

## PRELIMINARY STUDIES ON THE MODIFICATION OF GLASSY CARBON ELECTRODES WITH NICKEL HEXACYANOFERRATE SURFACE FILMS IN PRESENCE OF A CATIONIC SURFACTANT

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Modification of electrodes with various metal hexacyanoferrate films starting from the parent compound iron hexacyanoferrate (prussian blue) is a significant ongoing research activity in several laboratories globally. The promise for potential applications in various fields, such as electroanalysis, electrocatalysis, electrochromism, electrochemical power sources and photoelectrochemical systems, has triggered lot of interest in the study of these compounds for surface modification. Moreover newer strategies are adopted in getting tailor-made surface films with improved electrochemical characteristics. One such approach has been the addition of surface-active agent during surface modification. Among the surfactants studied cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) has been found to influence the electrochemical properties of nickel hexacyanoferrate surface film greatly. Results of the cyclic voltammetric studies carried out on these modified electrodes in the presence of various supporting electrolyte cations and their implications on surface modification are presented.

**Keywords:** Modified electrodes, Prussian blue, effect of surfactants.

### INTRODUCTION

Among the polynuclear metal hexacyanoferrates, ferric ferrocyanide or Prussian blue is the widely studied material for its electron transfer and ion transfer properties, spectral characteristics, electrochromism and battery application [1-16]. Nickel (II) hexacyanoferrate (NiHCF) appears to drag the attention of researchers, in an effort to devise mixed transition metal systems, but second only to Prussian blue. Besides  $K^+$  ions, nickel (II) hexacyanoferrate system has been demonstrated to intercalate various other alkali metal cations such as  $Li^+$ ,  $Na^+$ ,  $Rb^+$  and  $Cs^+$  [17-21] present in the supporting electrolyte. The structures of both oxidized,  $A Ni^{II}Fe^{III}(CN)_6$  and reduced  $A_2 Ni^{II}Fe^{II}(CN)_6$  forms (where  $A = Li, Na, K, Rb$  or  $Cs$ ) are contrary to Prussian blue and this system can very well be used as a model for studying the role of alkali metal transport during electrochemical charging of polynuclear metal hexacyanoferrates.

Kulesza *et al.* report on the stabilization of nickel hexacyanoferrate system via incorporation of Ag (I) into the microstructure [22]. In yet another study the authors [23]

employ electrochemical quartz crystal micro balance to monitor directly the growth of NiHCF and report the strict relationship between the amount of alkali metal ions incorporated into the film during reduction, or excluded from the film during oxidation, and the frequency changes during EQCM measurements.

Preparation of NiHCF on carbon substrates, electron transport and cation transport studies, its quantitative conversion to the celebrated nickel oxide/oxyhydroxide redox system and its electrochromic, ion sensing and catalytic properties have been reported for the first time from this laboratory [24-28]. The present study focuses attention on the electrochemical and cation transport properties of NiHCF film prepared in the added presence of the cationic surfactant CTAB at its critical micelle concentration. The special effects observed for NiHCF/CTAB films in presence of various supporting electrolyte cations are summarised and reported for the first time.

## EXPERIMENTAL

A three electrode cell, assembled with platinum counter electrode, normal calomel reference electrode and glassy carbon working electrode (area:  $0.03 \text{ cm}^2$ ) or platinum working electrode (area  $2 \text{ cm}^2$ ) was used.

All cyclic voltammetric experiments were carried out with a Potentiostat (Wenking Model LB 75) coupled to a Wenking Voltage Scan Generator VSG 72 and X-Y Recorder (Rikadenki -RW 201).

All chemicals were of Analar grade and used without further purification. Double distilled water was used for preparing solutions. Fresh solutions were used each time for modifying electrode surfaces with nickel hexacyanoferrate.

Prior to modification, the working electrodes were subjected to pretreatment as follows: Glassy carbon electrode was polished with emery papers of grades 1/0 to 4/0 (Premier, India & Oakey's, England) successively. Platinum electrode was subjected to ultrasonic cleaning and flame treatment before each modification. The modification of the electrodes with NiHCF film involves potential cycling of the electrode in the modifying mixture, which contains  $0.5 \text{ mM NiCl}_2 + 0.5 \text{ mM K}_3\text{Fe(CN)}_6$  in  $0.1 \text{ M KCl} + 0.02 \text{ N HCl}$ , from  $-0.2 \text{ V}$  to  $1 \text{ V}$  at the sweep rate of  $0.1 \text{ V s}^{-1}$  for 20 minutes.  $0.92 \text{ mM}$  of CTAB, which is its critical micelle concentration, was added, whenever required. The response of the modified electrode was observed in different pure supporting electrolytes (including in KCl), by cycling the potential of the electrode under the same recording conditions, used in the coating process.

Before subjecting the electrode to potential cycling in a supporting electrolyte, the cell, the reference electrode and the working electrode were thoroughly washed with distilled water. Solutions were clear prior to the addition of CTAB, but its presence turned the solutions to turbid.

## RESULTS AND DISCUSSION

Glassy carbon electrode was modified with nickel hexacyanoferrate (NiHCF) film, using the procedure described under experimental section. The film was found to grow in thickness with each cycle, as revealed by the increasing charge under the redox peaks. No further growth is observed after 17 to 18 min of cycling. When the electrode is thoroughly rinsed with double distilled water and its response is observed in pure  $0.1 \text{ M KCl}$ , it retained its CV response as shown in Fig. 1. The film formed is very stable over prolonged cycling of the potential between  $-0.2 \text{ V}$  and  $1.0 \text{ V}$ .

The CV exhibits two sets of redox peaks, one at  $0.35 \text{ V}$  and the other around  $0.48 \text{ V}$ . The observation is in agreement with the earlier reports [20,22]. However, the appearance of two redox peaks with GC electrode for NiHCF is in contrast to the single redox peaks in the cyclic voltammetric response with the nickel substrate electrode [19]. This points out to a possible difference in the nature of these analogues.

For understanding the nature of electron transfer and ion transfer within the NiHCF film, cyclic voltammetric experiments were carried out in two different concentrations of KCl, i.e. in  $0.01 \text{ M}$  and  $1 \text{ M}$ , which is one order less and one order more of the concentration of KCl used to obtain the CV in Fig. 1. It is noticed that at all these concentrations of KCl the second redox couple (at  $\sim 0.4 \text{ V}$ ) at more positive potential always responds to the concentration of the supporting electrolyte cation in solution. It is to be recalled that in case of Prussian blue (PB), the parent molecule of the family of metal hexacyanoferrates, the redox couple at  $\sim 0.2 \text{ V}$ , i.e., at less positive potential always responds to change in concentration of supporting electrolyte cation. The two redox centres at  $0.2 \text{ V}$  and  $0.8 \text{ V}$  in the case of PB are attributable to the high spin  $\text{Fe}^{3+}$  and low spin  $\text{Fe}^{\text{II}}$  ions respectively. In the absence of an outer sphere redox centre in the case of NiHCF, it is the low spin  $\text{Fe}^{\text{II}}$  which undergoes reduction or oxidation with or without the involvement of cations. The relevant redox reactions are represented as follows.

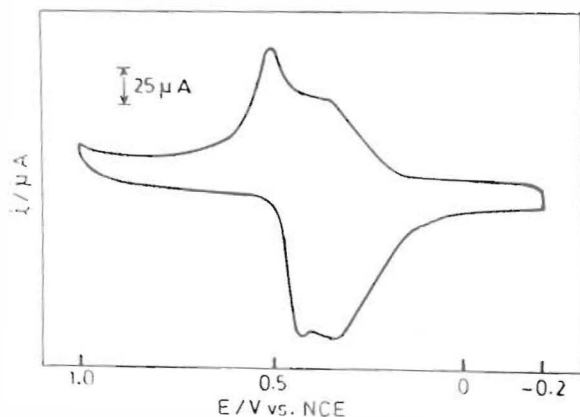


Fig. 1: CV response of a NiHCF modified GC electrode in  $0.1 \text{ M KCl}$  at  $0.1 \text{ V s}^{-1}$



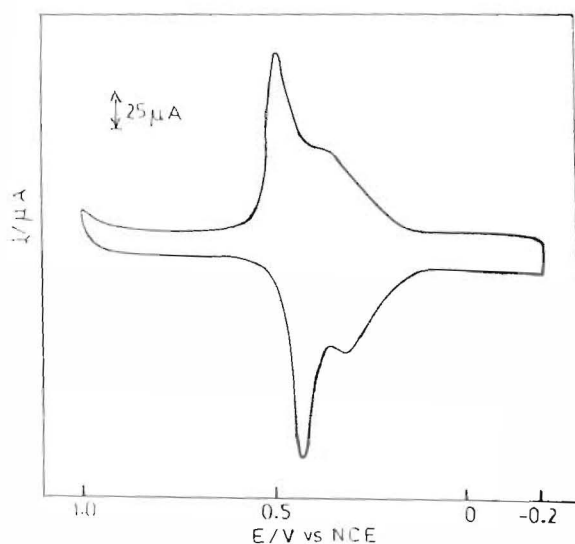
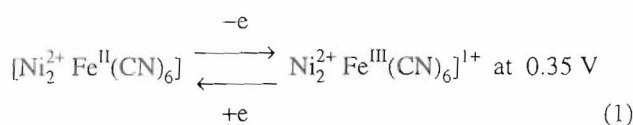
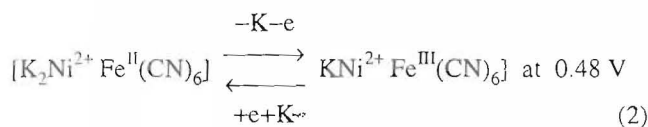


Fig. 2: CV response of a NiHCF + CTAB modified GC electrode in 0.1 M KCl at 0.1 Vs<sup>-1</sup>

Step 1:



Step 2:



Encouraged by the striking results obtained for surface modification of GC with PB film in presence of CTAB [29-31], the modification of the GC electrode with NiHCF film is carried out with the addition of 0.92 mM CTAB (corresponding to its c.m.c) to the modifying mixture. The response of this modified electrode in 0.1 M KCl is shown in Fig. 2.

As reported for NiHCF film without CTAB, two sets of redox peaks are obtained in presence of CTAB too. The first set of redox peaks appear at ~0.32 V and the second at ~0.45 V. The striking feature one could observe in the CV obtained in the presence of CTAB is the highly reversible nature of the redox peaks, being sharp and marked with exact symmetry over the X- axis, which is not usually observed in the absence of CTAB. The films formed with CTAB too are

very stable over prolonged cycling of the potential between -0.2 V and 1.0 V.

Tables I and II give the CV parameters of NiHCF and NiHCF + CTAB modified platinum electrodes respectively in 0.1 M KCl + 0.1 M HCl at different scan rates. From both the tables it can be seen that the CV's represent ideal reversible surface waves with  $\Delta E_p \rightarrow$  zero milli volts in all the cases, particularly in the case of films prepared in the presence of CTAB. Moreover enhancement of anodic and cathodic peak currents at all scan rates is noticed only for NiHCF film prepared in presence of CTAB (Table II). For both the electrodes modified in presence and absence of CTAB, voltammetric currents have been found to be proportional to the potential scan rates up to 200 mVs<sup>-1</sup>. In presence of CTAB the  $i_{pa}/i_{pc}$  ratio is nearly one at all the scan rates, whereas deviation from unity is noticed in absence of CTAB. Within the experimental limits of errors the  $i_{pa}/v^{1/2}$  and  $i_{pc}/v^{1/2}$  values are constant at scan rates above 0.08 Vs<sup>-1</sup>. Again as in the case of Prussian blue modified electrodes [29] there is a charge enhancement at all scan rates in case of electrode modified in presence of CTAB. The enhancement is more than double at the scan rate of 0.2 Vs<sup>-1</sup>.

Among the supporting electrolytes studied only KCl and LiCl gave two redox centers with NiHCF film, while NaCl and NH<sub>4</sub>Cl gave practically one redox center each at 0.1 Vs<sup>-1</sup>, irrespective of the fact whether the film is formed in presence or absence of CTAB. K<sup>+</sup> ion is the most preferred cation for transport through NiHCF or NiHCF + CTAB film, as evidenced from the larger currents obtained in KCl medium, in comparison to those in other media, i.e., in NaCl, LiCl

TABLE I: CV parameters of NiHCF - modified electrode in 0.1 M KCl 0.1 M HCl solution (Pt, area: 2 cm<sup>2</sup>)

Scan rate V/S	E <sub>pa</sub> V	E <sub>pc</sub> V	ΔE <sub>p</sub> V	I <sub>pa</sub> × 10 <sup>-4</sup> A	I <sub>pc</sub> × 10 <sup>-4</sup> A	i <sub>pa</sub> /i <sub>pc</sub>	I <sub>pa</sub> /v <sup>1/2</sup> × 10 <sup>-4</sup> A	I <sub>pc</sub> /v <sup>1/2</sup> × 10 <sup>-4</sup> A	Q <sub>a</sub> mC cm <sup>-2</sup>	Q <sub>c</sub> mC cm <sup>-2</sup>
0.005	0.48	0.47	0.01	3.5	4.0	0.88	49.51	56.58	1.75	1.90
0.010	0.48	0.47	0.01	5.0	6.0	0.83	50.00	60.00	1.85	1.95
0.020	0.49	0.47	0.02	8.0	10.0	0.80	56.58	70.72	2.13	2.15
0.040	0.49	0.46	0.03	13.0	16.5	0.79	65.00	82.50	1.67	1.69
0.080	0.50	0.45	0.05	21.0	27.5	0.76	74.26	97.24	1.58	1.59
0.100	0.50	0.45	0.05	24.5	32.0	0.77	77.48	101.20	1.38	1.39
0.120	0.50	0.45	0.05	27.5	36.0	0.76	79.39	103.83	1.30	1.31
0.140	0.50	0.44	0.06	30.0	39.0	0.77	80.17	104.22	1.23	1.23
0.160	0.50	0.44	0.06	32.5	42.0	0.77	81.25	105.00	1.14	1.14
0.180	0.50	0.44	0.06	34.0	44.5	0.76	60.13	104.88	1.05	1.06
0.200	0.50	0.44	0.06	35.0	46.5	0.75	76.27	103.98	1.00	1.01

**TABLE II: CV parameters of NiHCF + CTAB - modified electrode in 0.1 M KCl + 0.1 M HCl solution (Pt, area: 2 cm<sup>2</sup>)**

Scan rate V/S	E <sub>pa</sub> V	E <sub>pc</sub> V	ΔE <sub>p</sub> V	I <sub>pa</sub> x 10 <sup>-4</sup> A	I <sub>pc</sub> x 10 <sup>-4</sup> A	i <sub>pa</sub> /i <sub>pc</sub>	I <sub>pa</sub> /v <sup>1/2</sup> x 10 <sup>-4</sup>	I <sub>pc</sub> /v <sup>1/2</sup> x 10 <sup>-4</sup>	Q <sub>a</sub> mC	Q <sub>c</sub> mC
0.005	0.46	0.46	0.00	3.5	3.5	1.0	49.51	49.51	1.90	1.85
0.010	0.46	0.46	0.00	5.5	5.5	1.0	55.00	55.00	1.85	1.90
0.020	0.47	0.46	0.01	9.5	10.0	0.95	67.19	70.72	1.88	1.85
0.040	0.47	0.45	0.02	17.5	15.5	0.95	87.50	82.50	1.81	1.81
0.080	0.48	0.44	0.04	31.5	34.0	0.93	111.39	120.23	1.65	1.67
0.100	0.45	0.44	0.04	37.5	41.0	0.92	118.60	129.66	1.56	1.55
0.120	0.49	0.43	0.06	43.0	47.5	0.91	124.13	137.13	1.53	1.53
0.140	0.49	0.43	0.06	48.5	54.0	0.90	129.61	144.31	1.46	1.46
0.160	0.49	0.43	0.06	54.0	60.0	0.90	135.00	150.00	1.42	1.42
0.180	0.49	0.43	0.06	59.0	66.0	0.89	139.05	155.55	1.38	1.37
0.200	0.49	0.43	0.06	63.0	72.0	0.88	140.88	161.00	1.33	1.32

and NH<sub>4</sub>Cl; that is Na<sup>+</sup>, Li<sup>+</sup> and NH<sub>4</sub><sup>+</sup> transport in NiHCF film is not as facile as K<sup>+</sup> ion transport in it, whether the film is formed in presence or absence of CTAB. It is interesting to note that the original response of KCl is obtainable, after having subjected the electrode for potential cycling in other supporting electrolytes, however with reduced charges; this fact holds good whether the film is formed in presence or absence of CTAB. The reduction of charge in regained KCl response, compared to the original KCl response is about 30-40%. This observation indicates that Na<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup> ions either have blocking effect on NiHCF channels to a lesser or greater extent or are capable of partially solubilizing the film; the results also show that CTAB has no influence in this respect. The results in the absence of CTAB are readily comparable with the earlier observations in the supporting electrolytes of Na<sup>+</sup>, Li<sup>+</sup> and NH<sub>4</sub><sup>+</sup> made in this laboratory [24].

The above observations lead us to believe that CTAB does not alter the channel size of NiHCF film. It further indicates that the micelles present during the NiHCF film formation have only catalytic role and do not change its chemical composition.

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