deliberately added electroactive material, are shown in Fig. 1A for various scan rates. The observation of well-defined and persistent cyclic voltammetric peaks after 100 cycles provides evidence for prolonged surface attachment of the film. We observed that these peaks were not affected by stirring of the electrolyte, offering more proof that the material is well associated with the electrode surface. As seen in Fig. 1A, a single and well-defined redox couple (with peak potentials $E_{pa} = 0.550$ V, $E_{pc} = 0.490$ V) appeared in this electrolyte solution. Since the Ni^{2+} cations in the modifying film are not expected to be electroactive in the potential range examined (0.0–0.8 V), the reaction should be attributed to the reversible redox behavior of hexacyanoferrate(III/II) in the film. The peak currents of the voltammograms are linearly proportional to the scan rate between 20 and 200 mV s^{-1} (Fig. 1B). The ratio of i_{pa}/i_{pc} remains almost equal to unity, as is expected for surface-type behavior. The peak potential separation ΔE_p is at least 15 mV for a potential scan rate of 20 mV s^{-1}. This slight deviation of the redox process from the ideal surface redox process ($\Delta E_p = 0$) appearing even at low scan rates may be attributed to several factors, but mainly to the limitations associated with charge propagation in the film [8]. At scan rates higher than 200 mV s^{-1}, a wider splitting appears indicating the limitation arising from the charge transfer kinetics. The anodic and cathodic peak currents are linearly

Fig. 1 A Cyclic voltammograms of the Pt-NiHCF|Zn electrode in 0.5 M K$_2$HPO$_4$, potential scan rates 25–200 mV s^{-1}(25 mV s^{-1} interval) and 200–1,000 mV s^{-1}(100 mV s^{-1} interval), and plot of anodic (*a*) and cathodic (*b*) peak currents versus **B** potential scan rate *v*, and **C** square root of scan rate $v^{1/2}$
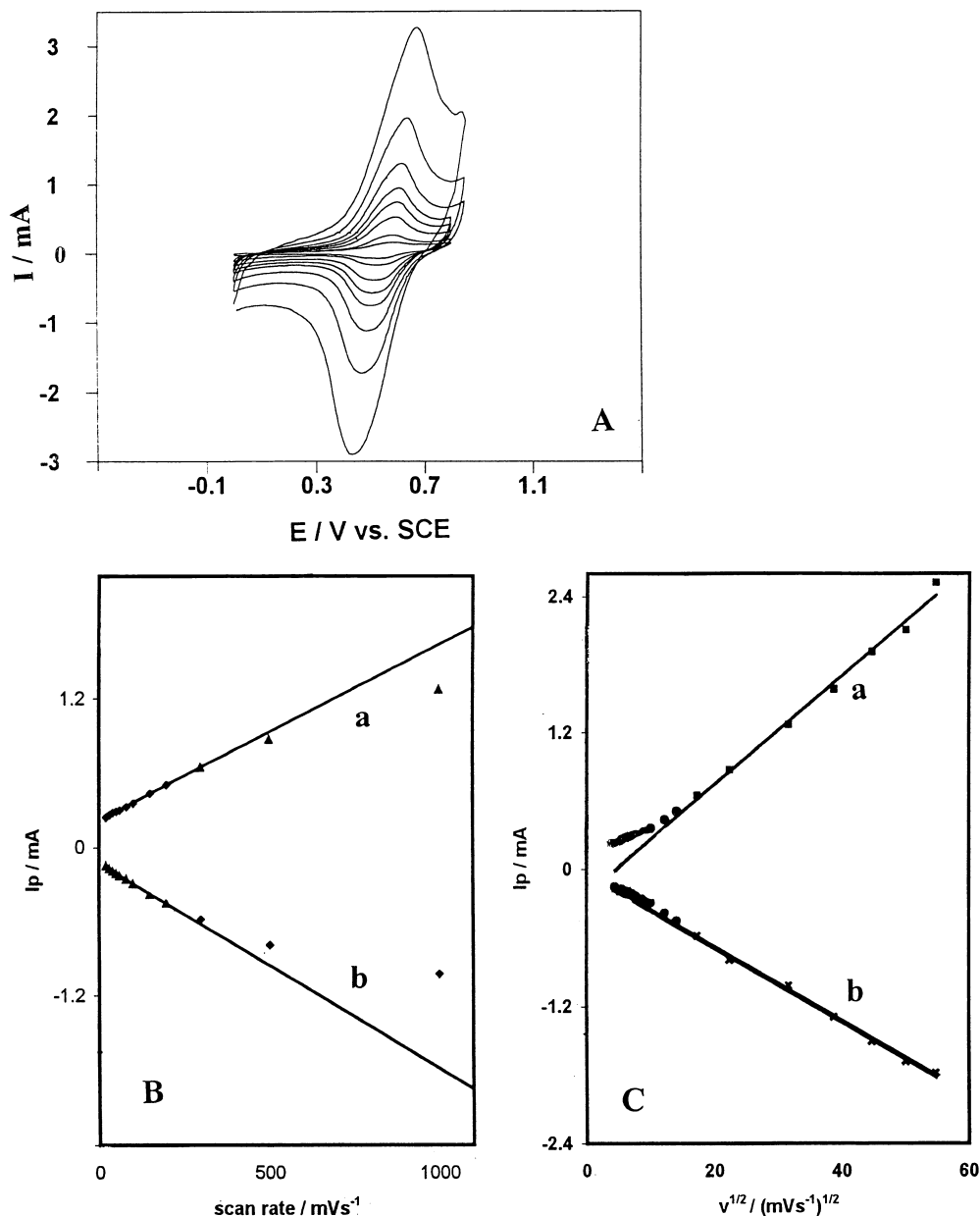
proportional to the square root of scan rate, $v^{1/2}$ ($r = 0.998$) (Fig. 1C), which is expected for a diffusion-controlled electrode process.

Effect of pH

The bare zinc electrode in alkaline cation phosphate solutions over the pH range 5–11 is not electrochemically stable. The voltammetric behavior of the Pt-NiHCF film-modified zinc electrode was characterized at various pHs by CV. As seen in Fig. 2, the peak potential and peak currents of the Pt-NiHCF|zinc electrode in 0.5 M potassium phosphate of pH 3–12 (adjusted by addition of concentrated H$_3$PO$_4$ or 10 M KOH solutions) remained unchanged, and the Pt-NiHCF film showed a considerable protective effect on the zinc

substrate against electrochemical corrosion. However, repetitive potential scanning at the Pt-NiHCF film-modified zinc electrode in solutions of pH lower than 3 and higher than 12 leads to film degradation. Therefore, a suitable pH range of 4–11 (pH = 7.0) was chosen for the electrochemical experiments.

Effect of alkali metal cations

In order to maintain the electroneutrality of the modified film during the electrochemical process, ions usually enter or leave the immobilized film, so ions have a considerable effect on the electrochemical behavior of the modified electrodes. The effect of alkali metal cations on the voltammetric behavior of the Pt-NiHCF film was studied by CV. Figure 3A shows the cyclic voltammo-
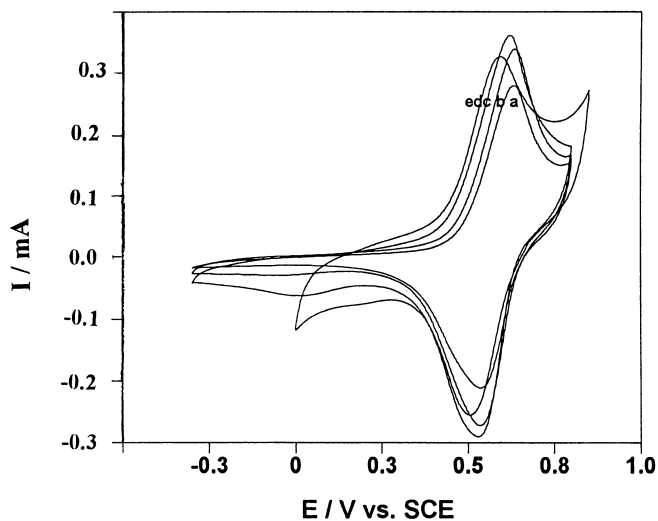
Fig. 2 Cyclic voltammograms of the Pt-NiHCF|Zn electrode in 0.5 M K$_2$HPO$_4$ at pH *a* 3, *b* 5, *c* 7, *d* 9, *e* 11; potential scan rate 300 mV s^{-1}

grams of the Pt-NiHCF|Zn modified electrode recorded in the presence of different alkali metal cations: Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ of the same concentration. The cyclic voltammograms are well-defined in the presence of all the cations, indicating that they can freely penetrate the Pt-NiHCF crystal lattice.

The electrochemical behavior of the modified electrode may be indicative of some characteristics of the film, depending on the nature or size of the alkali metal cations in the solution. These are discussed from five different aspects as follows.

Redox potential of the film

The surface redox potential $E^{0\prime}$, taken to be the average of the anodic and cathodic voltammetric peak positions $((E_{pa} + E_{pc})/2)$, shifts monotonically with atomic number as one substitutes into the supporting electrolyte the various group 1A cations (Fig. 3B). The value of E$^{0\prime}$ changes by about 380 mV on going from Li$^+$ to Cs$^+$. This change rules out a simple shift in the Nernstian equilibrium as the source of ion-pair or complex formation with the anion in solution, at most 10–50 mV as a function of the cation present [4]. A possible explanation for the shift in $E^{0\prime}$ is that the different cations interact with the surface species in a way that perturbs the electronic energy of the surface species and thus $E^{0\prime}$. The interaction would have to be reversible, since the change in $E^{0\prime}$ is reversible and reproducible with electrolyte. Note that the peak potential shifts with radius of hydrated alkali metal cation as well as its free energy of hydration ($\Delta G^0_{hyd.}$), but the change is not monotonic (Fig. 3C).

Affinity of the film

In the analysis of cation size it is assumed that the surface interactions are taking place under conditions in
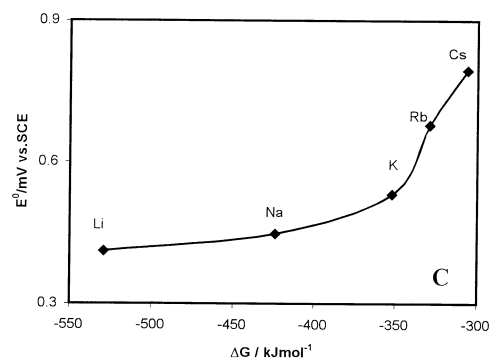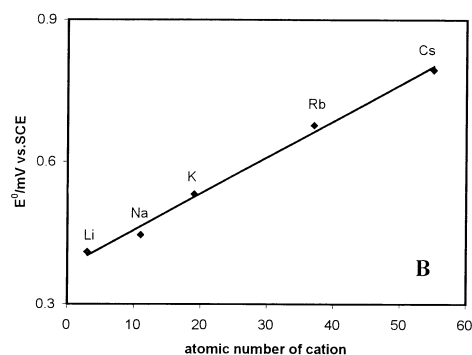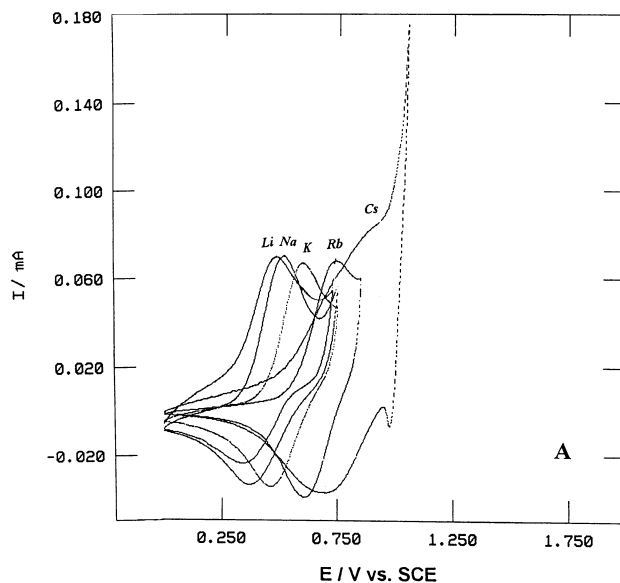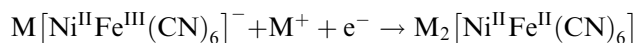

Fig. 3 A Cyclic voltammograms of the Pt-NiHCF|Zn electrode in the presence of different alkali metal cation phosphate supporting electrolytes at the same concentration (0.5 M); potential scan rate 100 mV s^{-1}. **B** Plot of $E^{0\prime}$ vs. atomic number of alkali metal cation. **C** Plot of $E^{0\prime}$ vs. $\Delta G^0_{hyd.}$ of alkali metal cation

which the cations are hydrated [19] or partially hydrated [20], according to the solution conditions and morphology of the surface layer. Therefore, the cation size is determined by the ionic radius plus the radius of the hydration sphere, making Cs$^+$ the smallest ion and Li$^+$ the largest. The assignment of ionic size is based on the observation that the surface can be synthesized with relatively fast substitution kinetics for Cs$^+$ (the smallest hydrated cation) incorporation, but slow kinetics for

Li$^+$ (largest hydrated cation) incorporation. This proposition can be established from competition experiments. For example, with addition of Rb$_2$HPO$_4$ to the solution with a concentration less than that of Na$_2$HPO$_4$, the Na$^+$-associated peaks disappeared and the Rb$^+$-associated peaks appeared at a more positive potential. In contrast, the Rb$^+$-associated cyclic voltammograms observed in 0.2 M Rb$_2$HPO$_4$ solution did not change or shift with addition of Na$_2$HPO$_4$at a concentration over more than four times the Rb$_2$HPO$_4$ concentration. This clearly indicates a preference for Rb$^+$ over the Na$^+$ cation. On the basis of the results obtained from similar studies for the other alkali metal cations, we concluded that the Pt-NiHCF film shows the following surface affinity ranking: Cs$^+$ > Rb$^+$ > K$^+$ > Na$^+$ > Li$^+$.

This ordering parallels the observed change in $E^{0\prime}$ or thermodynamic tendency of the film for cations, due to the size of the hydrated cation and thus its ability to enter into the crystal lattice during the electrochemical reduction process as follows:

$$M\left[Ni^{II}Fe^{III}(CN)_6\right]^- + M^+ + e^- \rightarrow M_2\left[Ni^{II}Fe^{II}(CN)_6\right]$$

Charge transfer rate in the film

For a Pt-NiHCF|Zn electrode, the peak-to-peak separation potential ($\Delta E = E_{pa} - E_{pc}$) of the cyclic voltammogram recorded for scan rates up to 200 mV s^{-1} was 80 mV in the presence of K$_2$HPO$_4$ as supporting electrolyte. At higher scan rates, this value increases indicating the limitation arising from some phenomena. These include: (i) a slow electron transfer between the Zn and Pt-NiHCF, (ii) a slow electron transfer from one redox center to the other inside the film (electron diffusion), (iii) slow diffusion of alkali metal cation in the film, and (iv) uncompensated ohmic drop. When the limitation is attributed only to charge transfer kinetics, Laviron derived general expressions for the cyclic voltammetric response according to the $\Delta E_p = E_{pa} - E_{pc}$ value observed [21].

For $\Delta E_p > 200/n$ mV obtained at very high scan rates, the following relations were proposed:

$$E_{pa} = E^0 + A\ln\left[(1-\alpha)/m\right] \quad (1)$$

$$E_{pc} = E^0 - B\ln(\alpha/m) \quad (2)$$

$$\log k_S = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nFv) \\ - \alpha(1-\alpha)nF\Delta E_p/2.3RT \quad (3)$$

where $A = RT/(1-\alpha)nF$, $B = RT/\alpha nF$, and $m = (RT/F)(k_s/nv)$. From these expressions it is possible to determine the transfer coefficient (α) by measuring the variation of the peak potentials with scan rate (v), as well as the apparent charge transfer rate constant (k_s) for electron transfer between the electrode and the surface-deposited layer. A plot of $E_p = f(\log v)$ yields two straight lines with slopes equal to $2.3RT/\alpha nF$ and $2.3RT/(1-\alpha)nF$ for the cathodic and anodic peaks, respectively. We have found that for scan rates higher than 4,000 mV s^{-1}, depending on the supporting electrolyte cation, the values of E_p were proportional to the logarithm of scan rate as indicated by Laviron. One typical example of these plots is shown in Fig. 4 for Pt-NiHCF film in the presence of 0.5 M K$_2$HPO$_4$.

For $\Delta E_p < 200/n$ mV commonly observed at low scan rates, and when the limitation arising from slow diffusion of electron or alkali metal cation in the film and uncompensated ohmic drop can be omitted, Laviron provided some working curves allowing determination of α and k_s. Using such working curves and experimental ΔE_p values measured at scan rates lower than 200 mV, the values of α and k_s were determined for the Pt-NiHCF|Zn electrode in the presence of alkali metal cations of the same concentration and are shown in Table 1. Note that the values obtained for α and k_s are nearly independent of the surface coverage (Γ) at a range 5×10^{-9}–5×10^{-8} mol cm^{-2}.

Permeability of the film

The height of the cyclic voltammogram peaks obtained for scan rates higher than 200 mV s^{-1} in the presence of different cations at the same concentrations in the electrolyte solutions is an important criterion, which can be related to the facility of cation diffusion in the modifier film [22]. The peak currents of cyclic voltammograms obtained for scan rates higher than 200 mV s^{-1}, in the presence of alkali metal cations are proportional to the square root of scan rate, $v^{1/2}$, indicating the diffusional nature of the process.
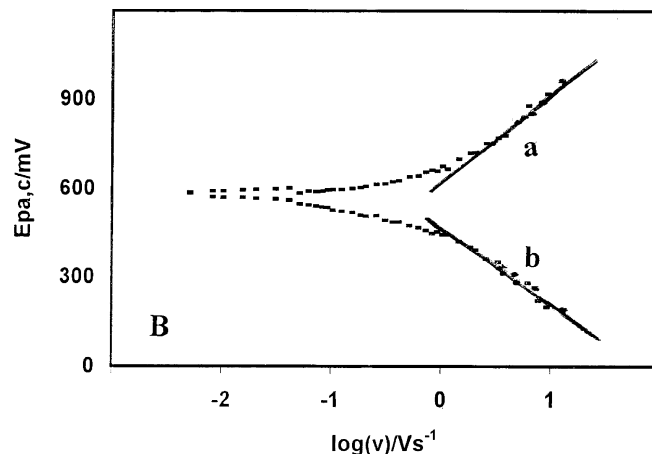

Fig. 4 Plot of E_p vs. log v for cyclic voltammograms recorded for Pt-NiHCF|Zn electrode in the presence of 0.5 M K$_2$HPO$_4$; *a* for anodic peaks, *b* for cathodic peaks

Assuming that in the presence of different alkali metal cations (with the same concentrations in the supporting electrolyte) the structure of the Pt-NiHCF film is identical, we could determine the diffusion coefficients of the cations in the film according to Eq. 4 at high scan rates [23]:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \tag{4}$$

where D is the diffusion coefficient of cation in the film (cm^2 s^{-1}), A the electrode area (cm^2), v the potential scan rate (V s^{-1}), i_p the peak current (A), and C the concentration of the electroactive sites in the NiHCF film (mol cm^{-3}).

As the reactivity of the redox sites in the film depends on the presence and concentration of the counter ion in the film, C in Eq. 4 may be replaced by the concentration of the counter ion in the modifier film. The values of C or cation concentration in the film were calculated by means of total moles of the cation in the film, obtained at any scan rate and total volume of the film on the surface of the electrode as follows:

$$C = \frac{\text{Total moles of cation in the film}}{\text{Total volume of the film}}$$
$$= \frac{Q_H/F}{(\text{Total moles of redox sites} \times M_w)/d}$$

or

$$C = \frac{Q_H/F}{[(Q_L/F) \times M_W]/d} \tag{5}$$

where Q_H and Q_L are the electric charges under cyclic voltammograms recorded at each scan rate higher than 200 mV s^{-1} and low scan rate (e.g., 50 mV s^{-1}), respectively, M_W is the molecular weight of NiHCF, and d is its density assumed to be 1.79 g cm^{-3} [8].

Using the peak currents measured from baselines for scan rates higher than 200 mV s^{-1}, and a plot of i_p versus $cv^{1/2}$, the diffusion coefficients are calculated from the slope of this plot and are given in Table 1. A typical example of these plots is shown in Fig. 5 for the cyclic voltammogram peaks recorded in the presence of K$^+$. On the basis of values of D obtained, the permeability of the Pt-NiHCF film follows the order: K$^+\approx$Rb$^+ >$ Cs$^+ >$ Na$^+\approx$Li$^+$ and we conclude that an

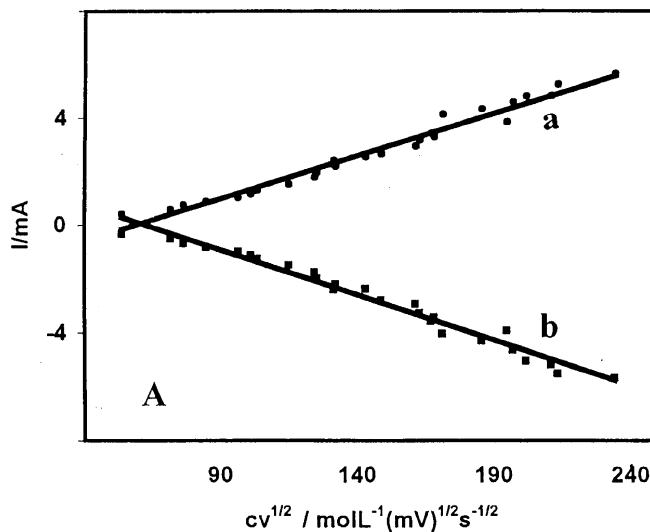**Fig. 5** Plot of i_p vs. $cv^{1/2}$ for cyclic voltammograms recorded for Pt-NiHCF|Zn electrode in the presence 0.5 M K$_2$HPO$_4$ at scan rates between 300 and 1,000 mV s^{-1}; a for anodic peaks, b for cathodic peaks

important factor affecting the value of D is the radius of the hydrated cation. If the transferring cation is large (Li$^+$), the large size does not allow easy diffusion into and through the lattice. In the case of small hydrated cations (Cs$^+$), the cation-induced microstructural distortion in the film may be a mass-transfer rate-determining factor.

Interaction of the redox sites in the film

The broadening of cyclic voltammogram peaks obtained at modified electrodes for truly thermodynamic equilibrium conditions (at extremely low scan rates) can be attributed to the presence of repulsive site-to-site interaction or the heterogeneity of the surface [24, 25]. These two factors, however, cannot be distinguished from each other. It should be noted that the surface peak of the Pt-NiHCF film in the K$^+$-containing electrolyte with a full width at half height (FWHH) value of 151 mV (for cathodic peak) at scan rate 10 mV s^{-1} is the narrowest one. With a change of supporting electrolyte cation from K$^+$ and Rb$^+$ to other alkali metal cations with smaller hydrated radii, such as Cs$^+$, or with larger hydrated radii, such as Na$^+$ and Li$^+$, the values of FWHH for the same modified zinc electrode increased in both cases (see Table 1). This indicates that the repulsive site-to-site interaction or the heterogeneity of the film can be increased in the presence of both smaller and larger cations. In the case of Cs$^+$, this may be due to the small size of hydrated Cs$^+$ causing a large lattice mismatch and thus spatially distinct interactions. On the other hand, the large radius of Li$^+$ also causes kinetic complication. Since the Li$^+$ has entered the surface structure, compressional effects have distorted the lattice, again enhancing intermolecular interactions.

Table 1 Diffusion coefficient (D) of alkali metal cations (0.5 M in the solution) in the Pt-NiHCF film, transfer coefficient (α), and charge transfer rate constant (k_s) obtained from cyclic voltammograms. The electrode area and its total surface coverage were 0.071 cm^2 and 2×10^{-8} mol cm^{-2}, respectively

Cation	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
$D\times10^{10}$/cm^2 s^{-1}	–	0.86	4.4	4.98	–
α	–	0.7	0.7	0.7	–
k_s/s^{-1}	–	1.8	1.9	0.3	–
FWHH/mV[a]	225	202	141	158	268

[a]Obtained for scan rate of 10 mV s^{-1}
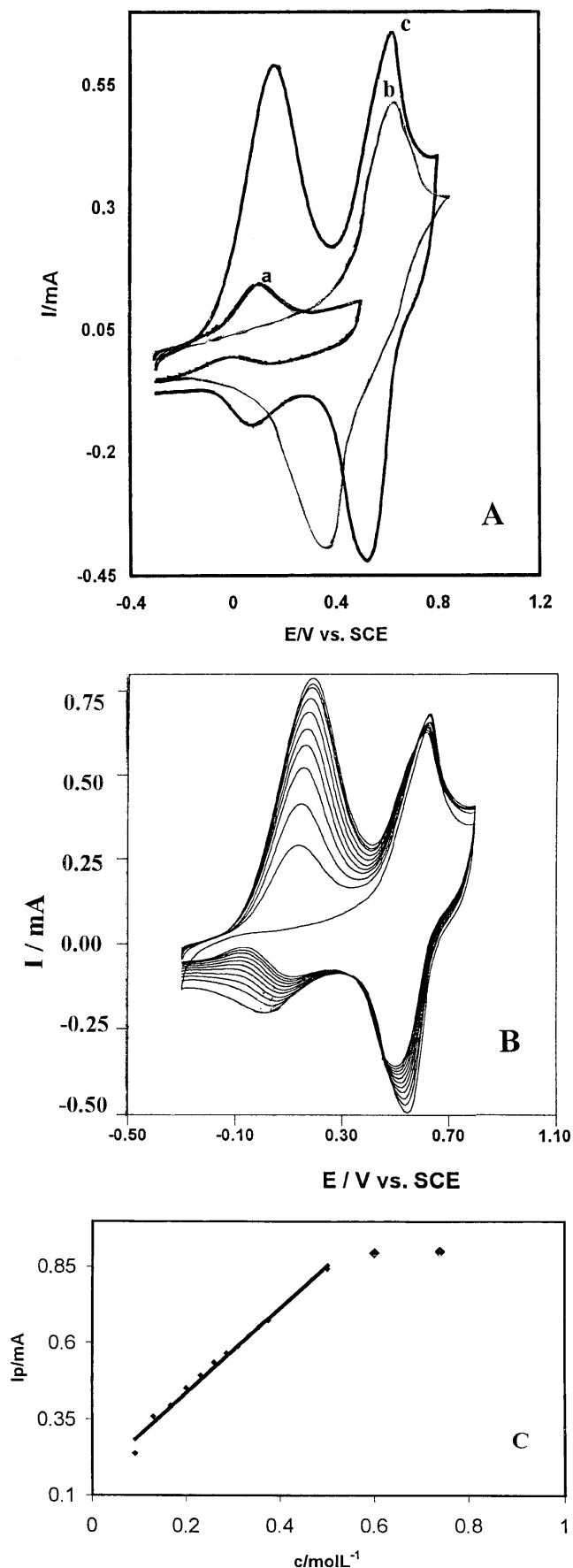
Effect of anions

Experimental investigation showed that the voltammetric characteristics of the Pt-NiHCF|Zn electrode were strongly affected by the anion present in the solution. In the presence of K_2HPO_4 buffer media, a well-defined and reproducible cyclic voltammogram was obtained. In the presence of some other anion supporting electrolytes (such as potassium salts), the characteristic peaks of the film were depressed and the order of this depressing effect was $ClO_4^- > Cl^- > NO_3^- > SO_4^{2-} > HCO_3^-$. Note that the characteristic peaks of the film observed in the K_2HPO_4 supporting electrolyte alone remain unchanged by the addition of other potassium salts of moderate concentration to the solution. This improved behavior of the modified electrode in the presence of the phosphate anions may be attributed to the formation of some nickel-substituted zincophosphate, stabilizing the Pt-NiHCF film on the zinc substrate.

Electrocatalytic oxidation of methanol on the electrode

Figure 6A shows the typical cyclic voltammograms of 0.2 M CH_3OH in 0.5 M potassium phosphate, on the bar Pt electrode (curve a), NiHCF|Zn (curve b), and Pt-NiHCF|Zn (curve c) modified electrodes. As seen in Fig. 6A, methanol is oxidized on both the Pt and Pt-NiHCF film-modified zinc electrodes at less positive potential (150 mV vs. SCE) compared with the original peak potential of the modifier film (520 mV vs. SCE), but methanol is electroinactive on the NiHCF|Zn electrode, because any anodic peak was not discernable at the less positive potential. A comparison between curves a and c in Fig. 6A leads us to conclude that the modification of the zinc surface by NiHCF, and then deposition of metallic Pt on the modifier film, ultimately reinforces significantly the efficiency of the platinum catalyst via oxidation of methanol, producing a considerable increase in the oxidation current.

Effect of methanol concentration

Figure 6B shows the effect of methanol concentration on the anodic current of the methanol oxidation. As seen in Fig. 6C, the anodic peak current increases with increasing methanol concentration and levels off at concentrations higher than 0.55 M. This effect may be attributed the saturation of active sites at the surface of the electrode. In accordance with this result, the
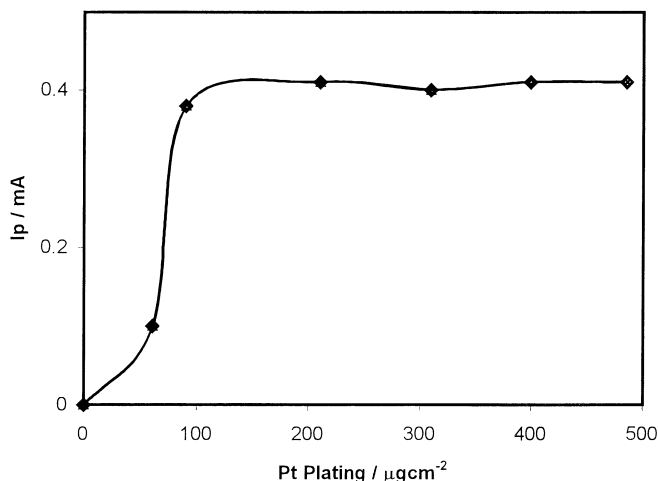
Fig. 7 Plot of the methanol oxidation peak current versus amount of metallic platinum incorporated in NiHCF film on the Zn electrode, solution conditions as Fig. 6

optimum concentration of methanol to obtain a higher current density may be considered as about 0.5 M.

Further work is currently being conducted in our laboratory in order to gain more detailed insight into the role of the Pt-NiHCF film.

Effect of Pt amount

Figure 7 shows the voltammetric response of the Pt-doped NiHCF film-modified zinc electrode prepared by doping with various amounts of platinum, in potassium phosphate buffer solution (0.5 M, pH 7) containing 0.1 M CH_3OH. The current response of the electrode increases with Pt amount and levels off at 100 $\mu g \, cm^{-2}$ Pt, indicating the saturation of the NiHCF surface sites.

Effect of solution pH

The voltammetric response of the Pt-NiHCF-modified zinc electrode in the presence of potassium phosphate buffer (0.5 M) containing 0.1 M CH_3OH was characterized at various solution pHs. We have found that the height of the electrocatalytic peak for methanol oxidation does not change over the pH range 5–11, but decreases in acidic medium (pH lower than 5). Therefore, the utility of the modified electrode is limited to neutral and weakly basic solution.

Conclusion

The experimental results reported above demonstrate clearly that: (i) the Pt-NiHCF film can be firmly immobilized onto the zinc electrode by chemical means; (ii) the Pt-NiHCF film has a protective effect on the electrode substrate, against electrooxidation; (iii) the radius of the hydrated alkali metal cation of the supporting electrolyte has a considerable effect on the electrochemical behavior of the film; (iv) unlike Prussian blue, all alkali metal cations can freely enter the Pt-Ni-HCF crystal lattice and an electrolyte solution containing K^+ or Rb^+ provides a good electrochemical characteristic for the modified electrode; (v) the kind of anion affects strongly the stability of the electrode and a well-defined and reproducible cyclic voltammogram is obtained in the presence of phosphate and hydrogen carbonate; and (vi) the prepared modified electrode is suitable for the electrocatalytic oxidation of methanol.

References

1. Itaya K, Akahoshi H, Toshima S (1982) J Electrochem Soc 129:1498
2. Cai C, Ju H, Chen H (1995) Anal Chim Acta 310:145
3. Cai C, Ju H, Chen H (1995) J Electroanal Chem 397:185
4. Bocarsly AB, Sinha S (1982) J Electroanal Chem 140:167
5. Lin C, Bocarsly AB (1991) J Electroanal Chem 300:325
6. Gao Z, Wang G, Li P, Zhao Z (1991) Electrochim Acta 36:147
7. Arent DJ, Hidalgo-Luangdilok C, Chun JKM, Bocarsly AB (1992) J Electroanal Chem 328:295
8. Pournaghi-Azar MH, Razmi-Nerbin H (1998) J Electroanal Chem 456:83
9. Pournaghi-Azar MH, Razmi-Nerbin H (2000) Electroanal 12:209
10. Bharathi S, Yegnaraman V, Rao GP (1995) Langmuir 11:666
11. Xu J, Wang G, Chen H (2000) Anal Sci 16:231
12. Dostal A, Meyer B, Scholz F, Schroder U, Bond AM, Marken F, Shaw SJ (1995) J Phys Chem 99:2096
13. Reddy SJ, Dostal A, Scholz F(1996) J Electroanal Chem 403:209
14. Ikeda O, Yoneyama H (1989) J Electroanal Chem 265:323
15. Pournaghi-Azar MH, Razmi-Nerbin H (2000) J Electroanal Chem 488:17
16. Pournaghi-Azar MH, Razmi-Nerbin H (2001) Electroanal 13:465
17. Razmi-Nerbin H, Pournaghi-Azar MH (2002) J Solid State Electrochem 6:126
18. Pournaghi-Azar MH, Dastangoo H (2002) J Electroanal Chem 523:26
19. Inzelt G (1990) J Electroanal Chem 287:171
20. Bacskai J, Martinusz K, Czirok E, Inzelt G, Kulesza PJ, Malik MA (1995) J Electroanal Chem 385:241
21. Laviron E (1979) J Electroanal Chem 101:19
22. Dong S, Jin Z (1989) Electrochim Acta 34:963
23. Ohsaka T, Okajima T, Oyama N (1986) J Electroanal Chem 215:191
24. Laviron E (1979) J Electroanal Chem 100:263
25. Sinha S, Humphrey BD, Bocarsly AB (1984) Inorg Chem 23:203