

Cobalt Hexacyanoferrate: Compound Stoichiometry and Photoinduced Electron Transfer

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The electrochemistry of Prussian blue and related metal hexacyanoferrates (MHCF) has been intensely studied in recent years (see Refs 1-3 for reviews). Cobalt hexacyanoferrate (CoHCF) is of particular interest from both fundamental and practical perspectives: (a) CoHCF has unique electrochromic properties with color changes not only dependent on the oxidation states of the Co and Fe redox centers, but also on the nature of the co-cation imbibed by the compound during electroreduction.⁴ (b) CoHCF exhibits the phenomenon of reversible photoinduced magnetization.⁵⁻⁷ (c) The ability of CoHCF to bind electrolyte cations can be exploited in environmental remediation scenarios as for the separation and transfer of Cs⁺ from high sodium waters.⁸ (d) CoHCF-modified electrodes have shown good electrocatalytic activity toward a variety of substrates including ascorbic acid, nitrite, hydrazine, *p*-chlorophenol, and hydroxylamine.⁹⁻¹¹ and (e) CoHCF, in addition to its electrochromic properties, also exhibits reversible thermochromism in the 25-85 °C temperature range.^{4a,12}

In spite of this extensive body of prior electrochemical work, a comprehensive study of the many possible compound stoichiometries in the CoHCF system as a whole, is currently lacking. Therefore, we report, using a combination of voltammetry, infrared spectroelectrochemistry, impedance spectroscopy, and X-ray photoelectron spectroscopy, how the CoHCF compound stoichiometry: (a) depends on the preparative history of the film; (b) evolves with the applied potential; and (c) dictates electron and ion transport between the film and the contacting electrolyte either in the dark or under photoexcitation.

CoHCF films were deposited on Au electrodes by three methods, namely: (a) potentiodynamic cycling on gold substrate, (b) coagulation plus potentiodynamic cycling, and (c) potentiodynamic cycling starting with a gold substrate at 1.2 V, that is, covered with an oxide layer.

Within the framework of our study, only CoHCF compounds bearing Co:Fe stoichiometries from 1.5 to 1.0 are pertinent. Co^{II}₃Fe^{III}(CN)₆]₂ and

M^ICo^{II}[Fe^{III}(CN)₆] represent the 1.5 and 1.0 end stoichiometries respectively, and M is the co-cation required to maintain electroneutrality. Intermediate stoichiometries give rise to a range of compounds represented by M^I_{3y-8}Co^{II}₄[Fe^{II}(CN)₆]_y, and the cobalt sites may exist in mixed II, III oxidation states, as in the structure M_{0.4}Co^{III}₁Co^{II}_{0.3}[Fe^{II}(CN)₆].

By considering all our data as a unit, a self-consistent redox scheme emerges, based on seven distinct CoHCF species with Co:Fe ratios in the 1.5-1.0 range. They are inter-linked through three independent pathways and charge transfer processes in the dark and activated by IR radiation. The photoinduced electron transfer from Co(III) to Fe(II) elongates the Co-N distance and thus improves the co-cation movement.

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