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# $Ni_x$ -Fe<sub>(1-x)</sub>Fe(CN)<sub>6</sub> hybrid thin films electrodeposited on glassy carbon: Effect of tuning of redox potentials on the electrocatalysis of hydrogen peroxide

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#### ABSTRACT

The electrochemical deposition of mixed  $Ni_x$ - $Fe_{(1-x)}Fe(CN)_6$  thin films on a glassy carbon (GC) electrode surface were carried out by electro-deposition under continuous potential cycling condition for the first time. The redox potential of the low spin iron in the hybrid film was found to depend on the ratio of metal centres. The improvement in the electrocatalytic property of the nickel hexacyanoferrate film with incorporation of iron ions in the film towards the electrocatalysis of hydrogen peroxide was studied in electrolytes like KNO<sub>3</sub> and NaNO<sub>3</sub>. The stability of hybrid film in Na<sup>+</sup> containing supporting electrolytes was examined. Detection limit of  $H_2O_2$  was about 1  $\mu$ M as determined by amperometry with the sensitivity of 192 nA/ $\mu$ M. The chemically modified glassy carbon electrodes with Ni<sub>x</sub>Fe<sub>(1-x)</sub>HCF hybrid films were characterized by cyclic voltammetry, impedance spectroscopy, energy dispersive X-ray analysis etc. These films may find extensive applications as redox mediators in biosensors which employ oxidase enzymes.

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# 1. Introduction

The 'metal hexacyanoferrate' (MHCF) is a class of compounds used for modification of electrochemical interfaces for the last 20 years due to their interesting ion transport, electrocatalytic, electrochromic and photoelectrochemical properties [1,2]. Possibility of using simple electrochemical control for preparing thin films of these compounds from a bath containing potassium ferricyanide and corresponding metal salt is exciting. In prototype transition metal hexacyanoferrate, ferric ferrocyanide (FeHCF) the iron coordinated with –N of cyanide ligand is termed as high spin iron and the other which is co-ordinated to –C of the cyanide is low spin iron, established from Mossbauer and infrared studies [2].

The intense blue colour in FeHCF is due to the charge transfer from Fe(II) in a carbon hole to Fe(III) in a nitrogen hole [3]. Modification of glassy carbon substrates with metal hexacyanoferrates were reported from our laboratory recently [4,5]. The modifications of the surfaces with metal hexacyanoferrates (MHCF) gain further importance owing to the fact that the interface can be modified with two MHCFs simultaneously. Electrochemical modification of electrode with NiHCF prepared in presence of Ag<sup>+</sup> make the electrode less catalytic to Fe<sup>2+</sup> oxidation [6]. Cataldi et al. reported that the CoHCF modified electrode on cycling in RuCl<sub>3</sub> solution gains extra stability without alteration in the electrochemical properties [7]. Modification of electrodes with mixed analogues of metal hexacyanoferrates with combinations such as Fe-Ni, Ni-Pd, and Ni-Tl were reported [8-10]. Dostal et al. demonstrated that the Prussian blue modified electrode can undergo lattice substitution during cycling in Cd<sup>2+</sup> containing solutions [11]. James et al. showed that the Prussian blue (PB) modified GC electrode can be converted to CuHCF modified GC completely on cycling in Cu<sup>2+</sup> solution [12]. Electrocatalytic hydrogen peroxide reduction on pure and mixed hexacyanoferrates of Cu, Ce and Pd were reported [13,14]. Bharathi et al. prepared mixed analogues of PB-NiHCF and PB-MnHCF mixed metal hexacyanoferrate electrodes [15]. They formed the mixed analogues of Prussian blue by potential cycling the glassy carbon electrode in a neutral medium containing metal salt and potassium ferricyanide to a very high anodic potentials where the ferricyanide decomposes to form ferric ions. The substitution of PB lattice by hetero atom is expected to alter the properties of the resulting mixed MHCF. However, there are not much systematic studies on the effect of substitution of PB lattice with another metal on the electrochemical properties. Scholz and Reddy prepared the mixed crystals of Fe–NiHCF with various ratios of Ni<sup>2+</sup> and Fe<sup>3+</sup> by chemical precipitation and incorporated these precipitate onto electrode by mechanical abrasion. Though the authors were able to show correlation between formal potential of the mixed crystal on composition, their voltammetric response show features of the existence of a small fraction of individual MHCF response also. In this work, we have demonstrated a simple electrochemical approach for the electrochemical formation of thin films of hybrid films of Ni-Fe-hexacyanoferrate directly onto the substrates. This film has applications in catalyzing the hydrogen

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peroxide oxidation/reduction electrochemically. Recently Karyakin et al. have demonstrated the record performance of Prussian blue modified electrodes in the detection of nanomolar level of hydrogen peroxide by electroreduction [16]. The PB type compounds are termed as 'artificial peroxidase' [17].

The redox potential of the ferro/ferricyanide couple was found to be dependent on the composition of metal ions in the hybrid films. Tuning of redox potential can be advantageously used for creating new electrocatalytic interfaces. The ferric ferrocyanide has two electron transport channels namely high spin iron and low spin iron [18]. The introduction of heteroatoms Fe<sup>3+</sup> on the NiHCF network is expected to open up a new electron transport channel in the hybrid film. The ion transport properties of the hybrid film can be altered by the incorporation of selected metal ion in the MHCFs lattice. Considerable improvement of hybrid's electrochemical stability in sodium containing (Na<sup>+</sup>) electrolytes compared to that of PB is reported. Further, the effect of increasing iron content in the hybrid on the creation of electrocatalytic interface towards oxidation/reduction of hydrogen peroxide is described (Eqs. (5) and (6)).

# 2. Experimental

The electrochemical experiments were performed in a three electrode cell using a potentiostat, Autolab Model PGSTAT 30, Netherlands. The working electrode was a glassy carbon (GC) disc electrode (Bio Analytical Systems, USA, area 0.07 cm<sup>2</sup>). The working electrode was polished with 4/0 grade alumina coated emery paper. The polished electrode was subsequently cleaned by ultra sonication in Millipore water for 2-3 min. A large area platinum foil fused to a glass tube served as counter electrode. All the potentials were measured with respect to 1 M calomel electrode (NCE). All the solutions were prepared fresh in Millipore water of resistivity 18.2 M  $\Omega$  cm). The electrodes were modified by cycling the working electrode potential between 1.0 V and 0.0 V at scan rate of 0.05 V/s for 20 cycles, in 0.1 M KNO<sub>3</sub> medium containing 0.01 M HCl, 1 mM potassium ferricyanide and 1 mM of metal chlorides (total concentrations of ferric chloride and nickel chloride in the medium is 1 mM for corresponding hybrid synthesis). The films deposited on the electrodes were characterized for their electrocatalysis towards hydrogen peroxide by cyclic voltammetry. Energy-dispersive X-ray analysis (EDX) for the hybrids were conducted on films electrodeposited on glassy carbon (GC) electrode embedded in Teflon. AC impedance experiments for GC modified with films of FeHCF and  $Ni_x$ -Fe<sub>(1-x)</sub>Fe(CN)<sub>6</sub> were performed using an impedance analyser (Model IM6-Bio Analytical Systems, USA) in the frequency ranges from 1 mHz to 10 Hz. The amplitude was fixed at 10 mV (Number of data points per decade: 4). The impedance spectra were recorded at applied bias of mid-peak potential i.e. (Epa + Epc)/2.

#### 3. Results and discussion

Fig. 1A–F shows the cyclic voltammetric responses of NiHCF and FeHCF and their hybrid modified GC electrodes by the procedure described in the 'experimental section' in 0.1 M KNO<sub>3</sub>. The origin of redox processes of the modified electrodes are elaborately discussed in the literature [1,2]. FeHCF has two Fe redox sites one coordinated with carbon and the other coordination to the nitrogen of the cyanide ligand. The high spin iron (peak-I) coordinated with –N of the ligand undergo redox reaction at around 0.15 V as follows.

$$\begin{array}{ll} \left\{ {}^{K_{2}}Fe^{\textit{H}}_{\text{LS}}[Fe^{\textit{H}}_{\text{LS}}(\text{CN})_{6}] \right\}_{(s)} & \underset{\text{Cathodic}}{\overset{\text{def}}{\longrightarrow}} \left\{ {}^{K}\; Fe^{\textit{H}}_{\text{HS}}[Fe^{\textit{H}}_{\text{LS}}(\text{CN})_{6}] \right\}_{(s)} + K^{+} + e^{-} \end{array} \tag{1}$$

The low spin iron (peak-II) coordinated with –C of the ligand undergo redox reaction at higher potential is given below.

$$\begin{array}{l} \left\{ {}^{K_2} Fe^{H_{\text{HS}}}_{H_{\text{HS}}} \left[ Fe^{U_{\text{LS}}}_{L_{\text{S}}}(\text{CN})_6 \right] \right\}_{(s)} & \stackrel{\text{Anduc}}{\rightleftharpoons} \left\{ K \; Fe^{H_{\text{HS}}}_{H_{\text{HS}}} \left[ Fe^{U_{\text{S}}}_{L_{\text{S}}}(\text{CN})_6 \right] \right\}_{(s)} + K^+ + e^- \end{array}$$

Similarly GC electrodes can be modified with thin films of NiHCF by electrochemical cycling of electrode potential between 0.0 and 1.0 V in the medium containing 1 mM of  $K_3$ [Fe(CN)<sub>6</sub>] and 1 mM NiCl<sub>2</sub>. NiHCF modified electrode yield two sets of redox processes [19]. Fig. 1A shows the response of the NiHCF modified electrode in KNO<sub>3</sub>. The Ni<sup>2+</sup> does not undergo redox reaction under these experimental conditions. Hence the two redox processes ferro/ferricyanide are arising due to the presence of NiHCF with two different stoichiometric ratios between Ni and Fe [7,8]. The redox potential of the ferro/ferricyanide couple showed an anodic shift as a function of the concentration of iron ion in the modification mixture as seen from Fig. 1B–E. Linear variation of voltammetric peak potential of low spin iron as a function of composition of iron is observed as shown in Table 1.

When the GC electrode is cycled in the modification bath containing ferricyanide ions and mixture of NiCl<sub>2</sub> and FeCl<sub>3</sub>, we would expect the formation of NiHCF and FeHCF independently on the electrode surface. To our surprise, we observed two redox centres, one corresponding to redox process due to high spin iron and the other corresponding to low spin iron when the GC electrode was cycled in 0.1 M KNO<sub>3</sub> medium containing 1 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 0.5 mM of FeCl<sub>3</sub> and 0.5 mM NiCl<sub>2</sub> between the potential limit of 1.0–0.0 V at 0.05 V/s as seen from Fig. 1C. There was no broadening or splitting of the redox process due to low spin iron centre.

Occurrence of a single peak for the redox reaction corresponding to low spin iron is surprising. The redox peak potential corresponding to low spin iron in NiHCF films is shifted to more anodic values with the amount of ferric ion in the modification mixture. The possibility of merging two redox processes of NiHCF and FeHCF is ruled out as we did not observe any splitting of redox peaks in the voltammetric response of the hybrids even at sweep rates as low as 1.0 mV/s. The full width at half maxima (FWHM) is a parameter indicating the multiplicity of redox process or the attractive or repulsive interaction present in the film between redox sites [20]. The reversible surface redox process is expected to exhibit FWHM of 90.6/n mV. We observed FWHM of 100– 130 mV for the hybrid films which may be due to some repulsive interaction present in the hybrid films.

The chemical precipitation of hybrids containing FeHCF-NiHCF hybrid is performed by Reddy et al. The X-ray diffraction studies of these hybrids clearly proved the incorporation of second metal in the lattice of the primary metal hexacyanoferrate [21]. The formation of these hybrids by electrodeposition is complex due to the fact that the MHCFs are formed on the electrode surface by electro-reduction. To rule out the possibility of the formation of MHCF deposition at the initial potential, we have started the initial potential of cycling from 1.0 V in our experiment which ensures that there is no film formation on the electrode initially. Here we wish to state that there was no film formation noticed on GC surface when we potentiostated the electrode at 1.0 V vs. NCE. During reductive cycling, the ferricyanide ion in the medium gets reduced to ferrocyanide ion. The solubility product of many transition metal ions with ferrocyanide ion is less than the corresponding ferricyanide ion [22]. Hence both the metal ions simultaneously get precipitated on the electrode electrochemically as follows. At potential below 0.3 V,

$$[Fe(CN)_6]^{3-} + e^- \to [Fe(CN)_6]^{4-}$$
(3)

$$[Fe(CN)_6]^{4-} + (1-x)Fe^{3+} + x Ni^{2+} \rightarrow Ni_xFe_{(1-x)}Fe(CN)_6$$
(4)

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