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# Enhanced electrodeposition of indium hexacyanoferrate thin films through improved plating solution stability

Abstract An ordinary plating solution for indium hexacyanoferrate (InHCF) thin film deposition, mainly composed of equal concentrations of In^{3+} and $[Fe(CN)_6]^{3-}$, usually forms precipitates rapidly when either concentration is higher than few millimolar. This contributes to the plating solution's instability. Moreover, electrodeposited capacities are limited accordingly. In this work, the plating solution's stability and the electrodeposition of InHCF were greatly enhanced by adding a large amount of K^+ and/or H^+. It was found that a 10-mM plating solution added with 1 M HCl and 1 M KCl could be stored as fresh over a one-week period, whereas an unmodified plating solution became useless within a couple of minutes. Also, such cationic additions, especially adding H^+, increased the electrodeposited capacity ca. 18 times at least, as compared with that obtained from the unmodified plating solution. Furthermore, related enhancing mechanisms were proposed and verified. To sum up, this study offers a means for better InHCF electrodeposition and should promote the applications of InHCF films.

Keywords Electrochromic device · Electrodeposition · Indium hexacyanoferrate · Plating solution · Solution stability

Introduction

Indium hexacyanoferrate (InHCF) is a Prussian blue analogue [1] and undergoes a reversible redox reaction in a K^+-containing electrolyte. The following reaction is accompanied by a yellowish-to-colorless electrochromism [2, 3, 4, 5, 6]:

$$In[Fe(CN)_6](yellowish) + K^+ + e^- \rightleftharpoons$$
$$K[InFe(CN)_6](colorless) \tag{1}$$
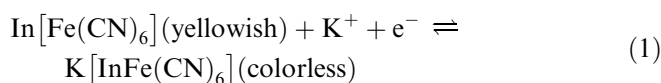
Therefore, InHCF can be considered as a superior transparent counter-electrode for complementary electrochromic devices [7, 8]. In addition, InHCF has been investigated for uses as a photoelectrode-stabilizing coating [9], a photoelectrochemical converting material [10], and a biosensor [11]. Although a variety of applications have been reported, the plating solution's instability has remained a bottleneck in limiting the practical uses of InHCF.

InHCF films can be prepared by cyclic voltammetric (CV) electrodeposition [2, 3, 4, 11], potentiostatic electrodeposition [5], and sacrificial anode deposition [6]. In general, the aqueous plating solution is composed of equal concentrations of In^{3+} and $[Fe(CN)_6]^{3-}$ [2, 3, 4, 5, 6, 11], which is similar to that of Prussian blue [1]. Because precipitates form in the plating solution within a short time when the concentration of either In^{3+} or $[Fe(CN)_6]^{3-}$ is higher than few millimolar, most of the plating solutions reported in the literature used a very dilute mixture of In^{3+} and $[Fe(CN)_6]^{3-}$ ($\leq$ 1 mM) [2, 3, 11]. However, such low-concentration plating solutions limit the electrodeposited capacity of the InHCF film. Thus, the applicability of InHCF is restricted. To overcome this issue, this work is devoted to the stabilization of a concentrated plating solution ($\geq$10 mM) for better InHCF electrodeposition.

Through literature reviews, it was found that Dong and Jin [4, 5] electrodeposited InHCF films using a solution containing 10 mM In^{3+}, 10 mM $[Fe(CN)_6]^{3-}$, and 2 M HCl. This 10-mM plating solution is required in order to form a film with a promising electrodeposited capacity, according to experience concerning assembling a PB-based electrochromic device [8]. As far as we know,

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their work employed the most concentrated InHCF plating solution, which is believed to be reasonably stable. Nonetheless, it is also noticed that such a plating solution is extremely acidic, as compared to other dilute solutions used [2, 3, 11]. This implies that an H^+-rich environment may help in stabilizing a concentrated In-HCF plating solution. Through our experimentations, when a 10-mM InHCF plating solution was added with plenty of KCl (say, 1 M) to form the "soluble-form" InHCF [1, 3, 11] during the CV electrodeposition, it was observed that the plating solution could be stored overnight. This infers that not only H^+ but also K^+ has a great influence in stabilizing the InHCF plating solution.

This paper addresses the effects of adding 1 M KCl and/or 1 M HCl on the 10-mM InHCF plating solution's stability. Furthermore, the influences of adding KCl and/or HCl on the CV electrodeposition and the corresponding film's electrochemical performances will also be discussed. By clarifying the roles of K^+ and H^+, this work aims to provide an approach to better InHCF electrodeposition.

Experimental

The main chemicals used in this work were $InCl_3$, $K_3Fe(CN)_6$, KCl, HCl, and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). All of them were ACS reagent grade and were not further purified. Deionized water (DIW) was used throughout. Transparent F-doped SnO_2-coated (FTO) glass substrates ($R_{sh} = 20$ Ω/sq.) were obtained from a local supplier (Sinonar Corporation, Hsinchu, Taiwan). Before using, the FTO glass substrates were ultrasonically cleaned in 0.1 M HCl for 5 min and then in DIW for another 5 min. After cleaning, the substrates were rinsed with DIW and dried in air. Afterward, a Cu tape (3M Company) was applied to one side of the FTO surface as the bus bar and an insulating tape was also applied to the same side to maintain an electrode area of 3.0×1.5 cm^2 for each substrate.

The absorptive spectroscopy was performed using a UV-visible spectrophotometer (Shimadzu, model UV-1601PC) to monitor the concentrations of four different plating solutions (solutions A, B, C, and D), consisting of 10 mM $InCl_3$ and 10 mM $K_3Fe(CN)_6$ in the absence of additives (A) and with the additives of 1 M KCl (B), 1 M HCl (C), and both (D), respectively. In addition to the optical probes, a simultaneous pH measurement (Orion, model 720A) was executed. Also, the CVs for the $[Fe(CN)_6]^{3-}/$ $[Fe(CN)_6]^{4-}$ redox couple on the FTO glass substrate under different additive conditions, corresponding to solutions A, B, C, and D, were recorded through a potentiostat/galvanostat (Auto-lab, model PGSTAT30).

InHCF thin films were deposited onto FTO glass substrates in solutions A, B, C, and D by CV electrodeposition [2, 3, 4, 11]. During the electrodeposition, a potential scanned back and forth between 0.2 and 1.3 V (vs. Ag/AgCl/sat. KCl) at a rate of 200 mV/s was applied to the FTO substrate for 20 cycles. As-prepared films were cleaned with DIW and then were dried in air at room temperature for at least 24 h. Afterward, the InHCF films were electrochemically characterized by a three-electrode CV using the above-mentioned potentiostat/galvanostat. To prevent the InHCF films from peeling off the FTO substrates, the KCl-saturated poly-AMPS (K-PAMPS) electrolyte with dimensions of $3.0 \times 1.5 \times 0.2$ cm^3 was employed during the electrochemical characterization. The preparation and properties of the K-PAMPS electrolyte are described elsewhere [8].

Results and discussions

Figure 1 gives the absorptive spectra of an $InCl_3$ aqueous solution, a $K_3Fe(CN)_6$ aqueous solution, and a fresh InHCF plating solution (an aqueous mixture of In^{3+} and $[Fe(CN)_6]^{3-}$) with the addition of K^+ and H^+. The $[Fe(CN)_6]^{3-}$ spectrum shown here totally agrees with that in the literature: a ferric cyanide aqueous solution exhibits three absorption bands at 263, 303, and 417 nm [12]. It was confirmed experimentally that the spectroscopic feature of a fresh InHCF plating solution is identical to that of $[Fe(CN)_6]^{3-}_{(aq)}$ (an absorption band at 417 nm [12]). This implies that adding $InCl_3$ does not affect the spectrum of $K_3Fe(CN)_6$. In addition, the presence of KCl and/or HCl does not affect the spectroscopic characteristics. Thus, the $[Fe(CN)_6]^{3-}$ concentration changes in solutions A, B, C, and D, due to the co-precipitation with In^{3+}, were quantified by measuring the absorbance change at 417 nm, based on Beer's law. The results are plotted in Fig. 2 to illustrate the influences of adding 1 M KCl and/or HCl on the stability of a 10-mM plating solution. Figure 2 shows that both K^+ and H^+, when present in large amounts, can greatly stabilize the plating solution. Furthermore, it was observed experimentally that the most stable plating solution (solution D, added with 1 M KCl and 1 M HCl) could remarkably be stored as fresh in air even over one week, whereas the ordinary, un-modified plating solution (solution A) became useless within a couple of minutes.

To explain the stabilizing mechanism by adding H^+, the InHCF plating solution's instability was considered, and the related mechanisms are suggested as follows:
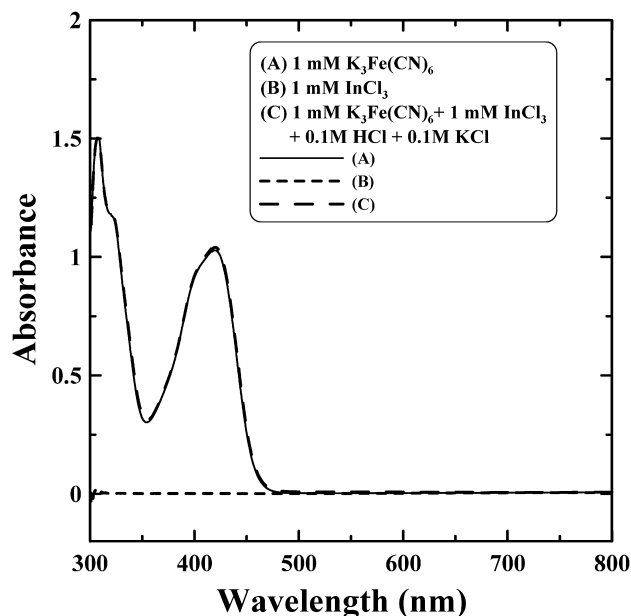

Fig. 1. UV-visible absorptive spectra of $InCl_{3(aq)}$, $K_3Fe(CN)_{6(aq)}$, and the fresh plating solution. The measured solutions were diluted to one tenth of their original concentration
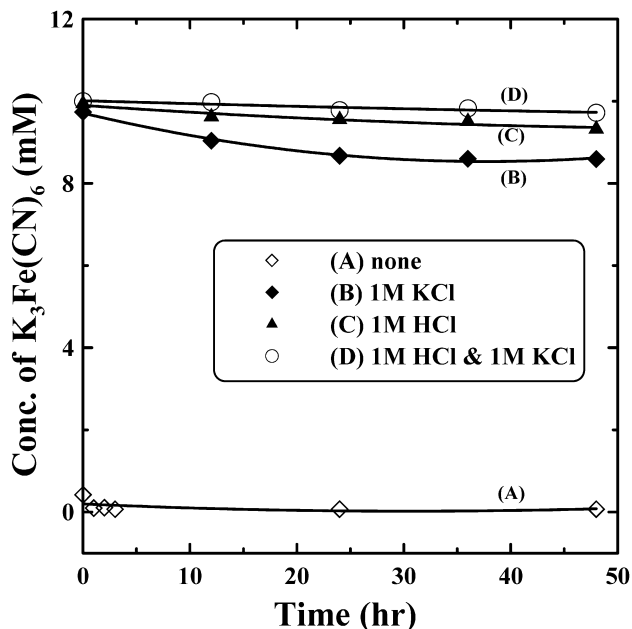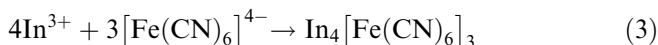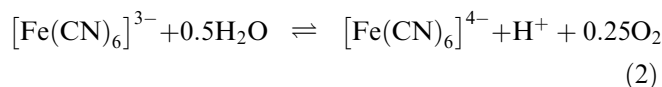
Fig. 2. The influences of adding 1 M KCl and/or HCl on the stability of a 10-mM InHCF plating solution. The unmodified plating solution (solution A) was composed of 10 mM InCl$_3$ and 10 mM K$_3$Fe(CN)$_6$

Fig. 3. The variation of the pH values monitored over a period of 48 h in various plating solutions

$$\left[Fe(CN)_6\right]^{3-} + 0.5H_2O \;\rightleftharpoons\; \left[Fe(CN)_6\right]^{4-} + H^+ + 0.25O_2 \tag{2}$$

$$4In^{3+} + 3\left[Fe(CN)_6\right]^{4-} \rightarrow In_4\left[Fe(CN)_6\right]_3 \tag{3}$$

These two reactions explain that the instability is attributed to the chemical reduction of $\left[Fe(CN)_6\right]^{3-}$ in the presence of water to form $\left[Fe(CN)_6\right]^{4-}$, which co-precipitates with In^{3+} instantaneously and yields $In_4[Fe(CN)_6]_3$ ($K_{sp}=2\times10^{-44}$ [13]). Reaction (2) was verified indirectly, over a period of 48 h, by observing slight decreases of the pH value in plating solutions with different additives during the co-precipitation. The variation of the pH values is plotted in Fig. 3 for all plating solutions used. Thus, the stabilization of plating solutions by adding plenty of H^+ is presumably due to the inhibition of the chemical reduction of $\left[Fe(CN)_6\right]^{3-}$ to $\left[Fe(CN)_6\right]^{4-}$, according to Le Chatelier's principle. As to the stabilizing effect of adding KCl, it is likely related to the deceleration in the co-precipitation of In^{3+} and $\left[Fe(CN)_6\right]^{4-}$, which was observed in a preliminary experiment and needs further proof.

CVs for the fresh InHCF thin films, plated from solutions A, B, C, and D, are given in Fig. 4. It can be calculated from Fig. 4 that the films deposited in the presence of 1 M HCl (C and D) both have ca. 18 times higher electrodeposited (redox) capacity, as compared with that deposited in solution A. In contrast, the capacity of the film prepared in solution B (added with 1 M KCl only) is ca. 3 times larger than that obtained from solution A. This means that K^+ addition shows a
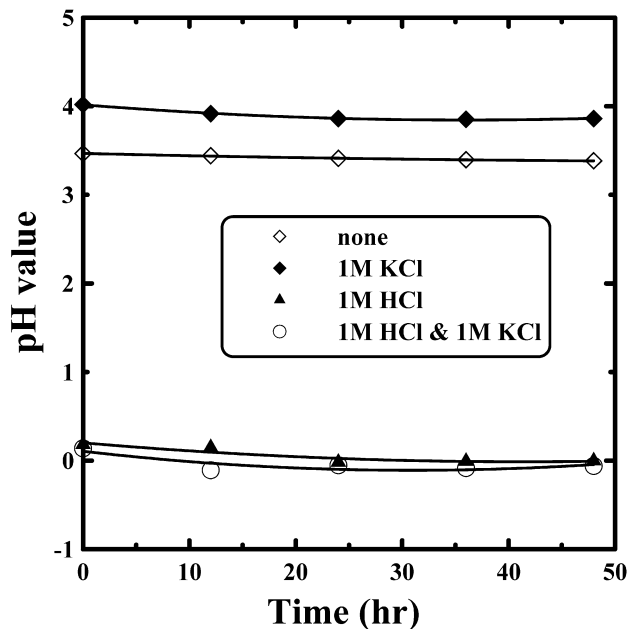
less positive influence on the electrodeposited capacity than H^+ addition does. The enhancement on the electrodeposited capacity in a H^+-rich (or K^+-rich) environment can be explained by the CV responses, which were recorded at the 20th plating cycle in solutions A, B, C, and D and are given in Fig. 5.

Notice that the CVs for the plating solutions containing 1 M HCl (C and D) both show cathodic peaks around 0.4 V (vs. Ag/AgCl/sat. KCl) in response to the reduction of $\left[Fe(CN)_6\right]^{3-}$ to $\left[Fe(CN)_6\right]^{4-}$, whereas the CVs for the plating solutions A and B do not shown such a cathodic peak. According to the CV electrodeposition mechanism reported by Kulesza and Faszynska [3], $In_4[Fe(CN)_6]_3$ should form first on the electrode surface prior to the growth of the InHCF film. That is, the formation of $\left[Fe(CN)_6\right]^{4-}$ on the FTO substrate is an essential step for the InHCF electrodeposition. Thus, the large enhancement on the electrodeposited capacity by adding 1 M H^+ should be attributed to the promotion on the electrochemical reduction of $\left[Fe(CN)_6\right]^{3-}$ to $\left[Fe(CN)_6\right]^{4-}$ by H^+, although H^+ is considered to inhibit the chemical reduction of $\left[Fe(CN)_6\right]^{3-}$ in the presence of H_2O. The corresponding evidence is given in Fig. 6.

Figure 6 compares the CVs for the $\left[Fe(CN)_6\right]^{3-}/\left[Fe(CN)_6\right]^{4-}$ redox couple on the FTO electrode under different additive conditions, corresponding to solutions A, B, C, and D. It is shown that the presence of 1 M H^+ (C and D) indeed promotes the redox reaction of $\left[Fe(CN)_6\right]^{3-}$ and $\left[Fe(CN)_6\right]^{4-}$ and shifts the cathodic peak to 0.4 V (vs. Ag/AgCl/sat. KCl), whereas the unmodified solution (A) and the solution containing only 1 M K^+ (B) show cathodic peaks at −0.45 V and 0.05 V, respectively. Since the InHCF film was deposited vol-
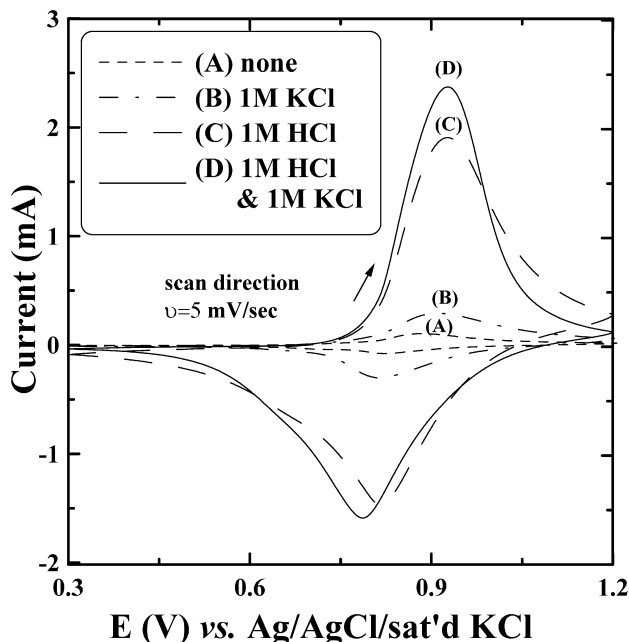
Fig. 4. CVs for the InHCF films prepared from solutions A, B, C, and D. The K-PAMPS electrolyte was employed for these CV experiments
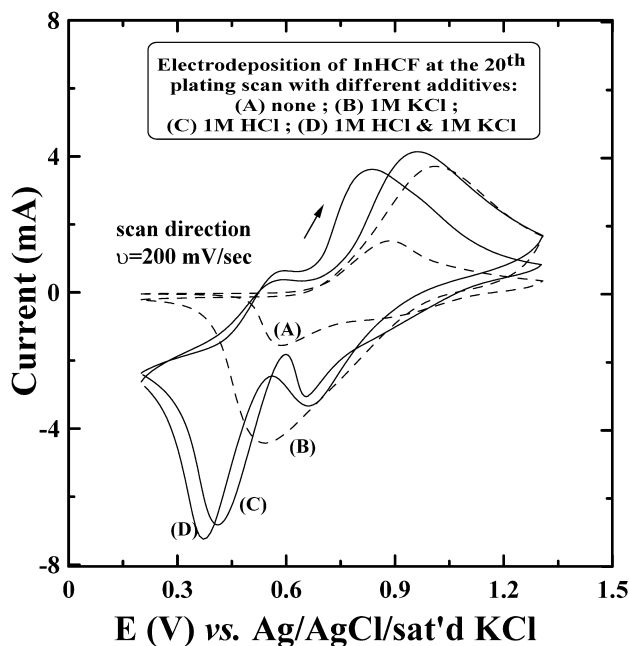

Fig. 5. CVs recorded at the 20th plating scan during CV electrodeposition with different plating solutions

Fig. 6. CVs for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple on FTO substrates under different additive conditions, corresponding to solutions A, B, C, and D. 10 mM $[Fe(CN)_6]^{3-}$ was present initially for each run. E' represents the estimated formal potential for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple

of the capacity gained per plating cycle and the plating potential window.

Conclusions

This work has demonstrated that adding a large amount of K^+ and/or H^+ can greatly stabilize the InHCF plating solution. It has also been shown that such cationic additions, especially adding H^+, can considerably increase the InHCF electrodeposited capacity. In addition, enhanced mechanisms have been proposed and can be used to explain the experimental findings very well. In particular, the interesting role of H^+ for the InHCF electrodeposition is identified: H^+ inhibits the chemical reduction of $[Fe(CN)_6]^{3-}$ in the presence of H_2O to form $[Fe(CN)_6]^{4-}$ and therefore improves the stability of InHCF plating solutions; on the other hand, H^+ promotes the electrochemical reduction $[Fe(CN)_6]^{3-}$ to form $[Fe(CN)_6]^{4-}$ on the FTO surface and thus increases the electrodeposition efficiency. These mean that the InHCF electrodeposition works better in an acidic environment. In conclusion, we believe that this work has achieved better InHCF electrodeposition and has broadened the applicability of InHCF thin films.

tammetrically between 0.2 V and 1.3 V (vs. Ag/AgCl/sat. KCl), no significant amount of $[Fe(CN)_6]^{4-}$, an essential anion to grow an InHCF film, will be produced if the solution's acidity is not high enough. As a consequence, for CV electrodeposition of InHCF films, H^+ addition is superior to K^+ addition from the viewpoints
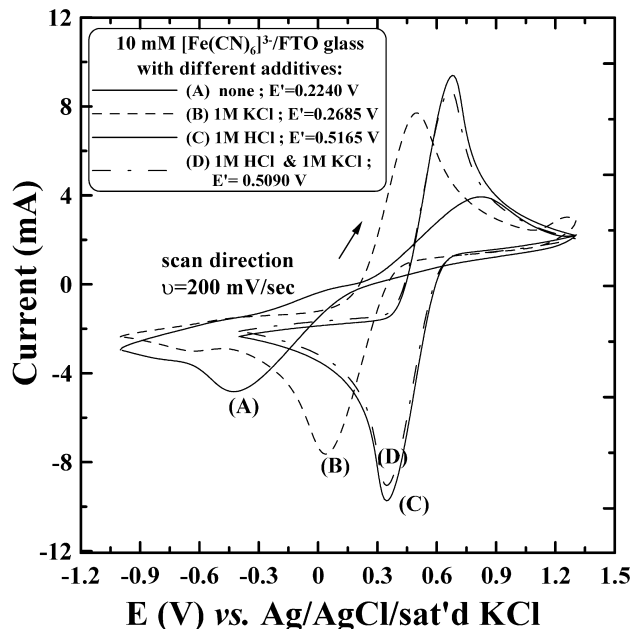
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