MODIFIED ELECTRODES WITH METAL HEXACYANOFERRATES

JAMES JOSEPH, H GOMATHI AND G PRABHAKARA RAO

Central Electrochemical Research Institute, Karaikudi-623, 006, INDIA

Metal hexacyanoferrates have generated much interest in the recent past. They find application in electrocatalysis, ion-exchange, electrochromism, photoelectrochemistry, etc. In this review, the preparation and characterization aspects of modified electrodes with hexacyanoferrates are presented. Analogues of hexacyanoferrates are also briefly discussed.

INTRODUCTION

Chemically modified electrodes offer interesting, novel and useful interfaces with electrolyte solutions. In contemporary electrochemistry, modified electrode is an electrode, the surface of which is manipulated by derivatizing it in such a way that the electrode thereafter exhibits the chemical, electrochemical, optical and other properties of the derivatised/immobilized molecules. Such modified electrodes with improved interfacial properties have potential applications in stereoselective electrosynthesis, photovoltaic generators, electroanalysis, etc. Substrate electrodes such as platinum, carbon or semiconductors (e.g. SnO_2) are permanently modified with substances containing easily oxidisable/reducible groups using procedures involving covalent linkage between the substrate and the modifying agent or by the irreversible adsorption of the adsorbate molecules. The large volume of literature on this topic has been reviewed by Murray [1].
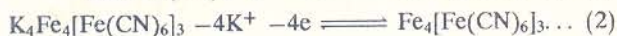
In recent years, the electrochemistry of metal hexacyanoferrates has gained good attention in view of the stable surface modification with these compounds [2]. The present review is an account of these developments highlighting the preparation and characterisation aspects of such modified electrodes along with some important properties pertaining to ion transport, photoelectrochemical behaviour and electrochromism of such modified surfaces.

HISTORICAL DEVELOPEMNT

Prussian Blue (PB) is an important pigment for paints, lacquers, and printing ink [3]. There are two proposed forms of PB, designated as "water insoluble PB" $Fe_4[Fe(CN)_6]_3$ and "water soluble PB" $KFeFe(CN)_6$ [4,5]. It has been shown that the chemical reduction and oxidation of PB can lead to Prussian white (Everitts salt) and Prussian green (Berlin green), respectively [4-6]. The PB and its analogues have f c c crystal structure with a lattice constant of about 10 Å [7].

Thin films of PB can conveniently be deposited by chemical means or electrodeposited by galvanostatic [8] potentiostatic [9] or potential cycling [10] methods. The presence of two redox centres in the PB molecule gives rise to two distinct redox peaks in the cyclic voltammogram as shown in Fig 1. These two redox transitions correspond to PW $\rightleftharpoons$ PB at 0.2 V and PB $\rightleftharpoons$ BG at 0.8V vs SCE, respectively, as depicted by equations 1-4.

At 0.2V

$$K_2FeFe(CN)_6 - K^+ - e \rightleftharpoons KFeFe(CN)_6 \quad \dots (1)$$

$$K_4Fe_4[Fe(CN)_6]_3 - 4K^+ - 4e \rightleftharpoons Fe_4[Fe(CN)_6]_3 \dots (2)$$

At 0.8V

$$KFeFe(CN)_6 - K^+ - e \rightleftharpoons FeFe(CN)_6 \quad \dots (3)$$

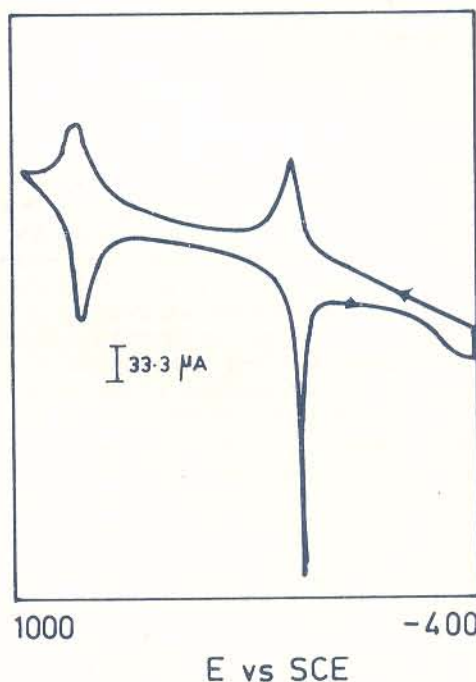$$Fe_4[Fe(CN)_6]_3 - 3e + 3A^- \rightleftharpoons Fe_4[Fe(CN)_6]_3 \dots (4)$$

Fig. 1: *Cyclic voltammetric response of PB modified electrode in 0.5M KCl. Scan rate 50 mV.s^{-1}*

ION EFFECTS

The fcc structure of PB and its analogues allows only alkali metal cations in their channelled structures. Therefore, the studies on the ability of different electrolyte cations to get into the cage structure have gained considerable attention. Such studies using electrodes modified by conventional procedures [5-7] are discussed in detail. The entry and exit of cations during oxidation/reduction necessitated by the electroneutrality considerations of the film have been studied by cyclic voltammothermometry by Ozeki et al [11]. A quantitative demonstration of the ion incorporation in the crystal structure referred to above was achieved through studying the weight change of the film during oxidation/reduction using a quartz crystal microbalance [12]. The ion permeability seems to depend on the hydrated diameter of the cation judging from studies similar to the above extended over a large number of cations viz. K^+, Na^+, NH_4^+, Rb^+, Cs^+, etc. Investigations using PB films prepared in our laboratory [13] revealed the unique reversible response characteristics in the presence of Na^+ in CV suggesting the uptake

and release of the sodium cation in the lattice of PB to be highly reversible (Fig. 2). Besides, the splitting of the CV peaks reveals the possible existence of two forms of sodium incorporated PB species. Similar observations are noted in the cobalt analogue of PB which will be discussed later.
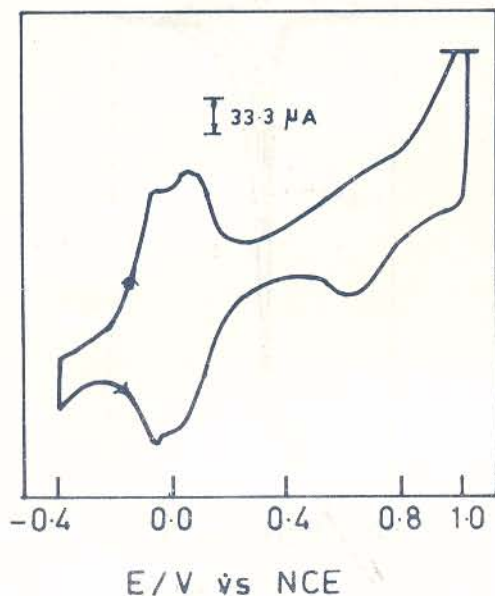

Fig. 2: Cyclic voltammetric response of PB modified electrode in 0.5 M NaCl. Scan rate 50 mV.s^{-1}

The shift in the Nernst potential amounting to 60 mV/decade concentration change exhibited by many PB or its analogues make them suitable candidates as ion selective electrodes. For device applications, appreciable specificity to a given cation in the presence of other alkali and alkaline earth cations is required. However, systematic studies on ion selectivity using PB and different analogues may be rewarding.

ELECTROCATALYSIS

The presence of two well defined reversible redox centres facilitates the electrocatalytic use of PB to mediate the electron transfer. Moreover, the two iron centres in PB, different in their channel environment (as a result of coordination to the adjacent carbon or nitrogen atom in the crystal lattice), can be profitably exploited for site selective electrocatalytic applications. Accordingly, it has been demonstrated [14] that ascorbic acid can undergo catalytic oxidation through mediated electron transfer at the first redox centre at 0.2 V involving ferrous/ferric moieties and the hydrazine sulphate at 0.75V involving ferro-ferricyanide moieties at the second redox centre, respectively. The surface bound outer sphere ferrous/ferric redox centre was also catalytic to the oxidation of the ferrocyanide in solutions [13]. The oxidation of ascorbic acid at the PB- modified glassy carbon electrode was also demonstrated by Dong et al [15]. Parallel efforts were made in our laboratory [15A] and by Dong [15] to modify Pt/carbon fibre microelectrodes with PB and study the catalysis of ascorbic acid oxidation using such modified microelectrodes. Such studies have wide applications in the in vivo analysis of biological systems. Our studies indicate that the thickness of PB on the electrode surface has profound effect on the electron transfer mediation abilities of PB. When the thickness is increased, catalytic currents for the ascorbic acid oxidation diminished; for thickness more than 3 μ M, the films were

not catalytic indicating that the charge transfer becomes slower at higher thicknesses.

POWER SOURCES

Since the PB is a mixed valent iron complex which can be both reduced and oxidised reversibly, it can store both negative and positive charges. Thus it could serve as an active material in both the anode and the cathode of secondary batteries. A secondary battery using PB at both the electrodes and with KCl in nafion as electrolyte was fabricated by Kaneko et al [16]. A photochargeable secondary battery with CdS/PB/ITO has been reported by the same research group [17]. The PB electrodes can be efficiently coupled with other reversible electrodes to get enhanced power density and are of current interest to several researchers.

ELECTROCHROMISM

The ability of PB to change its optical absorption characteristics with applied voltage in a stable and reversible manner (over 10^6 cycles) has opened up the possibility of its use in electrochromic devices [18]. Electrochromic cells with single film PB and with WO$_3$/PB, polyaniline/PB and PB/polymethyl viologen complementary cell have successfully been demonstrated [19-22].

The supporting electrolyte cations move in the PB lattice as hydrated ions. Ability of nonaqueous medium to affect the solvation sheath of the cation has been successfully used in the development of fast switching electrochromic devices [23]. An approach to prepare electroless deposits of amorphous PB also allows bigger cations such as Li$^+$, Ba^{2+}, etc. to enter the PB lattice [24]. Analogues of PB are not exceptions in exhibiting electrochromism and may even lead to the novel e.c. materials as found in the case of NiHCF in alkali [25].

PHOTOELECTROCHEMICAL STUDIES

In photoelectrochemical studies with conventional semiconductors [26-28] transitional metal cyanides or cyanide complexes are added as sensitizers. The enhancement in photocurrent, the stability of the material against photocorrosion etc. are attributed to the formation of charge transfer complexes of the type, PB and its analogues. The photoresponse of PB when present in a bilayer composition along with ruthenium bipyridyl has been reported [29]. However, photoelectrochemical studies on pure PB has not been studied except for a recent publication by Kaneko et al [30] who describe the photoresponse of a PB-coated graphite. Photoelectrochemical studies on the PB film prepared by us [31] showed n-type behaviour in contrast to p-type behaviour observed by Kaneko et al. The spectacular enhancement in n-type photoresponse we observed in the presence of I$_2$/I$^-$ (Fig. 3) redox system [29] is attributed to (1) the composition of the film being more in favour of reduced form of PB (i.e. PW as computed from the absorption spectral data (Fig 4) and (2) the possible chemical interaction between PB and I$^-$ (i.e. PB + I$^-$ $\rightleftharpoons$ PW to retain the PW state on the surface and hence its n-type character). Apart from PB, some analogues of PB such as InHCF have shown photoresponse characteristics. Further studies in this direction are in progress in this laboratory.

ANALOGUES OF PRUSSIAN BLUE

Nickel hexacyanoferrate

In an effort to arrest the surface instability of oxidatively unstable metals like nickel, ferro/ferricyanide solutions have been employed.
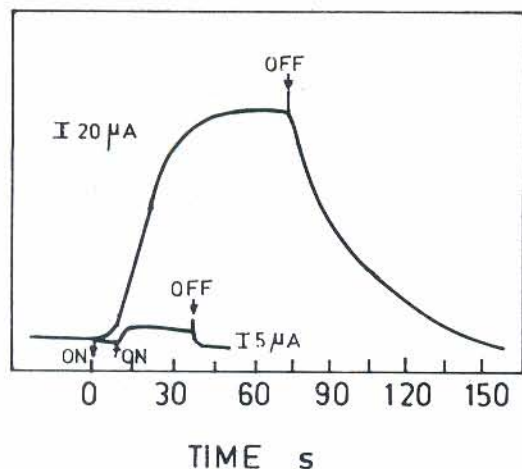
Fig. 3: Photocurrent response of PB modified GC electrode in 0.5 M KCl with and without I_2/I^-
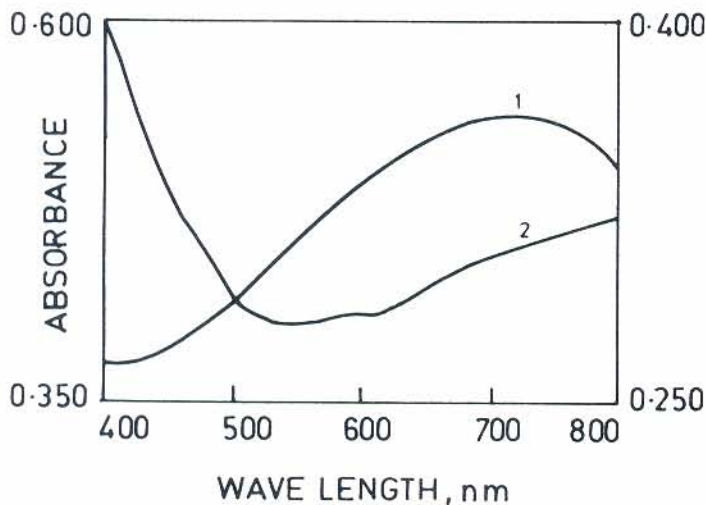

Fig. 4: Absorption spectra of PB modified ITO (1) p-type and (2) n-type

Fig. 5: Cyclic voltammetric response of NiHCF modified electrode in 0.5M KCl. Scan rates (a) $5mV.s^{-1}$ (b) $10mV.s^{-1}$ (c) $20mV.s^{-1}$

Stable surface derivatisation has been noticed due to the formation of nickel hexacyanoferrate redox species [32]. Subsequently the ion transport and electron transfer mediation properties of such films were studied [33]. The appearance of only one set of redox peaks is attributed to the oxidation/reduction of ferrocyanide/ferricyanide system in the NiHCF. Interestingly two redox centres were observed for the nickel analogue deposited on carbon substrates in our studies (Fig. 5) [34] and by Kulesza et al [35]. The two redox centres were attributed to the oxidation/reduction reaction of inner sphere ferro/ferricyanide couple in the NiHCF with two different energetics, designated as potassium incorporated and potassium non-incorporated forms of NiHCF. In various supporting electrolytes the cyclic voltammetric response was characterised by the extent of peak splitting/shifting with respect to the alkali metal cation present. The interesting behaviour of the NiHCF in NaCl medium can be described as follows. The voltammetric response of the NiHCF in NaCl showed a transformation from an initial less symmetric response to a more symmetrical response (Fig. 6) when aged in NaCl for 24 hrs. This change in the surface peaks can be attributed to the slow structural transformation of NiHCF in NaCl.
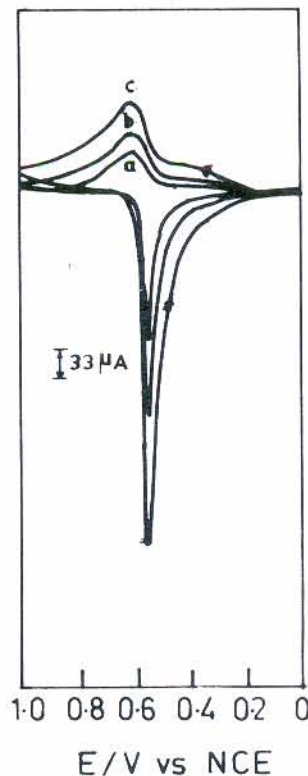
Another interesting observation on NiHCF modified electrode is that when the modified electrode was treated in alkali, it got further derivatised to $Ni(OH)_2$ (Fig. 7) on the substrate surface which incidentally is also electrochromic in nature. The coulombic conversion efficiency of NiHCF film to $Ni(OH)_2$ was found to be 95-100 %. The electrochromic switching time was 50 ms and the stability was extremely good. On the contrary, NiHCF film prepared on a nickel substrate is solubilised in alkali [25] which suggests that the composition of NiHCF prepared on Ni and glassy carbon may be different.

The mediated electron transfer mechanism has been demonstrated to be operative in the case of nickel surface derivatised with ferricyanide for the oxidation of ascorbic acid and hydrazine [36]. Thin films of NiHCF on glassy carbon has been used as stable and durable electrocatalyst for the reduction of Fe(III) in HPLC with electrochemical detection [37].

Cobalt hexacyanoferrate

The cobalt analogue of PB, exhibiting two excellent reversible redox centres very closely resembles PB in its CV response, was reported recently [38]. Both outer sphere cobaltous/cobaltic centre and the inner sphere ferro/ferricyanide redox centre are seen at 0.38 and 0.8V respectively, in 0.5M NaCl (Fig. 8). The excellent reversibility of CoHCF response in NaCl was similar to the behaviour of PB in KCl medium. The unique selectivity of CoHCF film for K^+ ion in the presence of 50 times excess of Na^+ ions (Fig. 9) makes these modified electrodes a suitable candidate for sensors for K^+.

Other analogues

Electrochemical preparation of various analogues such as InHCF, MoHCF, TiHCF, CuHCF, PdHCF and CrHCF were reported by various research groups. All the above analogues are characterised by a single redox centre at their characteristic potentials [39-44]. The electrochemical modification of carbon electrodes with
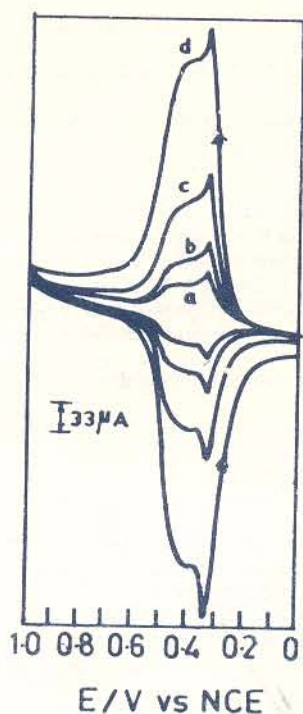
Fig. 6: Cyclic voltammetric response of NiHCF modified electrode in 0.5M NaCl after 24h. Scan rates (a) 5mV.s^{-1} (b) 10mV.s^{-1} (c) 20mV.s^{-1} (d) 50mV.s^{-1}

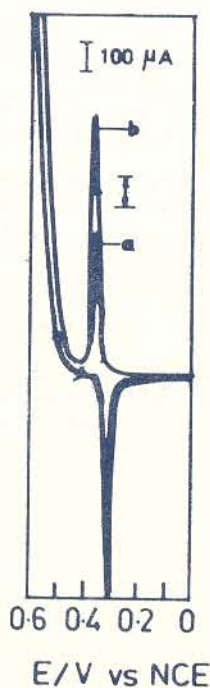*Fig 7: Cyclic voltammetric response of NiHCF modified electrode in 0.5 M NaOH. Scan rates (a) 5mV.s^{-1} (b) 10mV.s^{-1}*
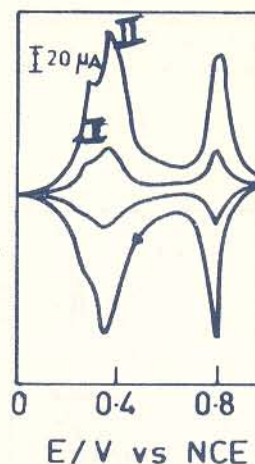
ZnHCF has also been reported [45].

Fig. 8: Cyclic voltammetric response of CoHCF modified electrode in 0.5M NaCl. Scan rates (I) 5mV.s^{-1} (II) 20mV.s^{-1}

Mixed metal hexacyanoferrates

The feasibility of preparing interfaces modified with mixed metal hexacyanoferrates was also studied [46]. Electrodes modified by PB-NiHCF and PB-MnHCF composites were prepared and electrochemically characterised. Figure 9 illustrates typical CV response of the PB -MnHCF modified electrode in KCl. Most of the metal hexacyanoferrates have f c c structure which allows the modification of the electrode with mixed hexacyanoferrates structurally compatible [47]. The multiredox centres in the mixed hexacyanoferrates make these systems as models for investigating the mechanism of propagation of electrons through redox chains, a topic of considerable significance both in inorganic and in biological systems.
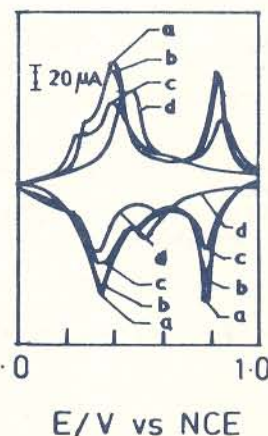

Fig. 9: Cyclic voltammetric response of CoHCF modified electrode in (a) 0.5M NaCl (b) 0.5M NaCl + 0.001M KCl (c) 0.5M NaCl + 0.01M KCl (d) 0.5M NaCl + 0.1M KCl. Scan rate 20mV.s^{-1}

CONCLUSIONS

Recent literature on the basic and applied aspects of PB and its analogues suggests their importance as materials for device applications in the near future. Even though structural similarity

exists between PB and its analogues [47], other differences in properties such as ion permeability, photo response, electrochromic properties, etc. do exist. Study of the various analogues in a unified way will help in the understanding of electronic structure-property relationships.
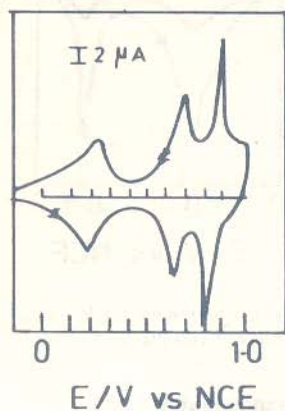

Fig. 10: Cyclic voltammetric response of PB-MnHCF in 0.5M HCl

REFERENCES

1. R W Murray in A J Bard (Ed) *Electroanalytical Chemistry*, Vol. 13, Marcel Dekker, New York. (1981) 169
2. K Itaya, I Uchida and V D Neff, *Act Chem Res*, **19** (1986) 162
3. V Krishnan, A L Xidis and V D Neff, *Anal Chim Acta*, **239** (1991) 7
4. K Itaya, T Ataka and S Toshima, *J Amor Chem Soc*, **104** (1982) 4767
5. V D Neff, *J Electrochem Soc*, **125** (1978) 886
6. K Itaya, H Akahoshi and S Toshima, *J Electrochem Soc*, **129** (1982) 1498
7. F Herren, P Fischer, A Ludi and W Halg, *Inorg Chem*, **19** (1980) 956
8. H Kellawi and D R Rossiensky, *J Electroanal Chem Interfacial Electrochem*, **131** (1982) 373
9. K Itaya, T Ataka, S Toshima and T Shinohara, *J Phys Chem*, **86** (1982) 2415
10. D Ellis, M Eckhoff and V D Neff, *J Phys Chem*, **85** (1981) 1225
11. T Ozeki, T Watanabe and S Ikeda, *J Electroanal Chem Interfacial Electrochem*, **236** (1987) 209
12. M R Deakin and H Byrd, *Anal Chem*, **61** (1989) 290
13. H Gomathi and G Prabhakara Rao, *J Appl Electrochem*, **20** (1990) 454
14. James Joseph, H Gomathi and G Prabhakara Rao (unpublished results)
15. S Dong and G Che, *J Electroanal Chem Interfacial Electrochem*, **315** (1991) 191
15A. James Joseph, D Jayakumar and G Prabhakara Rao (unpublished results)
16. M Kaneko, T Okada, *J Electroanal Chem Interfacial Electrochem*, **255** (1989) 45
17. M Kaneko, T Okada, H Minoura, T Sugicha and Y Ueno, *Electrochim Acta*, **35** (1990) 291
18. K Itaya, K Shibayama, H Akahoshi and S Toshima, *J Appl Phys*, **53** (1982) 804
19. M A Habib, S P Maheswari and M K Carpenter, *J Appl Electrochem*, **21** (1991) 203
20. N Leventis and Y C Chung, *J Electrochem Soc*, **137** (1990) 3321
21. M K Carpenter and R S Conell, *J Electrochem Soc*, **137** (1990) 2464
22. R J Mortimer, *J Electrochem Soc*, **138** (1991) 460
23. N Leventis and Y C Chung, *J Electrochem Soc*, **138** (1991) L21
24. Y Yano, N Kinugasa, H Yoshida, K Fujino and H Kawahara, *Proceedings of the ECS Symposium on Electrochromic Materials* (1990) 90-2, p 125
25. James Joseph, H Gomathi and G prabhakara Rao, *Solar Energy Mater*, **21** (1991) 1
26. D W De Berry and A Viehbeck, *J Electrochem Soc*, **130** (1983) 2439
27. E Vrachnou, M Grarzel and A J Mc Evay, *J Electroanal Chem Interfacial Electrochem*, **258** (1989) 193
28. H D Rubin, B D Humphrey and A B Bocarsly, *Nature*, **308** (1984) 339
29. M Kaneko, *J Macromol Sci Chem*, **24** (1987) 357
30. M Kaneko, S Hara and A Yamada, *J Electroanal Chem Interfacial Electrochem*, **194** (1985) 165
31. D N Upadyay, H Gomathi and G Prabhakara Rao, *J Electroanal Chem Interfacial Electrochem*, **301** (1991) 199
32. A B Bocarsly and S Sinha, *J Electroanal Chem Interfacial Electrochem*, **137** (1982) 157
33. A B Bocarsly and S Sinha, *J Electroanal Chem Interfacial Electrochem*, **140** (1982) 167
34. James Joseph, H Gomathi and G Prabhakara Rao, *Electrochim Acta*, **36** (1991) 1537
35. P J Kulesza, T Jedral and Z Galus, *Electrochim Acta*, **34** (1989) 851
36. C Lin and A B Bocarsly, *J Electroanal Chem Interfacial Electrochem*, **300** (1991) 325
37. P J Kulesza, K Brajter and E Dabek Zlotorzynska, *Anal Chem*, **59** (1987) 2776
38. James Joseph, H Gomathi and G Prabhakara Rao, *J Electroanal Chem Interfacial Electrochem*, **304** (1991) 263
39. P J Kulesza and M Faszynska, *Electrochim Acta*, **34** (1988) 1749
40. L M Siperko and T Kuwana, *J Electrochem Soc*, **130** (1983) 396
41. S Dong and Z Jin, *J Electroanal Chem Interfacial Electrochem*, **256** (1988) 193
42. M Jiang, X Zhou and Z Zhao, *J Electroanal Chem Interfacial Electrochem*, **287** (1990) 389
43. M Jiang, X Zhou and Z Zhao, *J Electroanal Chem Interfacial Electrochem*, **292** (1990) 289
44. M Jiang, X Zhou and Z Zhao, *J Electroanal Chem Interfacial Electrochem*, **292** (1990) 281
45. James Joseph, H Gomathi and G Prabhakara Rao, (unpublished results)
46. S Bharathi James Joseph, D Jeyakumar and G Prabhakara Rao, *J Electroanal Chem Interfacial Electrochem*, **319** (1992) 341
47. A G Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press: New York (1976)