Asian Journal of Chemistry Vol. 21, No. 9 (2009), 6752-6762

Platinum-Doped Cobalt Hexacyanoferrate Film-Carbon Paste Electrode for Electrocatalytic Oxidation of Methanol

REZA OJANI*, JAHAN-BAKSH RAOOF and BANAFSHEH NOROUZI
Electroanalytical Chemical Research Laboratory,
Faculty of Chemistry, Mazandaran University, Babolsar, Iran
Fax: (98)(112)5242029/5242002; Tel: (98)(112)5242025-7
E-mail: fer-o@umz.ac.ir; norouz2020@yahoo.com

The use of a carbon paste electrode (CPE) and the modification of its surface by means of a thin film of cobalt hexacyanoferrate (CoHCF) were developed. The electrochemical characteristic of this thin film of CoHCF was investigated. Thereafter, the deposition of platinum on the CoHCF modified CPE was described. This CoHCF/Pt modified CPE was used as an electrocatalyst for the electrooxidation of methanol in 0.1 M KH_2PO_4 solution. It has been shown that the presence of CoHCF film improves considerably the catalytic efficiency of deposited platinum microparticles toward the electrooxidation of methanol. The effect of some experimental factors such as platinum loading and concentration of methanol was investigated. Finally, the long term stability of modified electrode was studied.

Key Words: Electrocatalytic oxidation, Methanol, Platinum, Cobalt hexacyanoferrate, Cyclic voltammetry, Carbon paste electrode.

INTRODUCTION

Hexacyanometalates (HCM) possess characteristic features of redox active solid films. These features can be summarized as the ability to form a conducting polymer, resemblance to a zeolitic or intercalation material, as well as redox organic polymers. These features have been investigated in many studies such as electroanalysis, chemical sensing and electrocatalysis[1-3], in studies on interfacial charges, in ion exchange and electron transfer studies[4-6] and surface chemical composition[7]. The modification of the electrode surface with metal cyanoferrate is carried out by chemical or electrochemical formation of insoluble transition metal cyanoferrate[8-12] or immobilizing mechanically the metal cyanoferrate as microparticles on the surface of the electrode[13-15].

Among of many metal hexacyanoferrates, cobalt hexacyanoferrate can be considered as a model material for certain fundamental and applied studies[16] or many reasons. For example, the cobalt hexacyanoferrate system can contain a rich series of compounds that are inter-linked through various redox processes. This has been shown by Lezna *et al.*[16] using a combination of voltammetry, *in situ* infrared spectroelectrochemistry and X-ray photoelectron spectroscopy (XPS). Cobalt hexacyanoferrate exhibits well-defined and reproducible electrochemical responses because both the oxidized and reduced CoHCF structures seem to be fairly open and permit transport of alkali metal cations providing charge balance during the redox reactions. Cobalt hexacyanoferrate modified electrodes showed good electrocatalytic activity toward a variety of substrates including ascorbic acid, nitrite, hydrazine, *etc.*[17-21].

On the other hand, in direct methanol fuel cells (DMFCs), methanol is used as a fuel. In this respect, a great deal of interest exists in the development of materials with capability for the electrocatalytic oxidation of methanol, in order to decrease the typically large overvoltages encountered in its direct oxidation at most unmodified electrode surfaces.

One promising approach for minimizing overvoltage effects (related to the slow kinetic of reaction) is carried out the electrocatalytic process at chemically modified electrodes (CMEs)[22,23]. During the last 7-8 years, a large number of papers dedicated to the electrocatalytic properties of platinum group metals and their alloys incorporated into polymeric matrices have been published[24-26]. It has been shown that such modified electrodes with Pt microparticles exhibit a better catalytic effect than smooth platinum for the oxidation of organic fuels, which is methanol[27-29].

Recent research has demonstrated that coating of the electrode surface with polymeric films is an attractive approach for enhancing the power and scope of electrochemically modified electrodes[30-40]. This new class of electrode material has been found to improve the electrode sensitivity and selectivity and to reduce fouling effects in many applications[41,42]. Electrochemical polymerization offers the advantage of reproducible deposition in terms of film thickness and loading, making the immobilization procedure of a metal based electrocatalyst simple and reliable[43,44].

Previously, the functionalized polypyrrole modified electrodes for detection and electrocatalytic determination of ascorbic acid and dopamine[45,46] were employed. The advantageous features of polymer modification, dispersion of metallic particles into an organic polymer and carbon paste technology by construction of a poly(1-naphthylamine)/nickel modified CPE for successful electrocatalytic oxidation of some carbohydrates[47] and recently construction of a poly (1,5-diaminonaphthalene)/nickel modified CPE for electrocatalytic oxidation of methanol[48] are reported.

In this study, it is decided to combine the above mentioned advantageous features again, but in this work for the first time cobalt hexacyanoferrate matrix which is a conductive inorganic polymer and rigid matrix allowing a better dispersion of electrocatalyst particles and can be prepared by simple method on the CPE was used for the immobilization of platinum for electrocatalytic oxidation of methanol. It must be noticed, most research activities use Pt, Au or GC as matrices for the preparation of the hexacyanometallate modified electrodes, but we used carbon paste matrix because of low cost and its renewability and simple preparation procedure in our laboratory[45,46,49-51].

EXPERIMENTAL

Cobalt chloride, potassium hexacyanoferrate (III) and other chemical reagents were of analytical grade (Fluka). High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for carbon paste electrode (CPE). Graphite powder (particle diameter = 0.10 mm) from Merck was used as the working electrode substrate. The aqueous solutions were prepared using doubly distilled water.

The electrochemical experiments were carried out using a Metrohm potentiostat/galvanostat model 764 VA trace analyzer instrument. Voltammetry was conducted using a three-electrode cell. A CPE/CoHCF, a platinum electrode and Ag|AgCl|KCl (3 M) were used as working electrode, counter electrode and reference electrode, respectively.

Preparation of CPE/CoHCF: Graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (*ca.* 3.4 mm internal diameter). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste with a stainless steel rod and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

The electrochemical formation of the cobalt hexacyanoferrate (CoHCF) films at the surface CPE was performed by continuous cycling (in order to achieve morphological stabilization of the crystal lattice of the film) of the potential of the working electrode in a defined potential range (0-1 V) in a supporting electrolyte aqueous solution of $K_3Fe(CN)_6$ (1 mM) and Co^{2+} (1 mM).

Preparation of CPE/CoHCF/Pt: Metallic platinum was deposited on the CPE modified with CoHCF film by a galvanostatic deposition procedure with a current density of 2 mA cm^{-2} using a 5 mM solution of $PtCl_6^{2-}$ and 0.1M KH_2PO_4 as supporting electrolyte. The amount of platinum deposited onto the film surface is calculated from the integral of the cathodic charge passed during the deposition process, assuming that the reduction of Pt^{4+} to Pt^0 is realized with 100 % efficiency. Thus, the quantity electricity Q_{Pt} (mC cm^{-2}), resulting from the $PtCl_6^{2-}$ total reduction is used for the evaluation of deposited Pt. The Pt loading (W in mg cm^{-2}) is then

$$W = Q_{Pt} M/zF$$

where M = 195.078 g mol^{-1} is the atomic weight of Pt, z = 4 the number of exchanged electrons and F = 96500 C mol^{-1}, the Faraday constant.

RESULTS AND DISCUSSION

Voltammetric responses of the CPE/CoHCF electrode: Fig. 1 shows successful growth of CoHCF (by repeated cyclic voltammograms) for the deposition of CoHCF at the surface of CPE from an aqueous 0.1 M KCl solution containing Co^{2+} and $Fe(CN)_6^{3-}$ ions in the potential range between 0.0 and 1.0 V (*versus* Ag|AgCl|KCl (3 M)). With increasing cyclic times, two sets of redox peaks at $E^{0'}$ of about 0.49

and 0.69 V, respectively, emerged and became higher and higher accompanied, which indicates the formation of polymerized CoHCF film on the CPE.

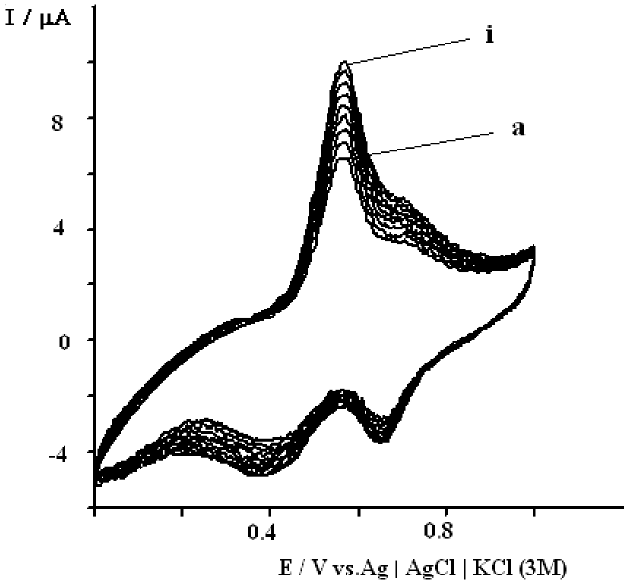


Fig. 1. Cyclic voltammograms related to growth of CoHCF film on carbon paste electrode [(a-i) show 7th to 15th cycles] in 0.1 M KCl solution, scan rate 50 mV s^{-1}

Fig. 2A shows the cyclic voltammetric response of the prepared CPE/CoHCF electrode at the various scan rates in the 0.1 M KCl solution. There are two pairs of redox peaks in each cyclic voltammograms. The corresponding formal potentials, $E^{0'}$ are 0.51 and 0.72, at a scan rate of 0.1 V s^{-1}. These values are almost the same as those for another electrode fabricated using the other method reported previously[17]. Using the most probable stoichiometric formulas for the oxidized and reduced CoHCF[52], where X^+ stands for K^+ or Na^+ and *etc.*, we can describe the system's redox reactions as follow:

$$X_2Co^{2+}[Fe^{2+}(CN)_6] \rightleftharpoons XCo^{2+}[Fe^{3+}(CN)_6] + X^+ + e^- \quad (1)$$

The fact that CoHCF film undergoes double reduction and double oxidation in potassium electrolyte can be attributed to the existence of two stable forms, probably $K_2Co^{2+}[Fe^{2+}(CN)_6]$ and $KCo_{1.5}[Fe^{2+}(CN)_6]$[52], which are electroactive at different potential.

It has been established that the structure of CoHCF is similar to those of hexacyanoferrates of copper and nickel and easily allows the flux of alkali metal cations with different sizes in the electrolyte during the redox reactions. The transfer of an electron is always accompanied by the simultaneous motion of a counter-cation to maintain charge balance during the redox reaction.

The peak currents of the voltammograms are linearly proportional to the scan rate up to 0.1 V s^{-1} (Fig. 2B) which is expected for surface-type behaviour. At scan rates higher than 0.1 V s^{-1}, peak currents are linearly proportional to the square root of the scan rate, which is expected for a diffusion-controlled electrode process.

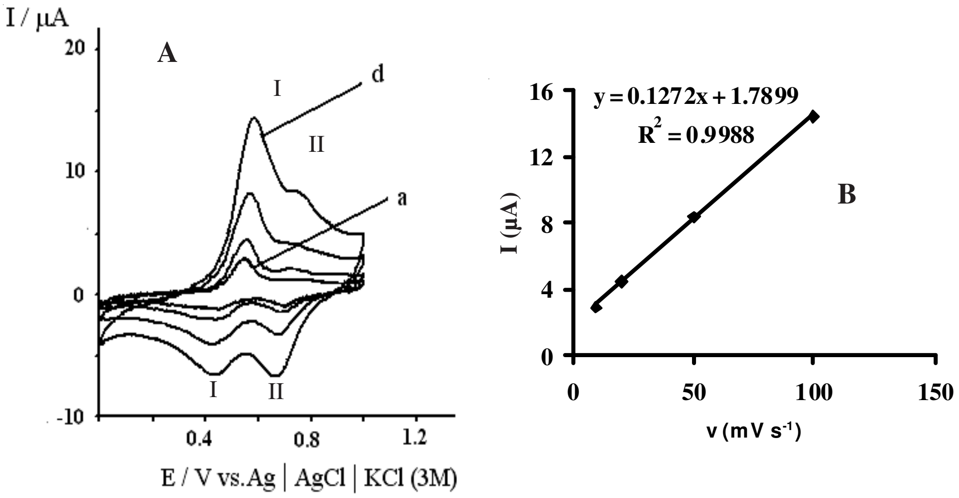


Fig. 2. (A) Cyclic voltammograms of CPE/CoHCF in 0.1 M KCl solution for various scan rates: (a) 10, (b) 20, (c) 50 and (d) 100 mV s^{-1} (B) Plot of anodic peak currents *vs.* scan rate

The electrochemical responses of the CPE/CoHCF electrode in an electrolyte solution with different alkali metal cations are shown in Fig. 3. It was found that two pairs of well-defined redox peaks can be observed, when K^+ containing electrolyte solution was used (curve a). When Na^+ (Fig. 3, curve b) or Mg^{2+} (Fig. 3, curve c) containing electrolyte solution was used, two pairs of broad and ill-defined redox peaks were observed. Furthermore, the peak currents decreased drastically compared with that in K^+ containing electrolyte solution. The above results indicated that the size of K^+ matches best with the cavity of the CoHCF film. The different electrochemical behaviour of the CPE/CoHCF electrode in different supporting electrolytes may be due to the size of the alkali metal cations. The CoHCF film seems to possess greater selectivity for K^+ ion as a counterion.

Fig. 4 shows the cyclic voltammograms of the CPE/CoHCF electrode in KCl solutions of different concentrations. It is observed from Fig. 4 that the potentials of both pairs of redox peaks shift in the negative direction with a decrease in the concentration of KCl (this behaviour is in accordance with eqn. 1). Peak current also increases with an increase in the concentration of KCl.

Electro-oxidation of methanol: At the beginning of the experiment, the CPE/CoHCF/Pt was immersed in the supporting electrolyte 0.1 M KH_2PO_4 and the potential was cycled between 0.0 and 1.0 V with sweep rate of 20 mV s^{-1}. Fig. 5 shows

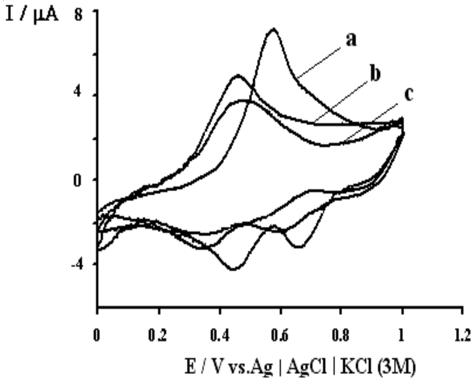


Fig. 3. Cyclic voltammograms of CPE/CoHCF in 0.1 M (a) KCl, (b) NaCl, (c) $MgCl_2$ solutions, Scan rate 50 mV s^{-1}

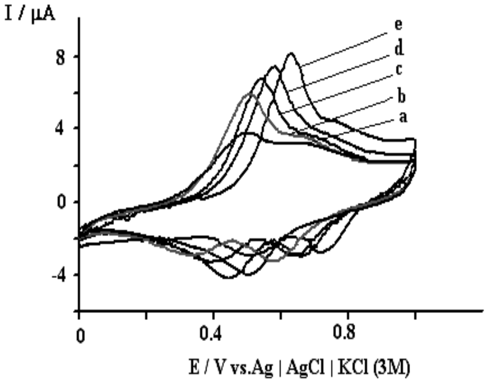


Fig. 4. Cyclic voltammograms of CPE/CoHCF in (a) 0.0001, (b) 0.001, (c) 0.01, (d) 0.1 and (e) 1 M KCl solution, Scan rate 50 mV s^{-1}

a typical voltammogram for methanol electrooxidation on the CoHCF/ Pt modified carbon paste electrode in the solution of 0.1 M KH_2PO_4. Like the other platinum dispersed in electrode substrates the anodic oxidation current for methanol is started from 0.05 V with low anodic current and by sweeping to the more positive potentials the peak of anodic current appears at about 0.53 V (Fig. 5(a), peak I). At more positive potential than region I the oxidation current decrease due to the formation of platinum oxide and peak II appears. When the potential scan was reversed, there appears a reduction current peak III due to the reduction of platinum oxide. With the clean platinum available, the methanol oxidation takes place more easily and therefore the current peak IV for methanol oxidation appears. The height of this peak depends on the residue poisoning species on platinum surface that can be removed, *i.e.*, by increasing temperature. The oxidation current of methanol (for both peaks I and IV) increased linearly with the scan rate v (not illustrated), suggesting that the methanol oxidation reaction is an adsorptive process. For comparison, the voltammogram of methanol at CPE/Pt is shown in Fig. 5(b). As seen in Fig. 5(b) the methanol shows the same electro-oxidation behaviour at CPE/Pt electrode observed at CPE/CoHCF/Pt electrode, but the CPE/CoHCF/Pt electrode yields much higher peak currents than CPE/Pt electrode. This may be attributed, to the large real surface area of the Pt particles in the CoHCF film. In addition, the polymeric structure prevents the microparticles agglomerating and coalescing during deposition and also stabilizes them on the electrode[53]. These observations can explain clearly the role of the CoHCF film on the enhancement of electrocatalytic currents. Indeed the CoHCF is a good and proper bed for immobilization of Pt particle.

Effect of platinum loading: The anodic current of methanol oxidation depends on the amount of Pt incorporated in the film. The variation of the anodic peak currents, which appear in the positive going sweeps, as a function of Pt loading are given in Fig. 6. As is seen in Fig. 6, Ipa increases with increasing mass of the Pt incorporated in the film and level off at 0.25 mg cm^{-2}. Indeed thereafter, any extra platinum loading does not increase the catalytic activity of the electrodes, probably because of a constant active surface area.

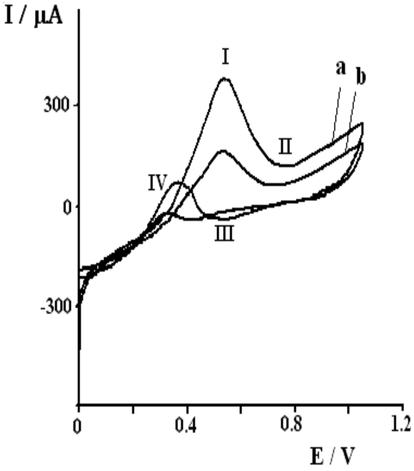


Fig. 5. Cyclic voltammograms of 0.1 M methanol on the (a) CPE/CoHCF/Pt and (b) CPE/Pt electrocatalysts in 0.1 M KH_2PO_4 solution; scan rate: 20 mV s^{-1} and Pt loading 0.25 mg cm^{-2}

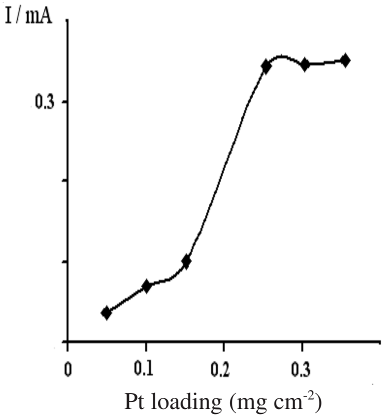


Fig. 6. Plot of the anodic peak currents of 0.1 M methanol at the surface of CPE/CoHCF/Pt, in 0.1 M KH_2PO_4 solution as a function a function of platinum loading

Effect of methanol concentration: Fig. 7A shows the effect of methanol concentration on the anodic current of the methanol oxidation. As seen in Fig. 7B, the anodic peak current increases with increasing methanol concentration and levels off at concentrations higher than 0.46 M. This effect may be due to the saturation of active sites at the surface of the electrode.

SEM characterization of the electrodes surfaces: Electrodeposition method of electrocatalysts in the polymeric matrix is able to produce small crystallites even at large amount of electrodeposited Pt particle. This is a good property to bring out in large surface area. The morphology observed by SEM revealed that the catalytic particles have commonly, micro size and practically spherical shape with rough surface[54]. Fig. 8 present the SEM images obtained from CPE/CoHCF and CPE/CoHCF/Pt containing 0.25 mg cm^{-2} of Pt prepared. Image (A) shows, the CoHCF particles formed on the CPE surface, were not regular in shape and were not spread uniformly on the substrate; however, they expose a rather developed surface area. Concerning the coating adherence of the film to the electrode surface, the CoHCF film is strongly adhered to CPE surface and shows considerable promise as matrix for dispersing of the catalyst particles. Image B shows the morphology of the CPE/CoHCF after deposition of 0.25 mg cm^{-2} of Pt. As seen in image B the large spherical aggregates even 0.5 µm in diameter may be formed.

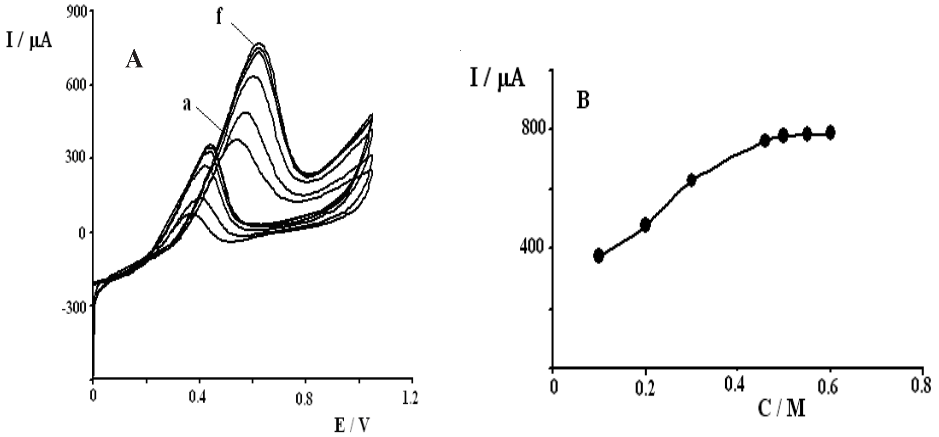
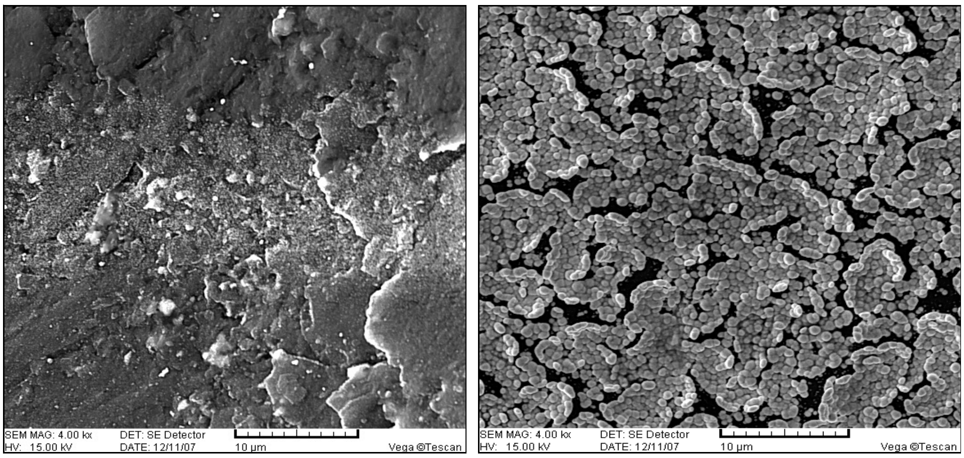


Fig. 7. (A) Cyclic voltammograms of CPE/CoHCF/Pt in 0.1 M KH_2PO_4 solution with addition of different methanol concentrations: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.46 M (e) 0.55 and (f) 0.62 M. (B) Plot of anodic peak current as a function of methanol concentration on the CPE/CoHCF/Pt film in 0.1 M KH_2PO_4 solution; scan rate: 20 mV s^{-1}



(A) (B)

Fig. 8. SEM images of (A) CPE/CoHCF (B) CPE/CoHCF/Pt; Pt loading as in Fig. 5

Stability of the electrode: The stability of CPE/CoHCF/Pt electrode was examined by successive potential cycling in 0.1 M KH_2PO_4 plus 0.1 M methanol solution. The results obtained showed that the response of electrode increase in the first three cycles of potential then they become constant. The stability of the modified electrode was also investigated by posing it in air. The results indicate that, neglecting the weak decrease in peak current during 2 weeks. Such stability seems to be acceptable for most practical applications.

Chronoamperometric studies: Chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrochemical processes at CPE/CoHCF/Pt. Fig. 9A represents the current-time profiles obtained by setting the working electrode potential at 0.8 V for various concentrations of methanol. Chronoamperograms show an increase in methanol concentration accompanied by increasing in anodic currents obtained when the potential step (0.8 V) is applied. Therefore, the results obtained show that the oxidation of methanol can be catalyzed by CPE/CoHCF/Pt.

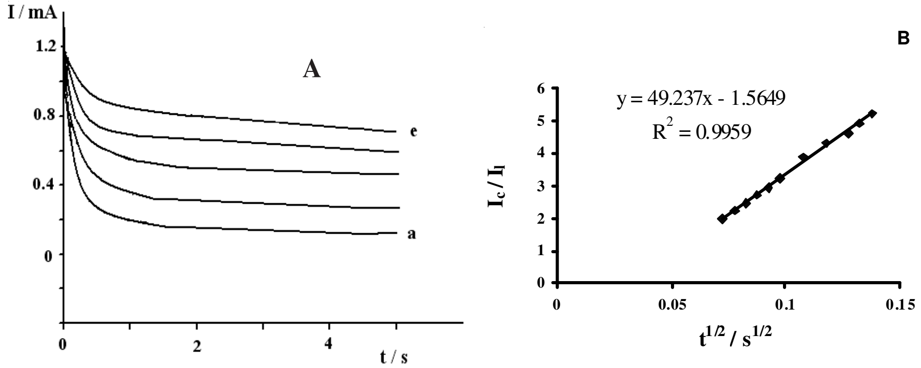


Fig. 9. (A) Chronoamperograms obtained at the CPE/CoHCF/Pt in absence (a) and presence of (b) 0.04, (c) 0.08, (d) 1.5 and (e) 2.5 M of methanol, potential step was 0.8 *vs.* Ag/AgCl, in 0.1 M KH_2PO_4 solution. (B) Dependence of I_c/I_L on $t^{1/2}$ derived from the data of chronoamperogams of (a) and (e) in part A

The rate constant for the chemical reaction between the methanol and redox sites of CPE/CoHCF/Pt (k), can be evaluated by chronoamperometry according to the method described in the literature[55].

$$I_C/I_L = \gamma^{1/2}[\pi^{1/2} \operatorname{erf} (\gamma^{1/2}) + \exp (-\gamma)\, \gamma^{1/2}] \qquad (2)$$

where I_C is the catalytic current of the CPE/CoHCF/Pt in the presence of methanol, I_L is the limiting current in the absence of methanol and $\gamma = kc_ot$ (c_o is the bulk concentration of methanol) is the argument of the error function. In the cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2} (kc_ot)^{1/2} \qquad (6)$$

where k, c_o and t are the catalytic rate constant ($cm^3\ mol^{-1}\ s^{-1}$) methanol concentration ($mol\ cm^{-3}$) and time elapsed (s), respectively. From the slope of the I_C/I_L *vs.* $t^{1/2}$ plot the value of k can be calculated for a given concentration of substrate. Fig. 9B shows one such plot, constructed from the chronoamperogram of the CPE/CoHCF/Pt in the absence and presence of 2.5 M methanol. The mean value for, k was found to be $3.09 \times 10^2\ cm^3\ mol^{-1}\ s^{-1}$.

Conclusion

Cobalt hexacyanoferrate (CoHCF) film was deposited on the carbon paste electrode using a chemical method by the successive cyclic voltammetry. The electrochemical behaviour of this film was described in 0.1 M KH_2PO_4. Modification of the electrode surface by a thin film of CoHCF and then electrodeposition of Pt on this film improves the reactivity of electrode toward the methanol oxidation. Overall, the anodic peak current of methanol oxidation at a CPE/CoHCF/Pt is two half times greater than a CPE/Pt, indicating the crucial effect of CoHCF film on the electrode reaction kinetics. This modified electrode can improve methanol oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction of methanol.

REFERENCES

1. S.M. Chen, *J. Electroanal. Chem.*, **521**, 29 (2002).
2. S.M. Chen, *J. Electroanal. Chem.*, **401**, 147 (1996).
3. S.M. Chen, *Electrochim. Acta*, **43**, 3359 (1998).
4. M.B. Soto and F. Scholz, *J. Electroanal. Chem.*, **521**, 183 (2002).
5. A. Dostal, G. Kauschka, S.J. Reddy, F. Scholz and H. Mehner, *J. Electroanal. Chem.*, **406**, 155 (1996).
6. H. Kahlert, U. Retter, H. Lohse, K. Siegler and F. Scholz, *J. Phys. Chem.*, **102**, 8757 (1998).
7. L.H. Kubota and Y. Gushikem, *J. Electroanal. Chem.*, **362**, 219 (1993).
8. C. Cai, H. Ju and H. Chen, *Anal. Chim. Acta*, **310**, 145 (1995).
9. C. Cai, H. Ju and H. Chen, *J. Electroanal. Chem.*, **397**, 185 (1995).
10. Z. Gao, G. Wang, P. Li and Z. Zhao, *Electrochim. Acta*, **36**, 147 (1991).
11. M.H. Pournaghi-Azar and H. Razmi-Nerbin, *J. Electroanal. Chem.*, **488**, 209 (2000).
12. J. Xu, G. Wang and H. Chen, *Anal. Sci.*, **16**, 231 (2000).
13. A. Dostal, B. Meyer, F. Scholz, U. Schroder, A.M. Bond, F. Marken and S.J. Shaw, *J. Phys. Chem.*, **99**, 2096 (1995).
14. S.J. Reddy, A. Dostal and F. Scholz, *J. Electroanal. Chem.*, **403**, 209 (1996).
15. J. Joseph, H. Gomathi and G.P. Rao, *J. Electroanal. Chem.*, **304**, 263 (1991).
16. R.O. Lezna, R. Romagnoli, N.R. De Tacconi and K. Rajeshwar, *J. Phys. Chem. B*, **106**, 3612 (2002).
17. C.X. Cai, K.H. Xue and S.M. Xu, *J. Electroanal. Chem.*, **486**, 111 (2000).
18. S.M. Golabi and F. Noor-Mohammadi, *J. Solid State Electrochem.*, **2**, 30 (1998).
19. T.R.I. Cataldi, G. De Beredetto and A. Bianchini, *J. Electroanal. Chem.*, **447**, 42 (1999).
20. C.X. Cai, H.X. Ju and H.Y. Chen, *J. Electroanal. Chem.*, **397**, 185 (1995).
21. Z. Xun, C. Cai, W. Xing and T. Lu, *J. Electroanal. Chem.*, **545**, 19 (2003).
22. M.A. Abdel Rahim, H.B. Hassan and R.M. Abdel Hamid, *J. Power Source*, **154**, 59 (2006).
23. S.M. Golabi and A.N. Golikand, *Electroanalysis*, **16**, 199 (2004).
24. P.J. Kulesza, M. Matczak, A. Wolkiewicz, B. Grzybowska, M. Galkowski, M.A. Malki and A. Wieckowski, *Electrochim. Acta*, **44**, 2131 (1999).
25. F. Delime, J.M. Leger and C. Lamy, *J. Appl. Electrochem.*, **29**, 1249 (1999).
26. A.D. Jannakoudakis, P.D. Pagalos and N. Theodoridou, *Electrochim. Acta*, **38**, 1559 (1993).
27. S.M. Golabi and A. Nozad, *J. Electroanal. Chem.*, **521**, 161 (2002).
28. M.H. Pournaghi-Azar and B. Habibi, *J. Electroanal. Chem.*, **601**, 53 (2007).
29. W.T. Napporn, H. Laborde, J.M. Leger and C. Lamy, *J. Electroanal. Chem.*, **408**, 153 (1996).
30. R.P. Baldwin and K.N. Thomsen, *Talanta*, **38**, 1 (1991).
31. R. Ojani and M.H. Pournaghi-Azar, *Talanta*, **42**, 657 (1995).
32. R. Ojani and M.H. Pournaghi-Azar, *J. Solid State Electrochem.*, **3**, 392 (1999).
33. R. Ojani and M.H. Pournaghi-Azar, *J. Solid State Electrochem.*, **4**, 75 (2000).
34. P. Santhosh, A. Gopalan, T. Vasudevan and K.P. Lee, *Appl. Surf. Sci.*, **252**, 7964 (2006).
35. D. Profeti and P. Olivi, *Electrochim. Acta*, **49**, 4979 (2004).
36. S. Radhakrishnan and A. Adhikari, *J. Power Source*, **155**, 157 (2006).
37. L. Niu, Q. Li, F. Wei, X. Chen and H. Wang, *Synth. Met.*, **139**, 271 (2003).
38. L. Niu, Q. Li, F. Wei, S. Wu, P. Liu and X. Cao, *J. Electroanal. Chem.*, **578**, 331 (2005).

39. Ch. W. Kuo, L.M. Huang, T. Ch. Wen and A. Gopalan, *J. Power Sour.*, **160**, 65 (2006).
40. A. Kitani, T. Akashi, K. Sugimoto and S. Ito, *Synth. Met.*, **121**, 1301 (2001).
41. J. Wang, in ed.: A.J. Bard, Electroanal. Chem., Marcel Dekker, New York, Vol. 16 (1989).
42. S.A. Wring and J.P. Hart, *Analyst*, **117**, 1215 (1992).
43. T.R.I. Cataldi, E. Desimoni, G. Ricciardi and F. Lelj, *Electroanalysis*, **7**, 435 (1995).
44. S.J. Liu, *Electrochim. Acta*, **49**, 3235 (2004).
45. R. Ojani, J.B. Raoof and S. Rashid-Nadimi, *Electrochim. Acta*, **49**, 271 (2004).
46. R. Ojani, J.B. Raoof and S. Rashid-Nadimi, *Electrochim. Acta*, **50**, 4694 (2005).
47. R. Ojani, J.B. Raoof and P.S. Afagh, *J. Electroanal. Chem.*, **571**, 1 (2004).
48. R. Ojani, J.B. Raoof and R. Hoseini, *Electrochim. Acta*, **53**, 2402 (2008).
49. J.B. Raoof, R. Ojani and M. Kolbadinezhad, *Bull. Chem. Soc. (Japan)*, **78**, 818 (2005).
50. J.B. Raoof, R. Ojani and A. Kiani, *J. Electroanal. Chem.*, **515**, 45 (2002).
51. J.B. Raoof, R. Ojani and A. Kiani, *Bull. Electrochem.*, **919**, 17 (2003).
52. I.V. Tananaev, G.B. Séller, Yu. Ya. Kharitonov, V.G. Kuznetsov and A.P. Korol'kov, Ferrocyanide Chemistry, Nauka, Moscow (1971) (in Russian).
53. D.E. Weisshaar and T. Kuwana, *J. Electroanal. Chem.*, **163**, 395 (1984).
54. A.L. Santos, D. Profeti and P. Olivi, *Electrochim. Acta*, **50**, 2615 (2004).
55. A.J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley and Sons, New York (2001).

(*Received*: 1 September 2008; *Accepted*: 30 July 2009) AJC-7690