



Ni_x-Fe_(1-x)Fe(CN)₆ hybrid thin films electrodeposited on glassy carbon: Effect of tuning of redox potentials on the electrocatalysis of hydrogen peroxide

Alam Venugopal Narendra Kumar, Srinivasan Harish, James Joseph*, Kanala Lakshminarasimha Phani

Electrodics and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630 006, India

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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 KNO₃ and NaNO₃. The stability of hybrid film in Na⁺ containing supporting electrolytes was examined. Detection limit of H₂O₂ was about 1 μM as determined by amperometry with the sensitivity of 192 nA/μM. The chemically modified glassy carbon electrodes with Ni_xFe_(1-x)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⁺ make the electrode less catalytic to Fe²⁺ oxidation [6]. Cataldi et al. reported that the CoHCF modified electrode on cycling in RuCl₃ 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 Cd²⁺ 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 Cu²⁺ 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 Ni²⁺ and Fe³⁺ 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

* Corresponding author. Tel.: +91 4565 227550x441; fax: +91 4565 227779.

E-mail address: jameskavalam@yahoo.com (J. Joseph).

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