普魯士藍修飾電極之電化學鑑定及電致色變反應機制研究
On the Electrochemical Characterization and Electrochromic Mechanism of Prussian Blue Modified Electrodes

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1. ABSTRACT

The plating solution's stability and the electrodeposition for indium hexacyanoferrate (InHCF), an important analogue of Prussian blue (PB), were greatly enhanced by adding a large amount of K^+ and/or H^+. It was found that a 10-mM plating solution added with 1N HCl and 1N KCl could be stored as a fresh one over a week, whereas an unmodified plating solution became useless within couples of minutes. Moreover, the InHCF film grown in an H^+-rich environment showed comparatively higher cycle ability, based on the results of electrochemical characterizations. Besides, related enhanced mechanisms were proposed and verified. To sum up, this work has provided a means for better electrodeposition of PB analogues.

Keywords: electrochromic, indium hexacyano-ferrate, Prussian blue.

2. INTRODUCTION

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

$$In[Fe(CN)_6] + K^+ + e^- \leftrightarrow K[InFe(CN)_6] \quad (1)$$

(yellowish)　　　　　(colorless)
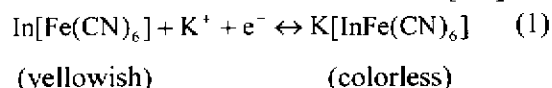
Therefore, InHCF has been regarded as a superior transparent counterelectrode for complementary electrochromic devices [7-8]. Although a variety of applications are reported, the plating solution's instability has been a bottleneck for using InHCF.

InHCF films can be prepared by the cyclic voltammetric (CV) electrodeposition [2-4], potentiostatic electrodeposition [5] and sacrificial anode deposition [6]. In general, the aqueous plating solution is composed of equally concentrated In^{3+} and $[Fe(CN)_6]^{3-}$ [2-6], which is similar to that of Prussian blue [1]. Because precipitates forms in the plating Although most of the plating solutions reported in literature used a very dilute mixture of In^{3+} and $[Fe(CN)_6]^{3-}$ ($\leq$ 1 mM) [2-3], such low-concentrated plating solutions limit the electrodeposited capacity of an InHCF film. Thus, the applicability of InHCF is constrained. To overcome this issue, this work is devoted to stabilize the concentrated plating solution ($\geq$ 10 mM) for InHCF and to achieve a better InHCF thin-film electrodeposition.
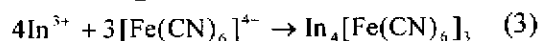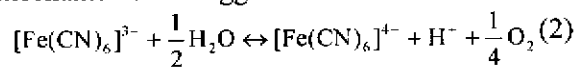
3. EXPERIMENTAL

InHCF thin films were deposited onto SnO_2 glass substrates (active area = 3.0×1.5 cm^2, R_{sh} = 20 ohm/sq.) in solutions A, B, C, and D by the CV electrodeposition [2-4] respectively. During the electrodeposition, a potential scanned back and forth between 0.2 and 1.3 V (vs. Ag/AgCl/sat'd KCl) at a rate of 200 mV/sec was applied to the SnO_2 substrate 20 cycles.

As-prepared films were cleaned with DIW and then were dried in air at room temperature for at least 24 hours. 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 SnO_2 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 is described elsewhere [8].

4. RESULTS AND DISCUSSIONS

It was confirmed experimentally that the presence of KCl and/or HCl doesn't affect the spectroscopic characteristic. 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 the Beer law. The results are plotted in Fig. 1 to illustrate the influences of adding 1N KCl and/or HCl on the stability of a 10-mM plating solution. Fig. 1 shows that both K^+ and H^+, in large amount, can greatly stabilize the plating solution.

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

$$[Fe(CN)_6]^{3-} + \frac{1}{2}H_2O \leftrightarrow [Fe(CN)_6]^{4-} + H^+ + \frac{1}{4}O_2 \quad (2)$$

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

These two reactions explain that the instability is attributed to the chemical reduction of $[Fe(CN)_6]^{3-}$ in the presence of water to form $[Fe(CN)_6]^{4-}$, which co-precipitates with In^{3+} instantaneously and yields $In_4[Fe(CN)_6]_3$ ($K_{sp} = 2 \times 10^{-44}$). Reaction (2) was verified indirectly by observing a decrease of the pH value of a plating solution during the co-precipitation.

CVs for the fresh InHCF thin films, plated from solutions A, B, C, and D, respectively, are given in Fig 2. It is calculated from Fig. 2 that the films deposited in the presence of 1N HCl (C and D) both have a *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 1N KCl only) is *ca.* 3 times larger than that obtained from solution A. It means that K^- addition shows a less positive influence on the electrodeposition capacity than H^- addition. The enhancement on the electrodeposited capacity by the 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. 3.

Notice that the CVs for the plating solutions containing 1N HCl (C and D) both show cathodic peaks around 0.4V (*vs.* Ag/AgCl/sat'd KCl) in response to the reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$, whereas the CVs for the plating solutions A and B have not shown such a cathodic peak. According to the CV electrodeposition mechanism reported by Kulesza *et al.* [3], $In_4[Fe(CN)_6]_3$ should be formed first on the electrode surface prior to the growth of the InHCF film. That is, the formation of $[Fe(CN)_6]^{4-}$ on the SnO_2 substrate is an essential step for the InHCF electrodeposition. Thus, the large enhancement on the electrodeposited capacity by adding 1N H^+ should be attributed to the promotion on the electrochemical reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ by H^+, although H^- is considered to inhibit the chemical reduction of $[Fe(CN)_6]^{3-}$ in the presence of H_2O. The corresponding evidence is given in Fig. 4.

Fig. 4 compares the CVs for the

$[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple on the SnO_2 electrode under different additive conditions, corresponding to those in solutions A, B, C, and D. It is shown that the presence of 1N H^+ (C and D) indeed promotes the redox reaction of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ and shifts the cathodic peak to 0.4 V (vs. Ag/AgCl/sat'd KCl), whereas an unmodified solution (A) and the solution only containing 1N K^+ (B) show the cathodic peaks at -0.45 V and 0.05 V, respectively. Since the InHCF film was deposited voltammetrically between 0.2V and 1.3 V (vs. Ag/AgCl/sat'd 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, H^+ addition is superior to K^+ addition for the InHCF's CV electrodeposition, from the viewpoint of the capacity gained per plating cycle and the plating potential window.

Fig. 5 shows the capacity loss during 100 CV scans for the InHCF films deposited from solutions A, B, C, and D. To prevent InHCF films from peeling off the SnO_2 substrates, the K-PAMPS electrolyte, which accommodates the conduction of both H^+ and K^+[8], was employed for the electrochemical characterizations. It is shown in Fig. 5 that the films prepared in the presence of 1N HCl (C and D) show a better cycle ability as compared with others. Again, it is presented that K^- addition works but has a less positive influence on the cycle life than H^- addition.

5. 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 shown that such cationic additions, especially adding H^+, can considerably increase the InHCF

electrodeposited capacity. Moreover, positive influences on the corresponding film's electrochemical cycle life are also presented. Besides the above facts, the related enhanced mechanisms have been proposed and can explain the experimental findings very well. In particular, the interesting role of H^+ for the InHCF electrodeposition is disclosed: 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 SnO_2 surface and thus increases the electrodeposition efficiency. These mean that the InHCF electrodeposition prefers a higher acidic environment. In conclusion, we believe that this work has provided a means for a better electrodeposition of PB analogues and has broadened the applicability of PB-derivative modified electrodes accordingly.

6. REFERENCES

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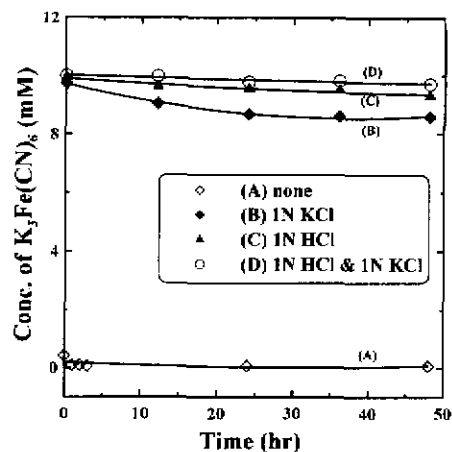
Fig. 1 The influences of adding 1N KCl and/or HCl on the stability of an InHCF plating solution.
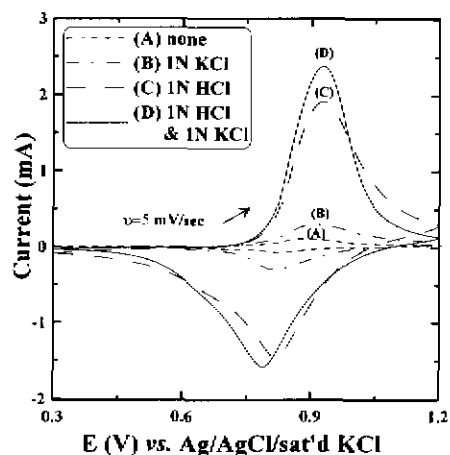

Fig. 2 CVs for the InHCF films, prepared in solutions A, B, C, and D, respectively. The K-PAMPS electrolyte was employed in these CVs.
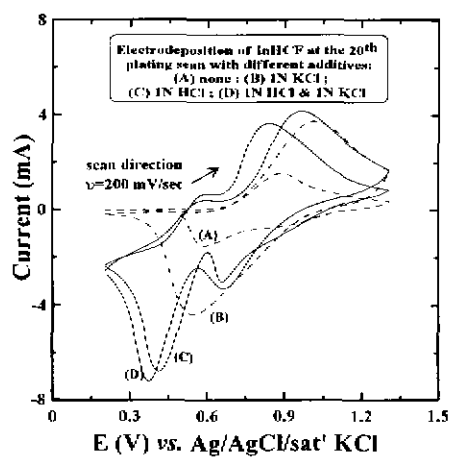

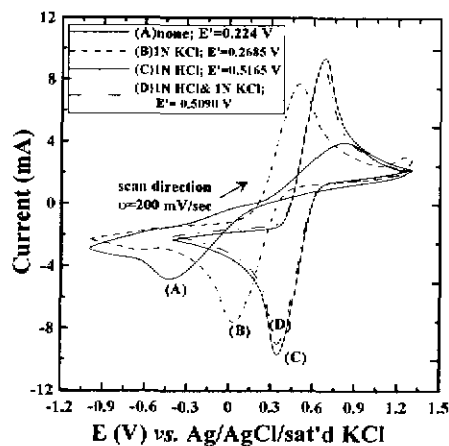Fig. 3 CVs recorded at the 20th plating scan during the CV electrodeposition.

Fig. 4 CVs for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple on a SnO_2 substrate under different additive conditions, corresponding to solutions A, B, C, and D.
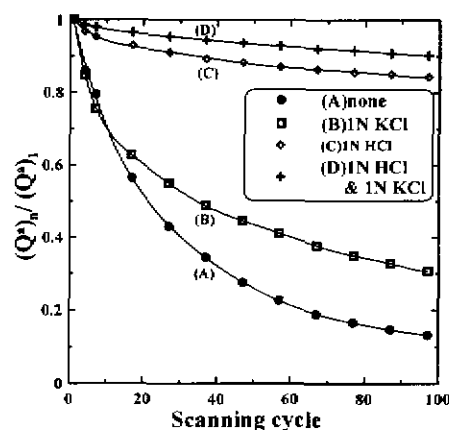

Fig. 5 Electrochemical stability for InHCF films prepared from the different plating solutions. The data were obtained from the CV experiments at a scan rate of 50 mV/sec and were recorded after three CV cycles.