

COMPARATIVE STUDY OF THE TRANSPORT CHARACTERISTICS OF METAL CATIONS IN METAL HEXACYANOFERRATE MATRICES

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The facility with which the inter-conversion of the different redox states occurs among the metal hexacyanoferrates (such as iron, nickel, cobalt, zinc, copper etc.) is largely dependent on the ease with which the uptake or release of a supporting metal cation into/from the host metal hexacyanoferrate is achieved concurrently with the associated electron transfer. The ramifications of the above as reflected in good reversibility or otherwise are quite important and crucial factors in deciding the successful application of these systems in a number of situations such as electrochromic devices, ion-sensors and mediated electron transfer catalysts. In this paper a detailed examination of the comparative data on the electrical charge associated with the intercalated metal species, transport characteristics of the metal cation and its diffusion coefficient would be presented with special reference to iron, nickel and cobalt hexacyanoferrate matrices and entry of K, Na and Li cations into them using electrochemical techniques.

Keywords: Hexacyanoferrates, intercalated metal species

INTRODUCTION

It is well known from current literature that Prussian Blue (PB), viz., ferric ferrocyanide and its analogues with Ni, Co, In, Zn, etc., can be formed as thin films on electrode surfaces and these metal hexacyanoferrates by virtue of their ordered zeolite cage like structure have specific transport characteristics towards alkali metal cations which form the basis of the projected application of these compounds in ion selectivity [1-2] electrochromism [3-8] and photoelectrochemistry [9-13] etc.

Relatively simple picture of the ion transfer behaviour depending on hydrated radii and channel size has been thought of in the case of PB [14] until *in situ* X ray diffraction measurements [15] of PB packed layers on electrodes have provided evidence for dynamic structural changes occurring as ions penetrate into PB lattice during redox reaction. Generally two concepts viz., ion mobility is a function of lattice channel size and conversely lattice structure can be modified by intercalated ions are prevailing [16] among which the second concept remains an open question for many analogues of PB. Moreover,

since the observed structure and ion-transport behaviour are also dependent on synthesis conditions an unified solution cannot be offered on the controversies, except to have the awareness that unit cell volume, the presence of lattice defects, and the water molecule frame work of the lattice are important parameters determining the ion exchange property.

Therefore in the present work, it is attempted to present a comparative study on the influence of mobile interstitial ions K^+ , Na^+ and Li^+ on the over layer structure of uniformly grown metal hexacyanoferrates of Fe, Co and Ni on glassy carbon substrate with the help of cyclic voltammetric and current time transient techniques.

EXPERIMENTAL

Glassy carbon electrodes were coated with the respective metal hexacyanoferrate of Fe, Ni or Co by cycling the electrodes between the potential limits 0-1 V vs. NCE at a sweep rate of 100 mVs^{-1} , for 15 cycles in the case of Fe and Ni and 7 cycles in the case of Co from the following solutions:

1. 0.5 mM each of $K_3Fe(CN)_6$ and $FeCl_3 + 0.5 M$ KCl + 0.1 M HCl
2. 0.5 mM each of $K_3Fe(CN)_6$ and $NiCl_2 + 0.5 M$ KCl + 0.1 M HCl
3. 0.5 mM each of $K_3Fe(CN)_6$ and $CoCl_2 + 0.5 M$ KCl + 0.1 M HCl

In the case of cobalt hexacyanoferrate film the growth was restricted to 7 cycles since the deposition charge was found to be equal to that of Fe and Ni complexes at this stage, and the amount of charge when computed for the electrodeposition of FeHCF, NiHCF and CoHCF was found to be $\approx 60 \pm 5 \mu c$.

The electrochemical experiments were performed with the use of a Wenking Potentiostat (POS 73) coupled to a Rikadenki Recorder (RW 201) and BAS 100 A (Bioanalytical system) Electrochemical analyzer. Three electrode cell assembly consisting of glassy carbon (area 0.38 cm^2) working electrode, platinum counter electrode and a Normal Calomel reference electrode (NCE) was employed.

Analytical grade chemicals were used. The solutions were prepared from triply distilled water and de-aerated by purging with nitrogen.

RESULTS AND DISCUSSION

Cyclic voltammetric studies

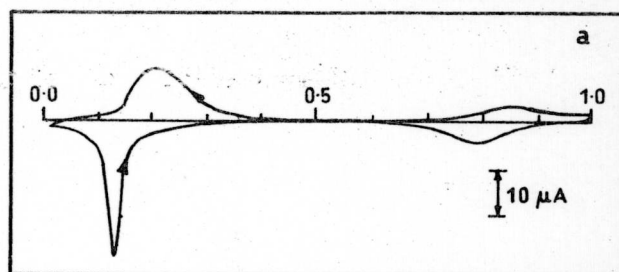
The Figs. 1a-c are the cyclic voltammetric responses of PB modified GC in 0.5 M KCl and 0.5 M NaCl and 0.5 M LiCl respectively at a sweep rate of 0.02 Vs^{-1} . The CV response obtained for the PB modified electrode in 0.5 M LiCl is not found to be stable. Figs. 2 and 3 present the CV responses of NiHCF modified and CoHCF modified GC electrodes respectively under the same experimental conditions.

Voltammetric parameters such as anodic and cathodic peak potentials (E_{pa} and E_{pc}) peak potential separation (ΔE_p), peak current values (i_{pa} and i_{pc}) peak current constant ($i_{pa}/v^{1/2}$) etc., were computed for the three hexacyanoferrates of Fe, Ni and Co from cyclic voltammetric experiments performed in the scan rate range 0.01 Vs^{-1} to 0.20 Vs^{-1} in the three supporting electrolytes studied viz., KCl, NaCl and LiCl. The

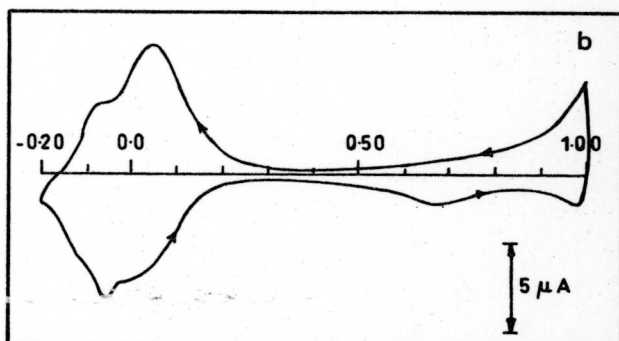
computed values of ΔE_p and ($i_{pa}/v^{1/2}$) for all the three systems in the three supporting electrolytes are given in Tables I and II.

The general cyclic voltammetric characteristics of Fe, Co and Ni hexacyanoferrates in K^+ , Na^+ or Li^+ containing supporting electrolytes are very similar to those reported by us earlier [17-19] under the present experimental conditions.

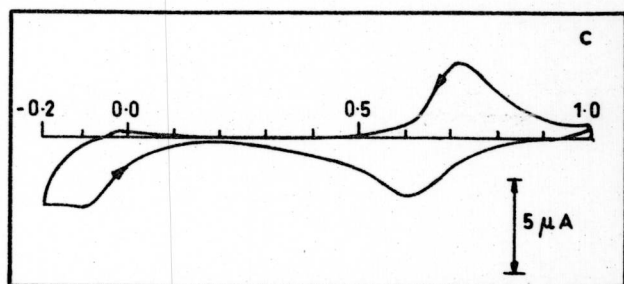
While considering the transport of K^+ ion in these three films, the peak (at $V = 20 \text{ mVs}^{-1}$) manifests sharpness in FeHCF compared to its response in NiHCF and CoHCF. Such a narrow sharp peak



E (VOLT)



E (VOLT)



E (VOLT)

Fig. 1: Cyclic voltammetric responses of PB modified GC in (a) 0.5 M KCl, (b) 0.5 M NaCl & (c) 0.5 M LiCl at 0.02 Vs^{-1}

unambiguously indicates the presence of attractive interactions [20] and facile and unique compatibility of channel size of FeHCF for K^+ ions. Even though the converse is not true in the case of transport of K^+ ions into CoHCF and NiHCF films there is variation in the degree and pattern of mobility of K^+ ions into the lattice of CoHCF and NiHCF ions. In other words it suggests that even though K^+ ion has a preferred entry into these metal hexacyanoferrate films there is an order of preference as follows:



The above proposition gains support from the peak current values which also follow the same order, the magnitude being much higher in the case of

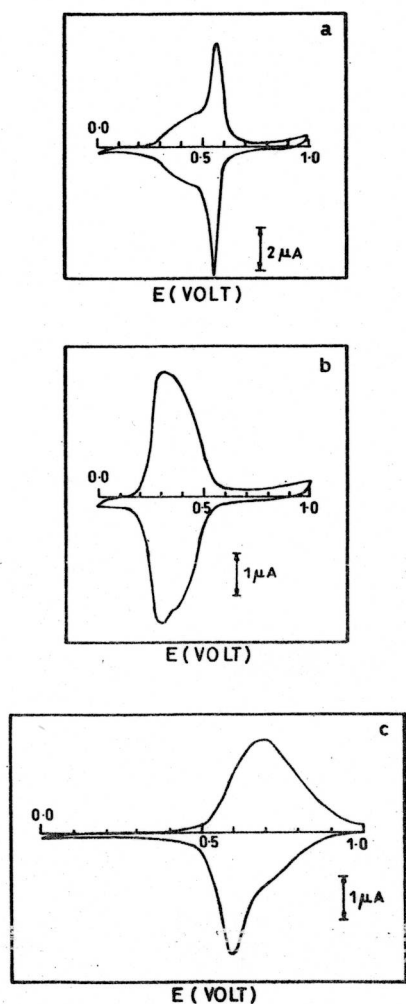
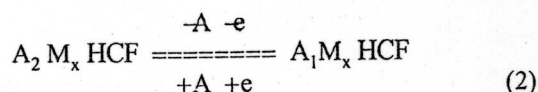


Fig. 2: Cyclic voltammetric responses of NiHCF modified GC in (a) 0.5 M KCl, (b) 0.5 M NaCl & (c) 0.5 M LiCl at 0.02 Vs⁻¹

FeHCF. While computing current values the following general reaction



where A is K^+ , Na^+ or Li^+ ; $M_x = Fe, Ni$ or Co involving alkali metal cation is taken into consideration in all the three cases.

When the three systems are analysed individually, it is seen that in the case of FeHCF there is no symmetry over the potential axis in KCl medium which does not auger for ideal modification [21] and ΔE_p values (Table I) also support this fact. However, it is clear that K^+ ions gain access into the lattice of modified film by diffusion as inferred from the $i_p/v^{1/2}$ constancy observed in the scan rate range 0.02 to 0.1 Vs⁻¹. On the contrary ΔE_p values in NiHCF & CoHCF for K^+ are less over the scan rates employed.

At this juncture it can be recalled that these MHCF films become much stable over a period of time without deterioration in peak currents by adopting a procedure of storing in KCl medium as demonstrated by us in the case of InHCF [12] during photoelectrochemical studies.

The ratio of peak current values (i_{pa}/i_{pc}) does not show vast difference in the case of CoHCF and NiHCF. Again the diffusion mode of transport is

TABLE I: Peak to peak separation (ΔE_p) in metal hexacyanoferrate film in different electrolytes

| Sweep rate | FeHCF | | NiHCF | | | CoHCF | | |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | KCl | NaCl | KCl | NaCl | LiCl | KCl | NaCl | LiCl |
| 0.01 | 0.050 | 0.020 | 0.010 | 0.050 | 0.060 | 0.100 | 0.060 | 0.290 |
| 0.02 | 0.060 | 0.030 | 0.015 | 0.060 | 0.060 | 0.130 | 0.060 | 0.300 |
| 0.04 | 0.065 | 0.050 | 0.025 | 0.070 | 0.060 | 0.160 | 0.040 | 0.320 |
| 0.06 | 0.075 | 0.060 | 0.040 | 0.090 | 0.065 | 0.185 | 0.050 | 0.340 |
| 0.08 | 0.080 | 0.080 | 0.045 | 0.100 | 0.075 | 0.195 | 0.060 | 0.355 |
| 0.10 | 0.085 | 0.095 | 0.055 | 0.110 | 0.085 | 0.210 | 0.060 | 0.365 |

TABLE II: Ratio of peak current of anodic peaks and square root of sweep rate in metal hexacyanoferrate films in different supporting electrolytes

| Sweep rate | FeHCF | | NiHCF | | | CoHCF | | |
|------------|-------|------|-------|------|------|-------|------|------|
| | KCl | NaCl | KCl | NaCl | LiCl | KCl | NaCl | LiCl |
| | V/s | | | | | | | |
| 0.01 | 195 | 85 | 113 | 60 | 65 | 88 | 52 | 58 |
| 0.02 | 222 | 84 | 145 | 75 | 81 | 102 | 66 | 74 |
| 0.04 | 245 | 90 | 140 | 91 | 92 | 112 | 97 | 82 |
| 0.06 | 244 | 89 | 149 | 100 | 99 | 118 | 118 | 85 |
| 0.08 | 254 | 104 | 157 | 107 | 103 | 127 | 134 | 91 |
| 0.10 | 265 | 107 | 162 | 114 | 107 | 132 | 147 | 94 |

inferred in these films too from the $i_p/v^{1/2}$ constancy (Table II) exhibited in the sweep rate range 0.02 Vs^{-1} to 0.10 Vs^{-1} .

Current time transient studies

The current time transient curves for the PB modified electrodes in KCl, NaCl and LiCl respectively for the potential steps of 50 mV are each well within the faradaic region. The current vs square root of time plots are linear for the forward step. Typical current-time transient curves for PB in KCl medium at potential steps (a) 0.0 V to 0.5 V and back to 0.0 and (b) 0.75 to 0.80 V and back to 0.75 V are given in Figs. 4a-b. Similar current-time transient curves were recorded for NiHCF and CoHCF in KCl, NaCl and LiCl at two potential steps selected based on the peak potentials in each case and the current vs square root of time plots were also found to be linear in all the cases. Typical $i-t^{-1/2}$ plot for the PB modified electrode in different supporting electrolytes is given in Fig. 5(a) to (f). From the slope of the linear plot diffusion coefficient of charge transport (D_{ct}) is computed and given in Table III for the three systems in all the three supporting electrolytes studied.

Diffusion coefficient values calculated from current time transients by assuming semi-infinite linear

diffusion (Table III) suggest surface bound reaction and the value $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ is quite comparable with the value obtained for vanadium hexacyanoferrate and other polymer films [22].

As against the response of these three metal hexacyanoferrates films towards K^+ ion, their behaviour towards Na^+ ion is generally marked with somewhat broader peaks with improved symmetry over the potential axis in all the three cases. However, the special features in presence of Na^+ ions is more pronounced in the case of CoHCF (see Fig. 3b). The peak potential values

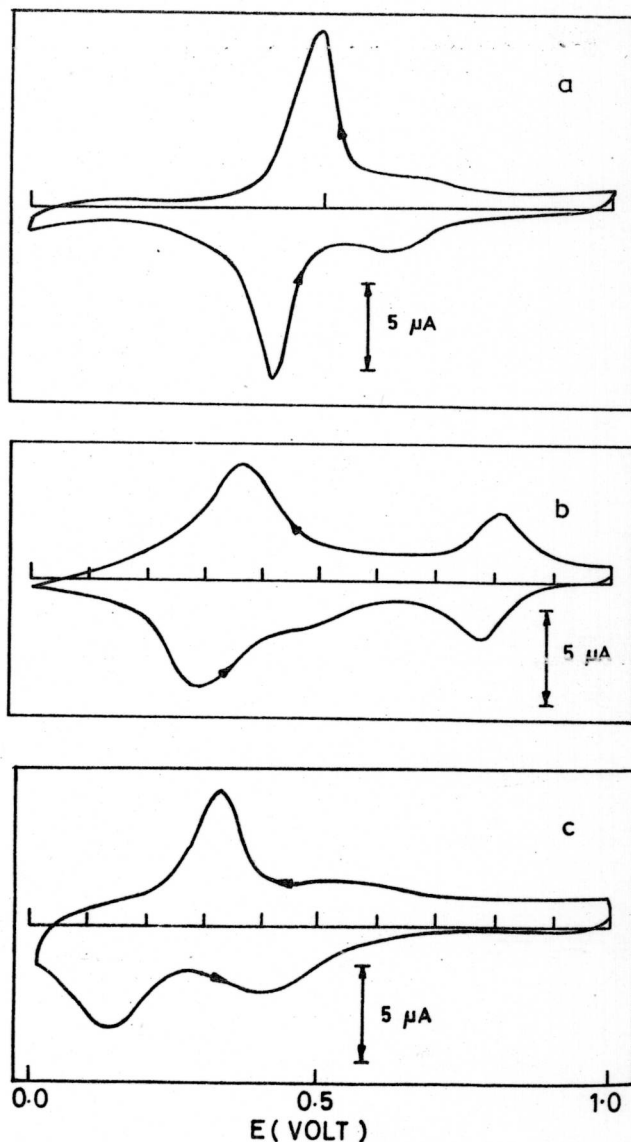
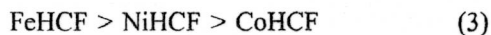


Fig.3: Cyclic voltammetric responses of CoHCF modified GC in (a) 0.5 M KCl, (b) 0.5 M NaCl & (c) 0.5 M LiCl at 0.02 Vs^{-1} .

suggest that transport of Na⁺ ion is energetically more favoured as follows:



Peak current values for Na⁺ ion transfer in these three films do not follow a uniform pattern. Anodic peak current is more in the case of CoHCF compared to NiHCF and FeHCF whereas cathodic peak current for the same is less compared to FeHCF and NiHCF, under the sweep rate conditions employed. Such a trend is peculiar in the case of Na⁺ ion transfer and may be associated with the resistance characteristics of the film and may also be associated with the structural changes of these films. However, further spectral studies are required to substantiate this proposition. Peak current constancy is observed in the scan rates range 0.01 Vs⁻¹. to 0.10 Vs⁻¹ in the case of FeHCF and NiHCF whereas deviations are observed in the case of CoHCF.

Diffusion coefficient of charge transfer for Na⁺ in all the three films is in the order 10⁻⁹-10⁻¹⁰ cm²s⁻¹ suggesting a faster surface diffusion and also falling in line with reported values [22].

As regards the transport of Li⁺ ion, FeHCF is unstable and solubilized in LiCl medium and no useful cyclic voltammetric data could be collected.

NiHCF shows better reversibility ($\Delta E_p = 0.06$ to 0.085 V) of Li⁺ ion compared to CoHCF ($\Delta E_p = 0.29$ -0.365 V) film. Peak current values show a decrease in both the films compared to K⁺ and Na⁺ transfer. Peak current constancy is observed for Li⁺ ion in both the films. Diffusion coefficient values are also of the same order as reported for K⁺ and Na⁺.

SUMMARY

From the cyclic voltammetric and current-time transient studies on PB, NiHCF and CoHCF a

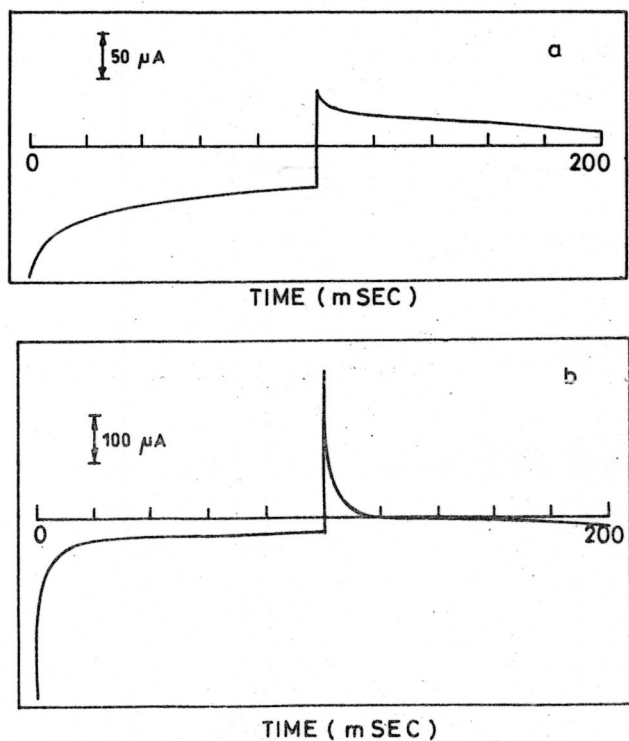
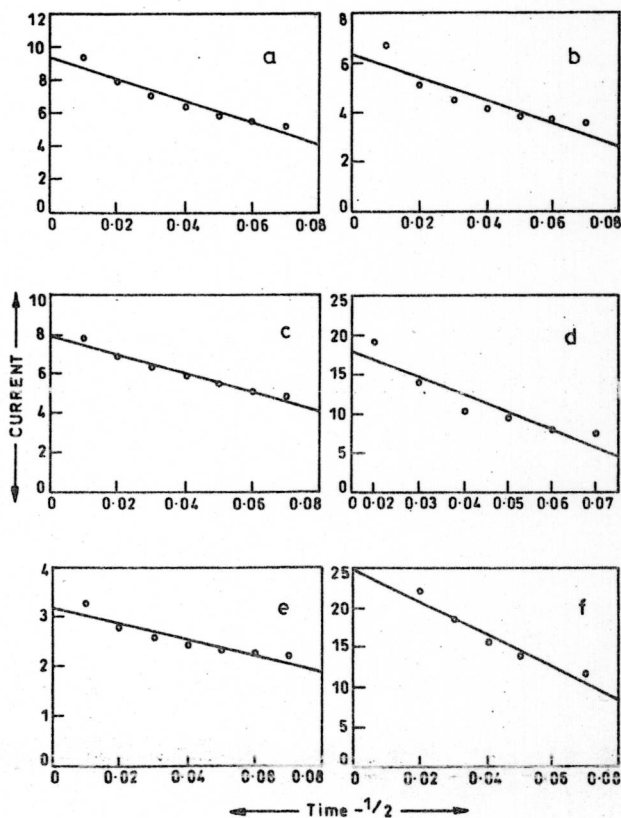


Fig. 4: Current transient curves for PB modified GC in 0.5 M KCl (a) potential step 0 to 0.05 V and back to 0 V and (b) potential step 0.750 V to 0.800 V & back to 0.750 V



Figs. 5(a) to (f) Plot of $i-t^{-1/2}$ plot for the Prussian blue modified electrodes in different supporting electrolytes

TABLE III: Diffusion coefficients of metal hexacyanoferrates in different supporting electrolytes

| MHCF | Diffusion coefficient (D_{cr}) cm^2s^{-1} | | |
|---------------|---|-------------------------|-------------------------|
| | 0.5 M KCl | 0.5 M NaCl | 0.5 M LiCl |
| Prussian Blue | 1.571×10^{-9} | 1.164×10^{-10} | 2.328×10^{-10} |
| | 5.238×10^{-10} | 1.164×10^{-10} | 5.824×10^{-11} |
| NiHCF | 1.455×10^{-9} | 1.047×10^{-9} | 4.655×10^{-10} |
| | 1.978×10^{-9} | 5.824×10^{-10} | 5.824×10^{-10} |
| CoHCF | 6.984×10^{-10} | 1.746×10^{-10} | 1.164×10^{-10} |
| | 9.984×10^{-10} | 2.328×10^{-10} | 2.328×10^{-10} |

meaningful comparison of the charge transport behaviour of K^+ , Na^+ and Li^+ ions into the channels of these surface modified electrodes could be achieved. Symmetry over the potential axis is not there for PB in KCl medium. Na^+ ion is generally marked with improved symmetry over the potential axis in all the three cases. Special features are more pronounced for CoHCF. Order of preference noticed for K^+ and Na^+ from peak current values is as follows

$$\text{FeHCF} > \text{NiHCF} > \text{CoHCF} \quad (4)$$

and in LiCl medium NiHCF shows better reversibility compared to CoHCF. Diffusion coefficient values are computed and reported for the ion transport studies carried out under suitable experimental conditions.

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