Electrochromic Switching Mechanism of Iron Hexacyanoferrates Molecular Compounds: The Role of Fe^{2+}(CN)$_6$ Vacancies

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On the basis of the structure of electrochemically prepared hexacyanometallate compounds, which was determined very recently and unexpectedly to be an *insoluble* structure (Bueno, P. R.; et al. *J. Phys. Chem. C* **2008**, *112*, 13264), a more detailed picture of the electrochromic switching mechanism in this kind of compound was proposed. It was demonstrated that the changeover mechanism is closely related to the electrochromic process. Specifically, it was shown that the coloring process is related to the changeover. Furthermore, by means of spectra-electrochemistry measurements in complement with the *insoluble* structural characteristics of the compound, it was proposed that the electronic charge preferentially occupies Fe^{3+}(NC)$_5$OH$^-$ clusters (i.e., pentacoordinated Fe^{3+} sites). All of these sites represent 25% of the total charge amount capable of being injected in the hexacyanometallate compounds. This is exactly the compositional point where the material starts bleaching and where the changeover is activated. After this compositional point, the Fe^{3+} sites of Fe^{2+}−CN−Fe^{3+} chains (hexacoordinated Fe^{3+} sites) begin to be occupied so that the polaronic mechanism responsible for the strong blue color of the compound is suppressed at this compositional point, and accordingly, the FeHCF is suddenly bleached, accompanied by a current peak that defines the changeover process.

Introduction

The possibility of using an electrochemical control to switch back and forth reversibly between ferrimagnetic and paramagnetic properties of hexacyanometallate compounds containing an alkali metal (e.g., Na$^+$, K$^+$, etc.) has already been demonstrated.[2] Furthermore, experimental studies have shown that structural defects such as Fe^{2+}(CN)$_6$ vacancies filled by (H$_2$O)$_6$ clusters are a prerequisite for photomagnetism.[2,3] This shows the importance of following the structural features of water, mainly its occupational positions in metal hexacyanometallate structures.

The existence of a changeover in the properties of iron hexacyanoferrates (FeHCF), particularly Prussian Blue (PB) materials during in situ compositional modulation, has been shown recently.[4] Furthermore, this changeover is also related to a magnetic change as proved by electroacoustic measurements.[5] This variation in the properties of FeHCF is controlled by a specific charge occupation in the compound structure that activates the changeover process, a mechanism that depends primordially on the structure and specifically on Fe^{2+}(CN)$_6$ vacancies,[1,6] that likely controls the electrochromic mechanism of the FeHCF compound, as shall be demonstrated herein.

For a more complete understanding of electrochemical magnetism and/or electrochromism modulations by means of compositional variation, it is very important to know the structure of the FeHCF K$^+$-containing alkali metal ions. It was demonstrated recently,[1] and very surprisingly, that the structure was found to be *insoluble*, and not *soluble*,[1] as generally mentioned in literature. Therefore, the general formula for electrochemical-stabilized FeHCF compounds is Fe$_4^{3+}$[Fe^{2+}(CN)$_6$]$_3 \cdot m$H$_2$O with the K$^+$ ion occupying the water crystalline structure.[1,7] Accordingly, a more precise description of the FeHCF structure was proposed as Fe$_4^{3+}$[Fe^{2+}(CN)$_6$]$_3 \cdot$[K$_h^+ \cdot$OH$_h^- \cdot m$H$_2$O].[1] The differences between the former picture and the actual one of the FeHCF compound lie mainly in the fact that the water crystalline substructure existing inside the Fe^{2+}(CN)$_6$ vacancies is affected by the presence of K$^+$ ions and such ions do not reside in interstitial sites inside the main FeHCF structure, formed by Fe^{2+}−CN−Fe^{3+} chains.

It is important to emphasize that according to neutron diffraction profile analysis conducted by Herren et al.[8] there are two types of crystalline water clusters. The first kind is a water shell structure (formed by oxygen atoms in 24e crystallographic sites), which is coordinated with the main structure framework by means of the Fe^{3+} atoms, which fill the empty nitrogen sites of the Fe^{2+}(CN)$_6$ vacancies. The second kind of structural water is formed by oxygen atoms occupying 8c and 32f sites and is not coordinated to the FeHCF-type main structural framework, Fe^{2+}−CN−Fe^{3+} chains.[8]

On the basis of this structural picture, the main purpose of the present work is to show that the changeover mechanism[4,5] controls the optical switching (i.e., the exchanging in coloring that is responsible for the electrochromic properties) observed during compositional variation. It will be shown that the changeover depends on the amount of Fe^{2+}(CN)$_6$ vacancies, so

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that the water substructure is considered very important in some switching mechanisms existing in the FeHCF compounds.

Indeed, the structural aspects that are related to these mechanisms are very important to be known since the changeover can be used to modulate electrochromic properties and electrochemical magnetic character of electrochemically tunable magnets.[9] Note that electrochemical magnetism is analogous to electrochromism.[9]

Experimental Section

The FeHCF compounds used here were prepared according to the procedures indicated in refs 4, 5, 7, 10, and 11 as well as the electrochemical analyses performed. Briefly, the electrochemical experiments were carried out in a typical three-electrode cell, where the working electrode was a transparent conductive electrode (ITO) with covering surface of 1 cm^2. A platinum plate was the counter electrode, and Ag/AgCl/KCl saturated was used as the reference electrode. FeHCF compounds were galvanostatically deposited. FeCl$_3$, KFe(CN)$_6$, and HCl were used for the synthesis of the FeHCF compounds. The galvanostatic experiments were carried out by means of a potentiostat-galvanostat (PAR model 263A). The working electrode was immersed into a 0.02 M K$_3$Fe(CN)$_6$, 0.02 M FeCl$_3$, and 0.01 M HCl solution and controlled with a cathodic current of 40 μA cm^{-2}, which was applied during 150 s to obtain the electrodeposited FeHCF electrodes. After that, the FeHCF films were stabilized before the spectra-electrochemistry measurements by means of cyclic voltammetry around the Everit's salt $\leftrightarrow$ FeHCF transition [0.60, −0.20] V in 0.25 M KCl, pH about 2.

Spectroscopic measurements were carried out in a typical electrochemical three-electrode cell. The spectroscopic measurements were performed by using the spectral range given by a HE1LOS b UV−visible spectroscopy (Spectronic Unicam).

Results and Discussion

On the basis of the structural analysis described in a previous work,[1] it was possible to infer some important information regarding the changeover observed in Fe$_4^{3+}$[Fe^{2+}(CN)$_6$]$_3 \cdot$[K$_h^+ \cdot$OH$_h^- \cdot m$H$_2$O] compounds during in situ compositional variation.[1] One important piece of information to be reinforced is that this changeover occurs exactly at a specific and characteristic point of the in situ compositional variation (modulated by ne$^-$ external variation), causing a tremendous increment in the current intensity; there is a current peak at this point, which is not accompanied by any mass variation,[4] according to electrogravimetric measurements (Figure 1 and refs 4 and 5).

Taking into account the aforementioned aspects and features of the changeover and the knowledge of the structural model, a more precise description will be proposed for the evidence that shows that the changeover mechanism is strongly related to the amount of Fe^{2+}(CN)$_6$ vacancies. According to some experiments in the literature,[14] it was observed that in this compositional point (changeover of the properties) there is also a change on the absorption, related to the coloring properties of the FeHCF compound.[14,15] At this particular changeover point, it is known that the FeHCF compound changes its color from blue (its name having been derived historically because of its natural coloration, a stable blue color compound) to an unstable transparent (the bleached compound is not stable in air if an electrochemical potential is not maintained, but the process is totally reversible during potential cycling in the electrolyte environment).
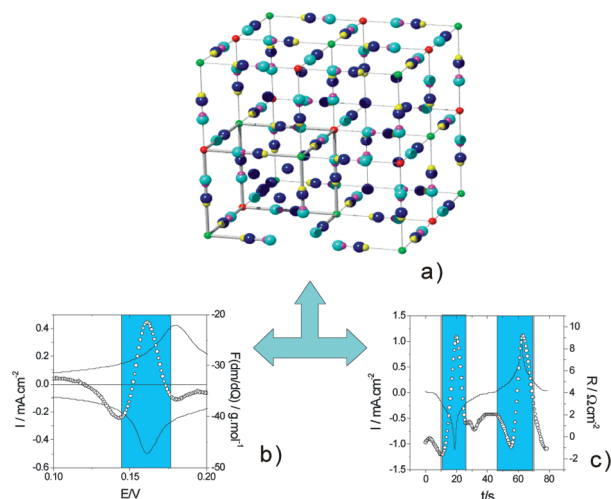

Figure 1. (a) Schematic representation of the stabilized FeHCF insoluble structure with Fe^{2+}(CN)$_6$ vacancies. (b) Voltammetric scan (solid line) and (○) *F*(d*m*/d*Q*) function.[4] (c) Current density as a function of time (solid line) (i.e., the voltammetric scan represented in a different way) and (□) the motional resistance.[5] The peaks are processes related to the changeover mechanism.[4,5]
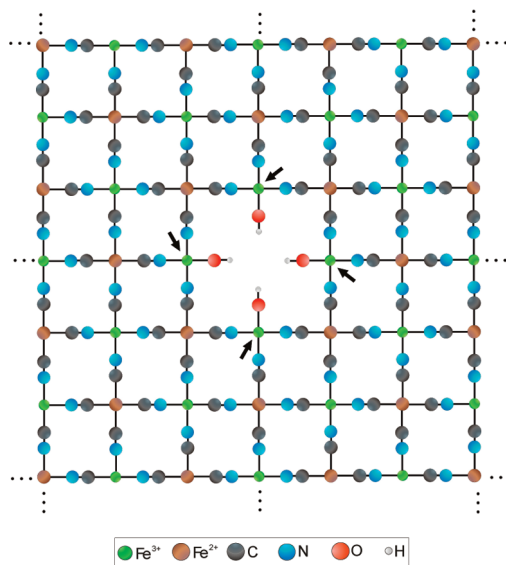

Figure 2. Planar schematic representation of a Fe^{2+}(CN)$_6$ vacancy environment in the role framework in FeHCF compound. The arrows indicate the preferential Fe^{3+}Fe^{3+}(NC)$_5$OH$^-$ clusters or entities where electronic charge is preferentially occupied before the changeover and the electrochromic process take place.

In the present situation, it is known that the total amount of electronic charge reaching the changeover point during in situ compositional variation is about 25% of the total charge of the processes in the range from −0.2 to 0.6 versus Ag/AgCl.[4] From an electronic charging point of view, the similarity between this amount of charge and that found from structural analysis, which is equivalent to the amount of Fe^{2+}(CN)$_6$ vacancies,[1,6] is very important.

Indeed, on the basis of this information, it is likely possible to suggest that the most probable electronic sites for electrons, before the changeover, are located in clusters of the Fe^{2+}(CN)$_6$ vacancies. These clusters can be referred to as [Fe^{3+}(NC)$_5$OH$^-$]$_6$ and probably are favorable electronic energy levels in which the electronic charge is inserted. Figure 2 illustrates these entities from a planar representation to facilitate the viewing. In other words, Fe^{3+}(NC)$_5$OH$^-$ acts as bridges between ionic vacancy

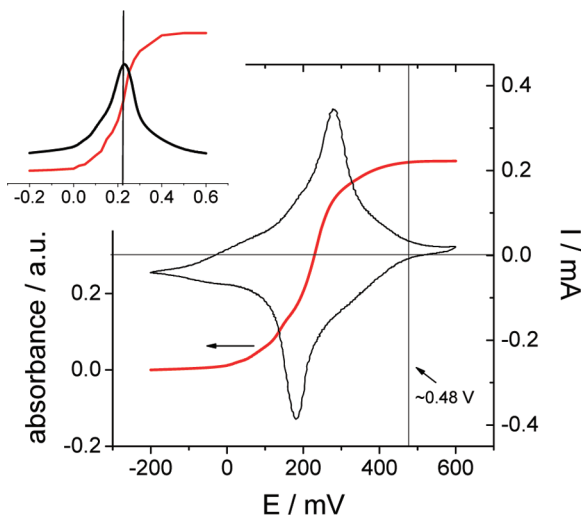**9918** *J. Phys. Chem. C, Vol. 113, No. 22, 2009*

Bueno et al.

Figure 3. Spectra-electrochemistry analysis at 687 nm corresponding to the energy for absorption of intervalence charge transfer between $Fe^{2+}-CN-Fe^{3+}$ chains of the *insoluble* PB structure. The 687 nm absorption peak is here monitored as a function of potential versus Ag/AgCl/KCl inside Ag/AgCl as the reference. Note that there is no absorption variation until the changeover potential starts to be reached (around 400 mV). Cyclic voltammetric pattern is shown as a background to show the region in which the processes starts. (Inset) Derivative of absorption as a function of potential. The derivative shows a peak around 0.2 V, which is exactly the potential value in which the changeover occurs, reaching its maximum crossover intensity. The behavior of the spectra-electrochemistry curve is reversible (not shown) as widely known since it follows the coloration cyclic behavior.[4,5,12,13] Note also that the variation in the motional resistance of Figure 1c is also reversible.[4,5]

environment and $Fe^{2+}-CN-Fe^{3+}$ chains. It is important to reinforce that this is in such an environment that the coordinated water is located and connected with the main structure framework ($Fe^{2+}-CN-Fe^{3+}$ chains). The later chain is formed by hexacoordinated Fe atoms and not pentacoordinated Fe as in $[Fe^{3+}(NC)_5OH^-]_6$ entities.

Considering the results obtained in refs 1 and 7, it is possible to conclude that the occupation of this electronic state (that correspond to 25% of the total charge) must be compensated by an ionic counterpart (i.e., K^+, H^+, and/or H_3O^+ ionic interplay around water crystalline counterpart), which is totally in agreement with the ionic interplay mechanism proposed in refs 7 and 16 and revisited in ref 1.

To verify the aforementioned statements, the absorption properties in 687 nm will be considered.[14] As classically known from coordination chemistry, the nitrogen pentacoordinated to Fe^{3+} metals (i.e., $Fe^{3+}(NC)_5OH^-$ clusters or entities) does not present absorbance in the UV−visible range.[14] On the other hand, the particular 687 nm wavelength has an energy whose absorption is attributed to $Fe^{2+}-CN-Fe^{3+}$ entities due to intervalence charge transfer (IVCT),[14] a very known mechanism that, in general, explains coloring changes in electrochromic materials.[12] The IVCT, or any polaronic model, considers that the coloration absorption in electrochromic compounds is due to a dynamic electronic intervalence exchange,[12] which in the case of FeHCF is given by $Fe^{2+}-CN-Fe^{3+}$ entities (i.e., a resonant movement of the electronic charge between Fe^{2+} and Fe^{3+} separated by −CN− cyanide group). The spectra-electrochemical signal of $Fe^{2+}-CN-Fe^{3+}$ entities, indicated by the absorbance spectra at 687 nm, is observed in Figure 3 as a function of potential with a voltammogram as a background to a better visualization of the changes as a function of compositional variation. As expected, there is no variation in absorption

before the changeover point around 400 mV versus Ag/AgCl. This means that the $Fe^{2+}-CN-Fe^{3+}$ entities are not being electronically occupied before the changeover point starts. The energy level (electronic states) of these entities starts to be occupied only in the changeover point, as clearly observed in Figure 3 by means of an abrupt variation of the absorption of this band (sigmoidal decrease of absorption and bleaching). This picture of the process is confirmed by the fact that $Fe^{3+}(NC)_5OH^-$ clusters or entities have a potential value of about 0.48 V versus Ag/AgCl,[14] which coincides with the potential in which the 687 nm wavelength starts varying, immediately before the potential value in which the changeover process arises (as indicated in Figure 3). The occupation of $Fe^{2+}-CN-Fe^{3+}$ entities indicates the decrease of the possibility of blue absorption in FeHCF due to the decrease in the Fe^{3+}/Fe^{2+} ratio inside the FeHCF structure and especially in $Fe^{2+}-CN-Fe^{3+}$ chains. As the $Fe^{3+}(NC)_5OH^-$ clusters represent an interface or surface that separates the FeHCF structure from the coordinated water substructure, after the occupation of these preferential electronic states the bleaching starts by means of the conversion of $Fe^{2+}-CN-Fe^{3+}$ chains to $Fe^{2+}-CN-Fe^{2+}$ ones. This picture of the electrochromic changeover process is also in agreement with the fact that electronic charges, if they have mobility (conductivity), tend to accumulate into the surfaces of the compounds or materials (the $Fe^{3+}(NC)_5OH^-$ are local surface clusters inside FeHCF structure).

Furthermore, as the magnetic properties change at this point,[5] after the electronic sites (likely the most favorable energetic electronic level) located at $Fe^{3+}(NC)_5OH^-$ clusters (and they represent 25% of the total Fe^{3+} to be electronically occupied in the FeHCF compound) are totally occupied, a structural electronic rearrangement related to superexchange interactions between Fe^{2+} and Fe^{3+} metallic electronic sites,[4] mediated by the CN bridges, most likely occurs.[4] According to motional resistance calculated at steady-state conditions (see Figure 2 of ref 5), it is possible to infer that there is also a structural rearrangement at this point.[5] Such a mechanism will be discussed in a future work supported by a more complete spectra-electrochemical analysis.

Electrochromic and Magnetic Switching Mechanism. The sites for electronic charge occupation injected from an external circuit during in situ compositional variation are Fe^{3+}. The full occupancy is thus reached when all the material's bulk has $Fe^{2+}-CN-Fe^{2+}$ chains (i.e., with all Fe^{3+} entities converted to Fe^{2+}). In the general formula, it means that $Fe_4^{2+}[Fe^{2+}(CN)_6]_3 \cdot [K_h^+ \cdot OH_h^- \cdot mH_2O]^1$ (i.e., all the 4a crystallographic sites receive an electron from the external circuit). However, before this state is reached, a previous state is preferentially occupied (i.e., $Fe^{3+}(NC)_5OH^-$ clusters). Therefore, accordingly, the IVCT mechanism cannot act when $Fe^{2+}-CN-Fe^{3+}$ chains are extended occupied and the material is thus transparent, with a minimal variation of the transmittance (bleached state), since polaronic dynamics between iron atoms mediated by −CN− chains totally vanished. Note then that there are two types of Fe^{3+} sites: (i) Fe^{3+} into the $Fe^{2+}-CN-Fe^{3+}$ chains and (ii) those adjacent to the $Fe^{3+}(CN)_6$ (i.e., $[Fe^{3+}(NC)_5OH^-]_6$) (Figure 2). These sites are represented by the $Fe^{3+}(NC)_5OH^-$ formula, which are related to Fe^{3+} sites adjacent to the $Fe^{2+}(CN)_6$ vacancies and coordinated by a first water shell crystalline substructure. There are, in the whole volume of the $Fe^{2+}(CN)_6$ vacancy entities, six of these units.

It will be assumed here that the sites for electronic charge occupation injected from an external circuit during in situ compositional variation are, because of energetic requirement,
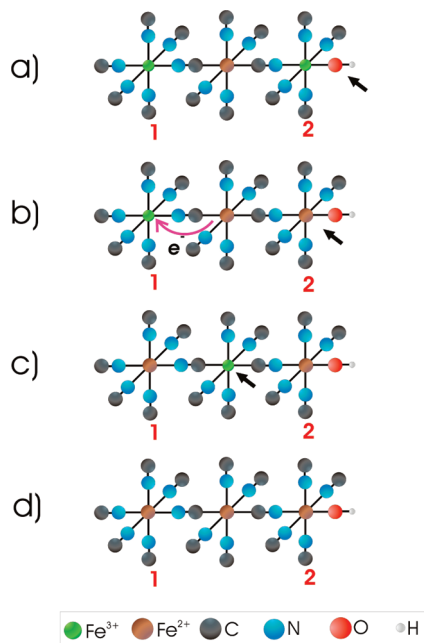
Electrochromic Switching Mechanism of FeHCFs

J. Phys. Chem. C, Vol. 113, No. 22, 2009 **9919**

Figure 4. Linear schematic representation of $Fe^{2+}(CN)_6$ vacancy environment and changeover and electrochromic mechanisms during electronic charging of the FeHCF compound. (a) Pentacoordinated Fe^{3+} in 4a crystallographic sites (octahedral coordinated by N atoms) (i.e., $Fe^{3+}(NC)_5OH^-$ clusters before electronic charging starts). The arrows in (a) indicate the OH^- entities where ionic compensating charges (H^+, H_3O^+, or K^+) must be located. (1) Fe^{3+} that does not have water substructure adjacent to it. (2) Fe^{3+} in 4a crystallographic sites adjacent to the water substructure. (b, c) Stage of the mechanism in which the changeover and bleaching process described in the text occur. (d) Final stage in which FeHCF compound is fully charged, when all Fe^{3+} is converted into Fe^{2+}.
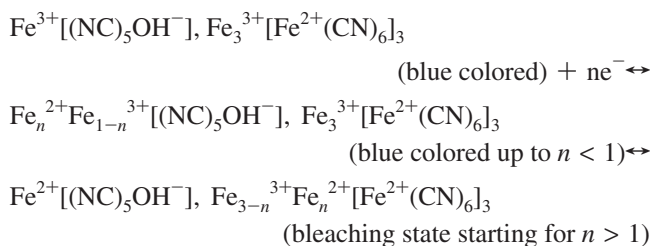
preferentially occupied by Fe^{3+} at $[Fe^{3+}(NC)_5OH^-]_6$ clusters. Therefore, it is being assumed that Fe^{3+} sites adjacent to the $Fe^{2+}(CN)_6$ vacancies are being preferentially occupied up to the changeover process starting, when the electrons occupy Fe^{3+} with unsatisfied $CN-Fe^{3+}$ chemical bonding adjacent to the vacancies. This particular site of the structure is a pentacoordinated Fe^{3+} instead of hexacoordinated Fe^{3+}, fully satisfying the chemical bonding. This explains why there is no color change up to 400 mV (i.e., around potential values just before the changeover starts taking place). This observation is related to the fact that these entities ($Fe^{3+}(NC)_5OH^-$ clusters) are inactive for UV–visible absorption.[14] This mechanism is totally in agreement to what was discussed concerning the spectra displayed in Figure 3. The intense blue absorption of FeHCF is thus due to IVCT mechanism associated with $Fe^{2+}-CN-Fe^{3+}$ charge transfer (polaronic dynamics), and the material is blue and magnetically active (before the changeover potential).

It is important to clarify that the OH^- entity is a consequence of the presence of the first water shell coordinated with the main structure framework (coordinated water).[1] It is a very important and particular environment of this structure because it is the bridge between the water substructure and the main framework represented by the $Fe^{2+}-CN-Fe^{3+}$ chains. Such bridge or connection is made mainly by means of the Fe^{3+} atoms at 4a crystallographic sites chemically bound to OH^- entities (first coordinated water substructure) as schematically displayed in Figure 4. The water crystalline substructure is a nonstoichiometric environment, and this characteristic is very important to control the occupancy of ionic sites by K^+, H^+, and/or H_3O^+ entities.[1,7]

Considering that the $Fe^{3+}(NC)_5OH^-$ site is favorably occupied by the electrons inserted from an external circuit during in situ

compositional variation (i.e., that this is the most energetically favorable site for occupation before the changeover), it is possible to say that, from the knowledge of the structure and from structural rules that arise with this particular *insoluble* structure, these sites shall saturate exactly when 25% of Fe^{3+} in the $Fe^{3+}(NC)_5OH^-$ environment is fully occupied. In other words, it is being considered that all the electronic charge imposed to the system up to the changeover point is going to fulfill the $Fe^{3+}(NC)_5OH^-$ sites. At this exact electronic charge fraction, when about 25% of all Fe^{3+} sites are being occupied, which is linked to the amount of $Fe^{2+}(CN)_6$ vacancies, the changeover occurs. This picture is in agreement with the proposal that all the charge is occupying exactly the $Fe^{3+}-(NC)_5OH^-$ entities (i.e., the entities that serve as bridge sites between the FeHCF main framework formed by $Fe^{2+}-CN-Fe^{3+}$ chains and water substructure) in the precise moment before the changeover process takes place.

Finally, it is important to mention that the picture of the changeover described here, by combination of ionic and electronic aspects, is totally in agreement with the fact that the K^+ ions are located in the water crystalline substructure and that this is crucial for the occurrence of the changeover. The role played by K^+ ions must still be better understood and clarified by future complementary measurements. However, the electrochromic mechanism in FeHCF compound is related to the changeover process and can be detailed as:

$$Fe^{3+}[(NC)_5OH^-], Fe_3{}^{3+}[Fe^{2+}(CN)_6]_3$$
$$\text{(blue colored)} + ne^- \leftrightarrow$$
$$Fe_n{}^{2+}Fe_{1-n}{}^{3+}[(NC)_5OH^-], Fe_3{}^{3+}[Fe^{2+}(CN)_6]_3$$
$$\text{(blue colored up to } n < 1)\leftrightarrow$$
$$Fe^{2+}[(NC)_5OH^-], Fe_{3-n}{}^{3+}Fe_n{}^{2+}[Fe^{2+}(CN)_6]_3$$
$$\text{(bleaching state starting for } n > 1)$$

Therefore, the process can be summarized considering that the total conversion to the bleached state occurs exactly when n reaches the unit value (i.e., 0.25 of total Fe^{3+} sites of the FeHCF compound), activating the changeover, a compositional point in which there is an injection of a great amount of electronic charge (current peak) with the subsequent occupation of iron metals (Fe^{3+} site) of $Fe^{2+}-CN-Fe^{3+}$ chains. At this point, the polaronic mechanism is suppressed and the charge transfer between valences is avoided so that the FeHCF is suddenly totally bleached.

Conclusions and Final Remarks

The changeover process is described here from a structural point of view according to a structural analysis that reveals that FeHCF compounds have about 25% of $Fe^{2+}(CN)_6$ vacancies. From such consequences and according to spectra-electrochemical analysis, it was shown that the electrochromic mechanism is related to the changeover process. The changeover occurs exactly when the $Fe^{2+}Fe_3{}^{3+}[Fe^{2+}(CN)_6]_3 \cdot [K_h{}^+ \cdot OH_h{}^- \cdot mH_2O]$ composition is reached (i.e., when all the Fe^{3+} (iron–nitrogen octahedral coordinated sites) is converted to Fe^{2+} in 4a crystallographic sites of the structure adjacent to the $Fe^{2+}(CN)_6$ vacancies).

Therefore, it was shown here that the changeover and electrochromic processes are activated exactly when 25% of total electronic charge is injected in the FeHCF compound by the ne^- external circuit, which corresponds to 25% of the total Fe^{3+} converted to Fe^{2+}. Furthermore, this fraction of Fe^{3+} converted was inferred to be exactly located at $Fe^{3+}(NC)_5OH^-$

clusters, that is, pentacoordinated Fe^{3+} iron metals that are the bridges between the main FeHCF framework ($Fe^{2+}-CN-Fe^{3+}$ chains and water substructure) by means of OH^- local chemical entities. The mechanism involved with the amount of $Fe^{2+}(CN)_6$ vacancies existing in the FeHCF compounds is capable of fully revealing and explaining the electrochromism of these materials.

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