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Facile Attachment of Uranium Hexacyanoferrate to Carbon Electrode by Reductive Electrodeposition

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Cyclic voltammetric scan of the glassy carbon substrate in an acidic solution containing both uranyl salt and ferricyanide can result in the new surface-deposition of an inorganic redox active film—polynuclear uranium hexacyanoferrate.

Chemically modified electrodes are the focus of considerable current research. Although most effort in this regard has been devoted to the synthesis and characterization of organic polymers and polyelectrolytes as the host for coating electrode surfaces,1,2) success has also been achieved with purely inorganic films. The latter are particularly attractive because of the greater stablity that can be envisioned by using solubility—limited systems rather than films in which the mediator is bound by an ion—exchanger or reaction adsorption. Remarkable success in the early work with inorganic coatings is encouraging. Very recently we reported the facile preparation, unique properties and comprehensive characterization of some novel hexacyanometallate film modified electrodes.3,4) To extend our idea along this line, we noticed that the electrodes modified with the uranium analogue of Prussian blue (PB) are exceptional — they possess excellent reversible redox centers very similar to those of PB, so for the first time their preparation and characteristics are given in this preliminary account.

Conducting substrates, such as glassy carbon, was immersed into the acidic KCl(1 mol dm $^{-3}$) solution containing equal amounts (0. 01 mol dm $^{-3}$) of $UO_2(NO_3)_2$ and $K_3[Fe(CN)_6]$ (pH=0), then electroreduction technique (cyclic voltammetry, potentiostatic or galvanostatic electrolysis) can be applied on the working conducting substrate. Typically the uranium hexacyanoferrate (UHCF) film can be homogeneously prepared by voltammetric cycling of a glassy carbon electrode in the above solution in the potential range of 1. 0—0. 0 V (*vs.* SCE, hereafter). In this respect, we had exploited the general knowledge that uranium ferrocyanide is less soluble than its ferricyanide form, hence the UHCF film would be accumulated during negative-going scanning.

Figure 1 shows the FT—IR spectra of UHCF film. The stretching vibrational absorbtion near 2100 cm $^{-1}$ corresponding to intermolecular cyanide group, which conforms with the general characteristics of ferrocyanide in PB and its related compounds.5) On the other hand, uranyl group in the film microstructure have been obviously confirmed due to the wide U=O stretching band around 900 cm $^{-1}$.6,7) The infrared absorbtion near 1600 cm $^{-1}$ (H—O—H bending) reveals the hydrated form of the film crystal.

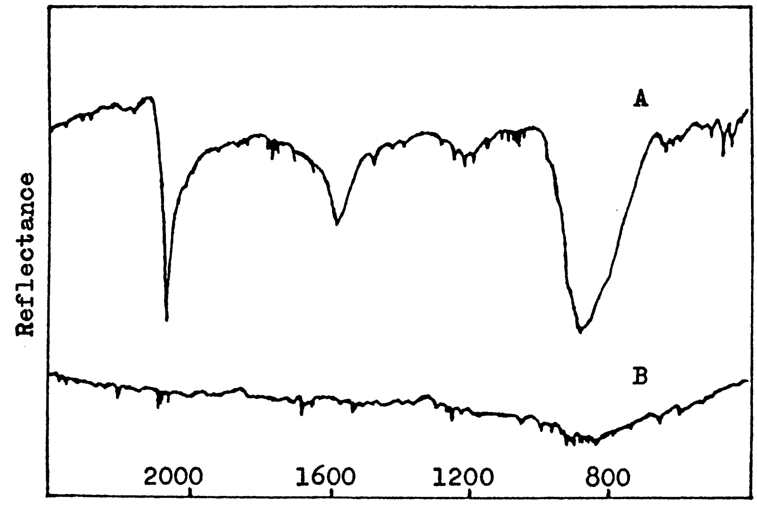

Fig. 1. Reflectance FT—IR spectra of the UHCF coating (A) on glassy carbon substrate (B).

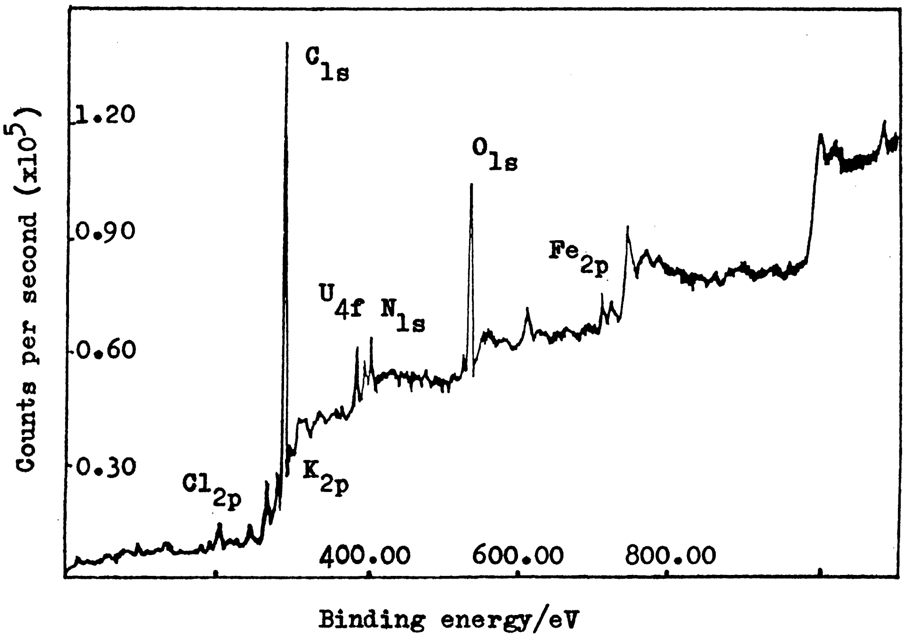

Fig. 2. ESCA spectrum of the UHCF film.

ESCA data of the UHCF film on glassy carbon have been given in Fig. 2. Direct evidence of the film components, i.e. uranium, iron, carbon, nitrogen, potassium, and oxygen, can be seen from their photoelectron peaks located at 382.6 eV (U: 4f$_{7/2}$), 709.0 eV (Fe: 2p$_{3/2}$), 288.2 eV (C: 1s), 399.8 eV (N: 1s), 293.4 eV (K: 2p$_{3/2}$), and 531.8 eV (O: 1s), respectively. The presence of small amount of chlorine, as impurities (near 200 eV), may be attributed to the contamination of supporting electrolyte. High resolution ESCA spectra of the film further exhibit the existence of ferro and ferri portion when the film was electrolized at 0.0 V (reduced state) and 1.0 V (oxidized state), respectively. These mean that the electroactive species in the film are Fe $^{II/III}$ portion.

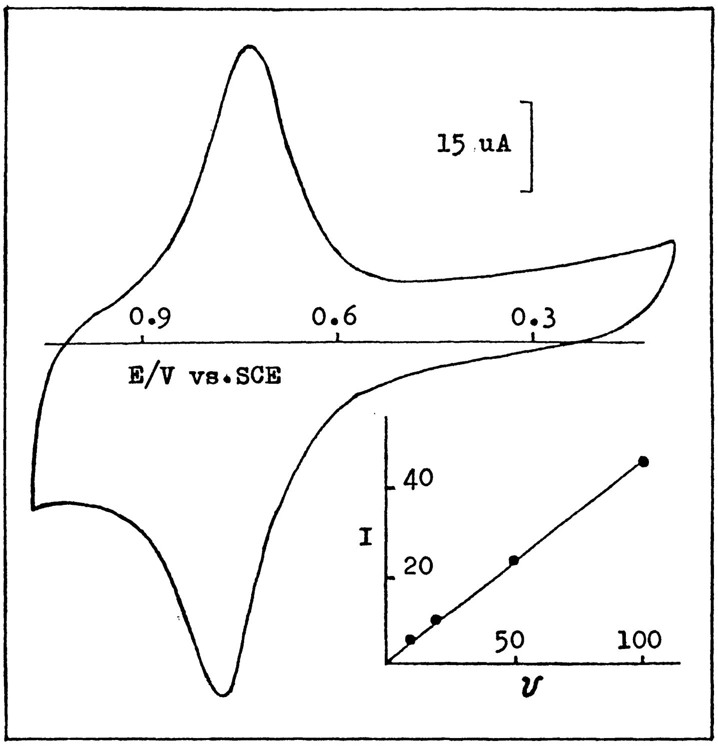

Fig. 3. Cyclic voltammogram of the UHCF film modified glassy carbon electrode in 1 mol dm $^{-3}$KCl + 2 mol dm $^{-3}$HCl solution, without any deliberately added electroactive species. Potential scan rate = 100 mV s $^{-1}$. Inserted plot shows the correlation between anodic peak current (I/uA) and scan rate (v/mV s $^{-1}$).

The UHCF modified electrode possesses an excellent electrochemical reversibility, which can be observed in its typical cyclic voltammogram (CV) in 1 mol dm $^{-3}$ KCl + 2 mol dm $^{-3}$ HCl solution (Fig. 3). Only one redox transition appears with reductive peak potential 0.75 V and oxidative 0.79 V. Both peak potentials are slightly dependent on the scan rate. Although the peak currents are directly proportional to the scan rate up to 100 mV s $^{-1}$ (see inserted plot in Fig. 3), distortion of the wave is observed at higher scan rates. This may be due to the Nerstian behaviour of a rapid surface process under slow plorized signal but charge limitations associated with charge propagation and complicated kinetic effect in the film will dominate at higher scan rates. Considering the cell parameter of UHCF crystal unit (a= 10.2 Å),[5] our estimation of charge consuming in the oxidative peak of Fig. 3 indicates that the concentration of UHCF molecules attached on the electrode surface is ca . $5\mathrm{x}10^{-8}$ mol cm $^{-2}$. Using the potential — step chronoamperometric technique introduced by Viehbeck and DeBerry,[8] the apparent diffusion coefficient of the film for charge transferring was calculated according to Cottrell equation and found to be ca. $2\mathrm{x}10^{-9}$ cm^{2} s $^{-1}$, which has the same order of magnitude as that of PB and its vanadium analogue modified electrode.[9,10] This reflects the similarity of charge transport kinetics in PB and its analogue family.

PB modified electrode exhibits two reversible redox transitions in KCl solution, corresponding to high—spin Fe $^{3+/2+}$ and low—spin Fe $^{II/III}$portions in the film microstructure respectively.[11)] For the UHCF film, however, the fact of only one single redox transition in the film electrochemistry (see above) makes it resemble some PB analogues,[3)] but somewhat different from PB itself.[11)]This suggests only one dominant electroactive species occur in the resulting film. Uranyl group is not expected to be electroactive in the potential range examined in Fig. 3 based on our diagnostic experiments and previous literature.[12)] Furthermore, ESCA tests also demonstrate Fe $^{II/III}$ portion are electroactive(see above). The electron—transfer mechanism in UHCF crystal can be formulated as follows by assuming the stoichiometric unit $K_2UO_2Fe(CN)_6$,[5)]

$$K_2UO_2Fe^{II}(CN)_6 - e^- - K \rightleftharpoons KUO_2Fe^{III}(CN)_6$$

Preliminary stability tests have shown that the film retains more than 95% of its initial electroactivity after 100 voltammetric cycles between 0.0 —1.0 V. The higher stability has been achieved by coating a thin layer of Nafion (E.I. du Pont) polyelectrolyte on the inorganic film. Because the film component uranium is radioactive, one can imagine that some radio— labelled techniques may be utilized to clarify the exact change in film microstructure accompanying electrochemical reaction and its charge—compensating ion effects. On the other hand, some fundamental (such as intercalation study) and practical (such as electrochromism and electrocatalysis) investigations can be anticipated to deepen the account mentioned above.

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