

Structure of Cathodically Deposited Nickel Hexacyanoferrate Thin Films

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Introduction

Nickel hexacyanoferrate (NiHCF), a polynuclear coordination compound in the Prussian blue family, is a candidate for separations involving alkali cations [1]. This family of compounds intercalates (deintercalates) alkali cations into (out of) interstitial sites in order to balance charge on its matrix. NiHCF has been shown to selectively intercalate Cs⁺ over other alkali cations [2]. When NiHCF is grown on a conductive substrate, the charge density of the matrix can be controlled, which, in turn, controls the intercalation and deintercalation of cations. NiHCF's efficiency as a separation medium depends on its ability to completely deintercalate cations as the charge density of the matrix is lowered; this property is a function of the stoichiometry and structure of the material. Bulk NiHCF exhibits a wide range of stoichiometries and structures that depend on the exact preparation method used. Although this range of structures is well established for bulk materials, the structure of cathodically deposited NiHCF has never been thoroughly studied [3].

By analogy to "soluble" Prussian blue as well as bulk NiHCF, the assumed structure of electrodeposited NiHCF consists of a perfect network of sixfold coordinated Fe-C≡N-Ni chains (~5 Å from Fe to Ni; lattice parameter of ~10 Å) [4]. This cubic network consists of eight interstitial sites per unit cell; these sites house the charge-balancing alkali cations. However, bulk NiHCF materials often have Fe(CN)₆ vacancies or, in some cases, excess Ni [3]. Recent data indicate that cathodically deposited NiHCF has an increased Ni:Fe ratio (~1.3:1), but it is not known how that ratio is achieved [5]. Variations in the material's structure, evidenced in the Ni:Fe ratio, are inherently linked to the nickel atom's average coordination. Nickel is sixfold coordinated in the assumed structure, but its coordination decreases as the number of Fe(CN)₆ vacancies increase. By using x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS), we set out to directly probe the structure of cathodically deposited NiHCF and compare it to what is known of bulk materials. We hope to confirm whether or not this material is cubic and to determine its average structure.

Methods and Materials

Thin films (~200-nm thick) of NiHCF were deposited onto mirror polished, polycrystalline Pt substrates by electrochemical cycling in a freshly prepared solution of 0.002M NiSO₄, 0.002M K₃Fe(CN)₆, and 0.25M Na₂SO₄. Multiple samples were prepared. The films were then cycled in 1 M solutions of CsNO₃, KNO₃, or mixtures of the two. The samples were then placed in either a reduced state (fully loaded with alkali cations) or an oxidized state (emptied of alkali cations). Each sample was then analyzed by using either XRD or EXAFS.

Conventional XRD experiments were unsuccessful; we were not able to get diffraction peaks from these thin, low-electron-density films. Thus, glancing angle experiments were performed at APS. Data were acquired from a 2θ of 10° to 80°. Samples were spun to average the response from ~20% of the surface area of the sample. Experiments were performed at room temperature.

Fe and Ni K edge EXAFS data were also acquired on spinning NiHCF samples at room temperature. Z-1 filters were used when the fluorescence data were being acquired. After background removal, the Ni and Fe EXAFS data were simultaneously fit to structural models by using the UWXAFS software package, which includes *feffit*2.32 and *FEFF*7. Multiple linear scattering paths were included in the fit; weaker triangular paths were ignored. The EXAFS data in K values of approximately 3-8 Å were Fourier transformed and fit in real space between R_{pseudo} of about 1-5.5 Å.

Results

Diffraction patterns for several different NiHCF thin films are shown in Fig. 1, which is a graph of intensity vs. degrees 2θ. The NiHCF films are intercalated with varying amounts of Cs⁺ and K⁺ (the Cs⁺ mole fractions shown in Fig. 1 were determined by using energy-dispersive x-ray [EDX] spectroscopy), and all are in the reduced state. Each diffraction peak is associated with a specific crystallographic plane. (The [400] plane is pointed out in Fig. 1.) Lattice parameters were calculated from the peak associated with this [400] plane and are plotted vs. the Cs⁺ mole fraction in Fig. 2.

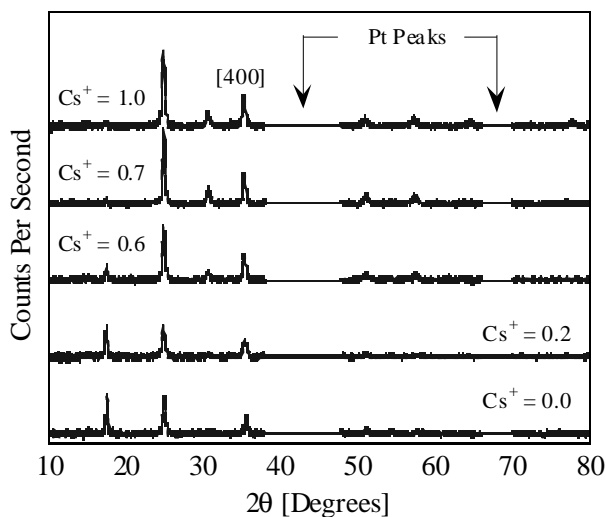


FIG. 1. XRD patterns of reduced NiHCF thin films. Cs^+ mole fractions reported above were found by using EDX spectroscopy.

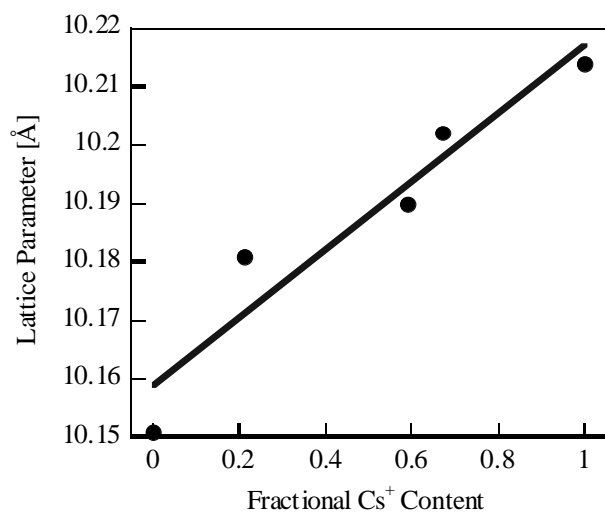


FIG. 2. Lattice parameters vs. mole fraction Cs^+ in NiHCF thin films, calculated by using [400] peak.

Background removed and Fourier transformed EXAFS data [$k^2\chi(k)$] are shown for the Fe K edge (shown as solid lines in Fig. 3) and for the Ni K edge (shown as solid lines in Fig. 4). The data are intentionally shifted along the y-axis for clarity, and R_{pseudo} is the distance from the probing atoms (Fe, Ni) without correcting for the phase shift. The NiHCF films shown in Figs. 3 and 4 are intercalated with either pure Cs^+ or pure K^+ and placed in either the reduced or oxidized state, as shown. The three main peaks seen in Fig. 3 are a result of Fe interactions

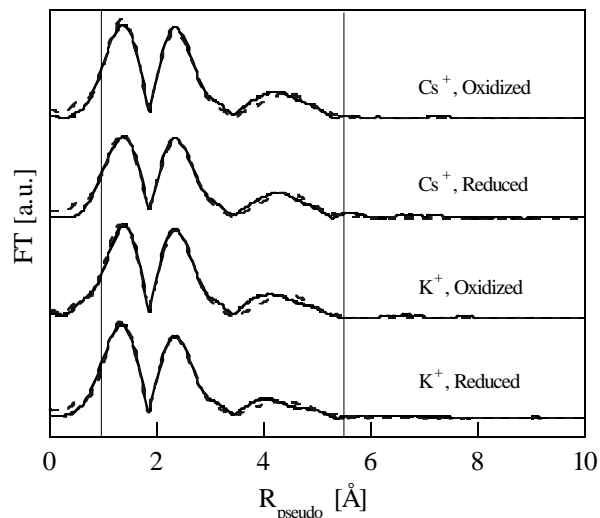


FIG. 3. Fe K edge EXAFS data were fit between the vertical lines and simultaneously with Ni K edge shown in Fig. 4.

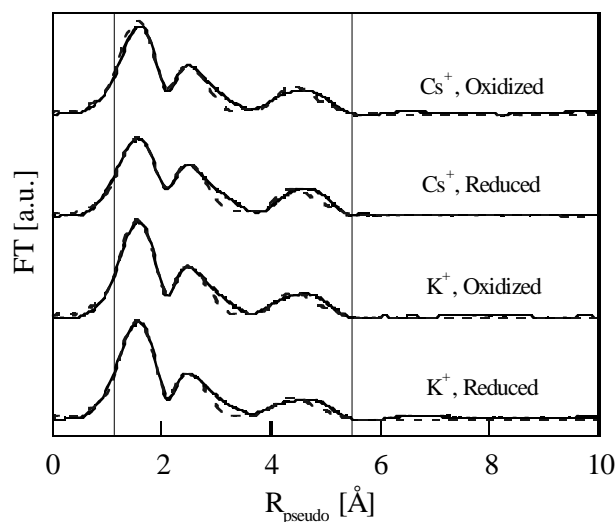


FIG. 4. Ni K edge EXAFS data were fit between the vertical lines. Ni coordination values were found to be between 4.4 and 5.1.

with the C, N, and Ni atoms at distances of $R_{\text{pseudo}} = 1.3, 2.5, \text{ and } 4.5 \text{ \AA}$, respectively. Likewise, the Ni interactions with the N, C, and Fe atoms are reflected in the three main peaks seen in Fig. 4 at $R_{\text{pseudo}} = 1.5, 2.5, \text{ and } 4.5 \text{ \AA}$, respectively. The actual interatomic distances average $R_{\text{Ni-N}} = 2.1 \text{ \AA}$, $R_{\text{C-N}} = 1.2 \text{ \AA}$, and $R_{\text{Fe-C}} = 1.9 \text{ \AA}$. Structural models were fit to the actual data and are shown as dashed lines in Figs. 3 and 4.

Discussion

The sharp, distinct peaks seen in Fig. 1 confirm that cathodically deposited NiHCF is indeed a polycrystalline material. Most of the peaks in Fig. 1 are seen to increase in intensity as the amount of Cs^+ in the matrix increases. The more electron-dense Cs^+ atoms lie within the planes whose diffraction peaks increase in intensity. Likewise, the lattice parameter increases with increasing Cs^+ content (Fig. 2). This also makes sense when one considers Cs^+ vs. K^+ ions; the larger Cs^+ ions stretch the NiHCF lattice slightly when intercalating, whereas the smaller K^+ ions are able to fit into these sites more freely (Cs^+ ionic radius = 1.8 Å; K^+ ionic radius = 1.5 Å). These results agree with recent XRD data taken of anodically derivatized NiHCF [6].

All of the structural variations known to exist in bulk NiHCF retain a cubic structure over a wide range of stoichiometries; thus, the low index peaks are conserved.

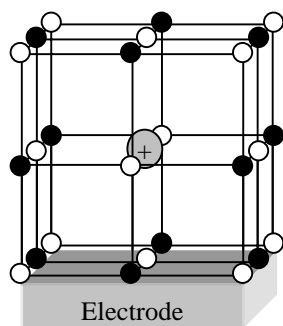


FIG. 5. The structure of cathodically deposited NiHCF in the oxidized state (space group: $Pm-3m$). ● = Fe, ○ = Ni, – = CN, and ⊕ = an intercalated alkali cation.

lattice parameters and confirmed that cathodically deposited NiHCF is a crystalline solid falling within the typical space groups found in bulk NiHCF.

The EXAFS data seen in Figs. 3 and 4 are similar to EXAFS data of other Prussian blues. Namely, the interactions with carbon and nitrogen dominate. Since metal hexacyanoferrates made from $\text{Fe}(\text{CN})_6$ precursors are typically sixfold coordinated, we were able to fix the Fe degeneracy at 6 when fitting structural models to the data. This, in effect, fixes the Debye-Waller factor when

These low index peaks are the only ones that can be resolved for these NiHCF films, as seen in Fig. 1. This leaves analysis of relative peak intensities as the means for refining the structure, which cannot be done reliably for textured materials. So, although these XRD data are not able to fully describe the material structure, they have provided useful

two related data sets are fit simultaneously. Values for the nickel coordination could then be determined independently; these values were found to be between 4.4 and 5.1. Ni coordination values less than 6 are indicative of $\text{Fe}(\text{CN})_6$ vacancies from the traditionally assumed structure; thus, the *average* structure best corresponds with the unit cell shown in Fig. 5. Lattice parameters calculated from the EXAFS data are approximately 0.1 Å larger than those found by using XRD. This trend is indicative of local disorder within the sample, giving further evidence that the structure is defected and $\text{Fe}(\text{CN})_6$ vacancies exist [7]. Thus, cathodically deposited NiHCF is a polycrystalline material with an average structure most closely resembling that shown in Fig. 5.

Acknowledgments

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