Structural study of the Cu$^{2+}$-loaded copper hexacyanoferrate electrode deposited on indium tin oxide substrate

M Giorgetti$^1$, G Aquilanti$^2$ and M Minicucci$^3$

$^1$Department of Physical and Inorganic Chemistry, University of Bologna, Bologna, 40137, Italy
$^2$Elettra - Sincrotrone Trieste S.C.p.A., s.s. 14, km 163.5, 34149 Basovizza, Trieste, Italy
$^3$CNISM, School of Science and Technology, Physics Division, Università di Camerino, 62032 Camerino (MC), Italy

E-mail: giuliana.aquilanti@elettra.trieste.it

Abstract. We report the structural characterization by XAFS spectroscopy at the Cu K-edge of three different CuHCF-based electrodes deposited on ITO (indium tin oxide) substrate. The electrochemical characterization confirms the occurrence of typical CuHCF films on the ITO surface. The EXAFS analysis evidences the strong multiple scattering effects in these compounds which makes the EXAFS probe effective for distances up to 5 Å from the photoabsorber. The presence of Cu-N-C-Fe linear chains with a high multiplicity has allowed us to determine accurately the local environment of Cu which also includes the Fe atom. The XAFS characterization of the Cu$^{2+}$-loaded CuHCF shows the best agreement with the structural model for copper hexacyanoferrate, which also features $[$Fe(CN)$_6$$]^{3-}$ ion vacancies.

1. Introduction

Prussian Blue (PB) and related transition metal hexacyanoferrates belong to a class of polymeric inorganic compounds which have been extensively studied for many years [1]. The copper analogous CuHCF, has been successfully used for its electrocatalytic properties, demonstrating good capabilities in the determination of the hydrogen peroxide [2]. Recently, we have described a new experimental procedure, involving the insertion of Cu$^{2+}$ ions into previously deposited CuHCF films on graphite substrate, which leads to a Cu$^{2+}$-loaded CuHCF displaying an increased response sensitivity, with respect to the pristine electrode [3]. A structural study of several electrodeposited CuHCF based mainly on X-ray absorption technique [4] has clarified the key role of the subsequent Cu$^{2+}$ insertion step. In particular it has been observed that it is not possible to obtain a pure electrosynthesized CuHCF by one step because the film deposition is accompanied by a second component, the Prussian Blue (PB) and that a successive second step consisting of Cu$^{2+}$ ions intercalation enhances the amount of the pure CuHCF phase. The paper has also evidenced the strengths and limitations of the EXAFS approach in these systems, by presenting the comparison between the single metal edge data analysis (Cu or Fe) and the multiple-edge one, concluding that the best fit can be obtained by using the single-edge approach at the Cu K-edge. In the present paper, taking advantage of the former study [4], we present an EXAFS analysis of three CuHCF films deposited on an ITO substrate. As suggested from previous work, we considered the Cu K-edge data only, because the PB component spoils the EXAFS signal at the Fe K-edge making the structural refinement not reliable. The CuHCF films on ITO...
substrates have been recently proposed as precursors for hydroxide films which have catalytic ability towards alcohol oxidation, giving anodic current density of about 10 fold higher than that of any metal hydroxide modified electrodes reported [5].

2. Experimental
The modification of an ITO electrode surface with copper hexacyanoferrate (CuHCF) was performed with a CHI 660C (CH Instruments, Inc.) potentiostat, via potentiodynamic procedure[4]. A three-electrode conventional cell was employed, with an ITO electrode as the working, a saturated calomel electrode (SCE) as the reference, and a Pt wire as the counter electrode. Three electrodes were obtained: the oxidised CuHCF (1), the reduced CuHCF (2) and the Cu$^{2+}$-inserted CuHCF (3). X-ray absorption spectroscopy experiments were performed at the XAFS beamline of Elettra Synchrotron Light Laboratory, in Basovizza (Italy)[6]. The storage ring operated at 2.0 GeV in top up mode with a typical current of 300 mA. The beam was monochromatized using a fixed exit monochromator equipped with a pair of Si(111) crystals. The data were recorded Cu K-edges in fluorescence mode using a large area Si drift diode detector. Four to five spectra were collected and averaged to improve statistics. The energies were defined by assigning the first inflection point of the spectra of the metallic copper to 8979 eV. A spectrum of metallic Cu for calibration purpose was recorded simultaneously in each scan. The EXAFS analysis has been performed by using the GXNAXS package[7,8] that takes into account the multiple scattering (MS) theory. The theoretical signal is calculated ab-initio and contains the relevant two-body $\gamma^{(2)}$, the three-body $\gamma^{(3)}$ and four body $\gamma^{(4)}$ MS terms. The model includes the relevant set of MS signals obtained from typical structure of hexacyanoferrates[9].

![Figure 1. Cyclic voltammetry curves at two different scan rate of electrode 3 at 1 and 50 mV/s. Reference: SCE, Counter: Pt.](image1)

![Figure 2. FT curves (theoretical: continuous line and experimental: dotted line) of the EXAFS signals for electrodes 1, 2, and 3.](image2)

3. Results and Discussions
The voltammetric characterization of CuHCF deposited on ITO shows, as displayed in figure 1 for the electrode 3 at two different scan rate, a well defined redox system centred at about +0.65 V vs. SCE which is related to the redox reaction involving the ferric and ferrous states of the hexacyanoferrate [4]. The plot at 50 mV/s (red curve) displays a separation of the oxidation and reduction waves of about 100 mV, which is slightly more than the theoretical value of 59 mV per electron for a reversible system in a semi-infinite diffusion approximation (bulk). Interestingly, this peaks separation reduces to few mV when the scan rate is as low as 1 mV/s (blue curve), which is a typical behaviour of a thin layer (some hundreds of monolayers) of electroactive material. In addition since these curves have been recorded on the same electrodes after the XAFS measurements, they provide direct evidence for the absence of any beam damage on the electrodeposited material.
The EXAFS spectra of the investigated electrodes were fitted to a structural model based on the $Pm\overline{3}m$ structure of metal HCF in order to retrieve structural information of the electrodeposited film. The applied fitting procedure is similar to that presented in our previous publication [4] about electrodeposited films on a different substrate. The details on the structural model as well as on the choice of the single individual signals which mostly contribute to the overall EXAFS oscillations are available in reference 4.

![Figure 3](image)

**Figure 3.** Details of the EXAFS analysis for the investigated electrodes. Each panel of the figure displays the various single contribution to the EXAFS signals and the comparison of the experimental (-) and the theoretical signals (•). This figure underlines the peculiarity of the present EXAFS data analysis where the signal intensity of the four body contributions (signal marked in red) is comparable to the first shell ones.

The best-fit results at the Cu K-edge concerning the fitting procedure for the investigated electrode are illustrated in figures 2 and 3. Figure 3 reports the details of the EXAFS analysis, in terms of single contributions to the theoretical signals and the comparison of the total theoretical signal with the experimental one. The theoretical curves match well with the experimental ones, even though the small signal to noise ratio (S/N) of samples 1 and 2 makes the fitting procedure less reliable. The single theoretical contribution displayed in figure 3 confirm that all these atomic contribution above specified are important in the determination of the experimental signals and that the four body contribution due to the Fe atom (by the Cu-N-C-Fe linear chain) cannot be excluded because it modulates the entire EXAFS signal. Figure 2 shows the comparison between the calculated and the experimental Fourier transform moduli.

**Table 1.** Structural parameters from EXAFS fitting results of electrodes 1, 2 and 3. The estimated parameter errors are indicated in parentheses.

| Parameter                  | Sample 1 | Sample 2 | Sample 3 |
|----------------------------|----------|----------|----------|
| $d$(Cu-N)/ Å               | 1.98(3)  | 1.99(4)  | 1.97(2)  |
| $\sigma^2$(Cu-N)/ Å$^2$    | 0.006(3) | 0.004(3) | 0.004(2) |
| CN1 (Cu-N)                 | 3.5(5)   | 3.1(5)   | 2.1(2)   |
| $d$(Cu-O)/ Å               | 2.00(5)  | 2.03(5)  | 2.09(2)  |
| $\sigma^2$(Cu-O)/ Å$^2$    | 0.022(8) | 0.02(1)  | 0.019(4) |
| CN2 (Cu-O)                 | 1.0(5)   | 2.8(8)   | 2.6(2)   |
| Fe-C / Å                   | 1.90(3)  | 1.95(8)  | 1.90(2)  |
| $\sigma^2$Fe-C / Å$^2$     | 0.0015(9)| 0.009(5) | 0.009(3) |
| CN=N / Å                   | 1.15(2)  | 1.13(4)  | 1.16(2)  |
| $\sigma^2$CN=N / Å$^2$     | 0.002(2) | 0.002(2) | 0.007(3) |
| CN Cu-K (FIX)              | 0.2      | 2.9      | 1.4      |
| $E_0$, Cu                 | 8988(2)  | 8990(2)  | 8991.1(7)|
| $S_{2}^2$, Cu             | 0.82(8)  | 0.7(1)   | 0.96(4)  |
| GNXAS residual / (10$^{-6}$) | 28.1   | 62.1     | 6.0      |
Structurally speaking, considering that the FT curve is related to the radial atomic distribution around the photoabsorbing atom, the FT curves of figure 2 evidences three main peaks, which are related to three different main atomic shells around the copper atom. Specifically, the first shell is due to the N and O atoms, the second shell to the C atoms, and the third shell to the Fe atoms. The different intensities of the FT curves, especially those related to the –Cu-N-C-Fe chains, i.e. the peaks at about 5 Å, are related to the different extent of the “soluble” structure of the copper hexacyanoferrate, which can be related to the concentration of the [Fe(CN)₆]³⁻ ion vacancies [10].

The inter-atomic distances and the corresponding EXAFS Debye-Waller factor with their associated errors are shown in Table 1. They were determined by correlation maps (contour plots) for highly correlated parameters. Because of the noise of samples 1 and 2 the corresponding structural data obtained from the EXAFS analysis are associated not only to large errors with respect to those of electrode 3, but also to the higher values of the residual.

The atomic distances related to the Fe-C-N-Cu linear chain, i.e the Fe-C, C≡N, and Cu-N have found to be in line with the values of the bulk CuHCF compound [11] and in good agreement to those concerning Cu²⁺-inserted electrodeposited on graphite [4]. The coordination number Cu-K has been used as fixed parameter on the basis of the elemental analysis. The Cu-O distance, due to the ‘insoluble’ structure of metal hexacyanoferrate, has been quoted 2.09(2) Å with a coordination number (CN2) of 2.6(2). The coordination number for the Cu-N interaction (CN1) is found to be 2.1(6) which is lower than the ideal value of 4.5 for the insoluble structure. CN1 is related to the mean number of -Fe-C-N-Cu- linear chains, and CN2 indicates the number of water molecules linked to Cu. It is worth to recall that both Fe-C, C≡N distances are determined directly from the fitting of the four body χ(4) MS term. Those values are very close to that of the Cu²⁺-inserted electrodeposited on graphite [4] and indicates a number of [Fe(CN)₆]³⁻ ion vacancies close to 55%, in accordance to the recently observed samples of porous copper-based PB analogues [12].

4. Conclusions
The analysis of the -Cu-N-C-Fe- four-body contribution of the EXAFS signal in a set of three CuHCF electrodes synthesized on ITO substrates has been presented. Regardless the presence of two metal sites (Cu and Fe) which could be used for the data analysis, the presence of a two phases in different proportions constitutes a strong limitation for the EXAFS analysis of Fe K-edge data, and hence only the Cu K-edge data have been presented. Here, the most reliable data concern the Cu²⁺-inserted CuHCF, where the bond lengths associated to the -Cu-N-C-Fe- chain are similar to those of the bulk copper hexacyanoferrate. CuHCF on ITO also features a large presence of [Fe(CN)₆]³⁻ ion vacancies with respect to bulk samples.

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