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Cobalt hexacyanoferrate in PAMAM-doped silica matrix
1. Solid state electrochemistry and thermochromism

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Abstract

The solid-state electrochemistry and thermochromism of cobalt hexacyanoferrate (CoHCF) in a composite matrix comprising silica sol–gel and generation-4 poly(amidoamine) dendrimer was investigated and compared to analogous studies of CoHCF powders. The thermochromic behaviour over the range, 25–85 °C, of the reduced form in the sol–gel matrix differed from that of the powder. The results suggested that even in the presence of KCl in this matrix, the dominate form of the reduced CoHCF was $Co_2{}^{II}Fe^{II}(CN)_6$ rather than $K_2Co^{II}Fe^{II}(CN)_6$. In contrast, the thermochromic behaviour of the oxidized form of CoHCF was the same as that reported for the powders. The observed cyclic voltammetric behaviour of CoHCF in the sol–gel composite matrix was the same as that of powders in terms of the electrode processes, but the influence of scan rate on the current was dependent upon the cell configuration. With the CoHCF-doped composite contacted to a solution phase, this behaviour was consistent with anion intercalation/de-intercalation control, but in a solid-state cell, a transition from a surface-controlled to a mass-transport controlled current was observed.

Keywords: Cobalt hexacyanoferrate; Silica sol–gel; Thermochromism, Electrochemistry

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1. Introduction

Metal hexacyanoferrate Prussian Blue analogs are an interesting class of compounds studied for their electrochromic [1–3], electrocatalytic [4–9], magnetic [10–14], ion-sensing properties [15–17] and ion storage [18–20] capabilities. Among this class of compounds the cobalt analogue (CoHCF) shows peculiar chemical–physical behaviour. In particular reversible thermochromism of CoHCF was studied by Kulesza et al. [21,22] and is ascribed to the partial or total dehydration of the compound upon heating. Despite extensive studies in the past years, some basic aspects of their chemical physical properties are still unclear [23–25].

In the Prussian Blue analogs the redox process is coupled with an insertion-release of a cation, generally an alkali metal, in order to ensure the electroneutrality of the compound. The cyanometallates are studied as powders, films for electrode modification or guests in silica matrices.

The chemical–physical properties seem to be driven by the overall crystalline structure. In particular, the presence of soluble and insoluble form in various ratios in Prussian Blue analogues give the compound different characteristics [26–28]. For example, vacancies in the structure of the insoluble form created by a the lack of a $Fe(CN)_6$ unit leave the cobalt local environment flexible. This flexibility facilitates the oxidation of Co^{II} to Co^{III} that causes the shortening of the Co–N bond length from 2.13 to 1.90 Å. The inserted cation plays a key role in determining whether Co^{III} forms: in this regards Co^{III} seems to be

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obtainable only with structures containing potassium ions [12].

In studies of CoHCF, some authors report the presence of an additional Co^{2+}/Co^{3+} redox reaction, which results in two electrochemical processes in contrast to the behaviour found for other mixed hexacyanoferrates where the electrochemical behaviour is attributed only to the Fe^{+2}/Fe^{+3} redox couple in the studied potential range. In addition to the occurrence of Co^{III} species in CoHCF, its electrochemical behaviour seems to be dependent on the preparation route and on the nature of the interstitial countercation that can modulate the ratio between soluble and insoluble forms.

In our previous paper [29] we demonstrated that silica doped with polyamidoamine (PAMAM) dendrimers of different generations behaved as a good hosting material for Prussian Blue allowing solid-state electrochemical and spectral studies. A similar preparation route has been followed by Moore, who obtained nanoscale CoHCF by incorporating the material in a silica matrix as a host [30].

In this paper we describe the voltammetric and the thermochromic results obtained for CoHCF in a silica sol–gel doped with PAMAM. The results are compared to literature reports on CoHCF powders.

2. Experimental

Tetramethylorthosilicate, TMOS (99% pure) and polyamidoamine (PAMAM) dendrimers were purchased from Aldrich Chemical Co. (Milwaukee, WI). The generation 4 (G4) PAMAM (molecular mass, 14,215 Da; 64 surface amine groups) was 10 (wt.%) solution in methanol. Other chemicals were reagent grade from Fisher Scientific (Pittsburgh, PA). The water was purified with a Barnstead NANOpure II system to a conductivity of $17.5\,M\Omega\,cm^{-1}$.

The voltammetric experiments were performed with a CHI Model 630 Electrochemical Workstation (CH Instruments, Austin, TX). The cell used for the solid-state voltammetry, shown in Fig. 1, was designed and applied for XAS spectroelectrochemical experiments on biological compounds [31]. The modified silica (b) was put on a graphoil (Goodfellow cat. C 000200/2) sheet (a) that served as current collector in contact with a Pt wire as external electrical contact. The silver wire acted as a quasi-reference electrode. The counter electrode was a Pt wire in contact with the silica surface. To follow the behaviour of the gel in solution, a small piece of gel trapped in a Pt net and placed in a solution containing 1 M KCl. The reference electrode was a SCE; as counter electrode we used a Pt foil. Experimental set up for SSE (solid state electrochemistry) was similar to one in a previous report [29].

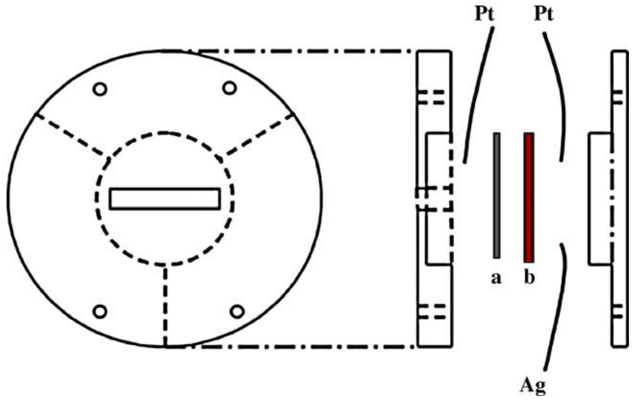

Fig. 1. Schematic view of the solid state electrochemical cell used for experiments. (a) Graphoil sheet; (b) modified silica monolith.

The UV–vis spectra were collected with an 8453A HP diode array spectrophotometer (Agilent Technologies, Waldbronn, Germany). The absorption spectra are referred to a blank recorded on a free CoHCF sample, when possible, or to the instrumental blank. The support for modified silica during thermochromic experiments on the optical axis of the spectrophotometer was an in-house made furnace with the temperature carefully controlled by an iron-constantan thermocouple connected with a heating system already described [22]. Silica monoliths were prepared by combining TMOS with 0.2 M KCl, 0.1 M HCl and 1 mM (methanol solution) PAMAM (of the desired generation) in a volume ratio of 1:1:1:1. The mixture was stirred for 30 min and dried for at least 10 days in 60 mm × 25 mm Falcon (plastic) covered Petri dishes (Fisher). The dimensions of the dried cylindrical monoliths were 1 mm thickness and 20 mm diameter. Unless otherwise stated, the doping of gels was performed by immersing them in 0.1 M $K_3Fe(CN)_6$ or 0.1 M $K_4Fe(CN)_6$. Immersion of glasses containing either $Fe(CN)_6{}^{3-}$ or $Fe(CN)_6{}^{4-}$ in 0.1 M $CoCl_2 - 1$ M KCl solution give rise to the formation of oxidized or reduced CoHCF. Based on the results obtained in preparation of the same glasses doped with Prussian Blue [29], the silica monolith was immersed in ferro-ferricyanide solution for 10 min and than in $CoCl_2$ for 20 min. This procedure ensures the formation of a layer of CoHCF of about 0.2 mm thick enough to record visible spectra and to perform electrochemical measurements. Attempts to improve doped layer increasing the immersion time was unsuccessfull. Anyway the doping kinetics was not fully investigated.

3. Results and discussion

3.1. Visible absorption

The inclusion of CoHCF in a silica sol–gel containing G4 PAMAM dendrimer has been pursued by following the procedure developed for modification with Prussian Blue [29].

According to the proposed scheme shown in Fig. 2, the protonated dendrimer contained in the silica reacts with hexacyanoferrate ions (3^- or 4^-) present in the modification solution. The visible spectra obtained from the modified monoliths show the bands typical for solutions containing $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$. The subsequent immersion of the