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## Electrochemical preparation and characterization of dysprosium hexacyanoferrate modified electrode

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**Abstract** An electroactive polynuclear inorganic compound of rare earth metal hexacyanoferrate, dysprosium hexacyanoferrate (DyHCF), was prepared by a procedure of electrochemical deposition on the surface of a glassy carbon electrode with a potential cycling procedure. The cyclic voltammogram of DyHCF exhibits two pairs of redox peaks with the formal potential of +210 and +362 mV (vs. SCE), respectively, at a scan rate of 10 mV/s in 0.2 mol/L KCl solution. The different electrochemical behaviors of DyHCF in various cation-containing supporting electrolytes were investigated by cyclic voltammetry. DyHCF was also characterized by scanning electron microscope (SEM), FTIR, XPS etc. techniques.

**Keywords** Cyclic voltammetry · Chemically modified electrode · Electrodeposition · Dysprosium hexacyanoferrate

### Introduction

Metal hexacyanoferrates belong to a class of polynuclear inorganic compounds. An interesting feature of these kind of compounds is that they resemble not only redox organic polymers, but also zeolitic or intercalation materials. Ever since the pioneering work of Neff [1] and Itaya et al. [2] on Prussian blue (PB)-modified electrodes, there have been many papers published over the years on the preparation and characterization of metal hexacyanoferrates as electroactive materials [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14] because they possess many intriguing properties, such as electrochromicity [15], capability to

store counter-cations [16], ion-exchange selectivity [17], ability to mediate electrochemical reactions [7, 8, 14, 18, 19, 20, 21, 22, 23], molecular magnetism [24] and used as electrode materials in solid-state secondary batteries [25], etc.

Rare earth metals (or ions) have received much attention in many fields, such as in the hydrogen storage materials of batteries [26], ion selective electrodes and chemical sensors [27], electrocatalytic hydrogenation of organic substrates [28] and as a promoter to facilitate the electron transfer of biological molecules, for example microperoxidase-11 [29], etc. Although there are considerable reports about the preparation and characterization of the transition metal hexacyanoferrates as well as their applications, there are only a few papers that, to our knowledge, reported the electrochemical preparation and characterization of rare earth metal hexacyanoferrates [3]. We [9, 10, 23, 30, 31, 32] have conducted several works on the electrochemical and chemical preparation and characterization of rare earth hexacyanoferrates, and found that there were great differences between the electrochemical characteristics of transition and rare earth hexacyanoferrates. Even among the rare earth hexacyanoferrates, there exist some significant differences in their electrochemical characteristics. We [31] also studied the effects of non-aqueous media on the solid-state electrochemistry of samarium hexacyanoferrate (SmHCF). However, much work needs to be done for fully exploring the electrochemical properties of rare earth hexacyanoferrates and understanding the differences in the electrochemical characteristics presented by transition and rare earth hexacyanoferrates.

Although there are some papers [33, 34, 35, 36] on the preparation, structural characteristics and applications of dysprosium hexacyanoferrate (DyHCF), which is a rare earth hexacyanoferrate, there is no report, to our knowledge, on the electrochemical preparation and characterization of DyHCF. In this work, DyHCF was prepared electrochemically on the surface of glassy carbon electrode to form a DyHCF-modified electrode (DyHCF/GC). The electrochemical characteristics of the

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DyHCF/GC electrode were studied by cyclic voltammetry. The DyHCF was also characterized by IR spectroscopy, scanning electron microscope (SEM), XPS, etc.

## Experimental

### Chemicals

Dysprosium chloride hexahydrate (99.9%) was obtained from Aldrich and used without further purification. All other chemicals were of analytical grade and used as received. All solutions were prepared with doubly distilled water.

### Apparatus

The electrochemical experiments were performed with a CHI 600 electrochemical workstation (Shanghai Chenhua Instruments Co.) and a three-electrode electrochemical cell. The DyHCF/GC electrode, a coiled Pt wire and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. The electric conductivity of hexacyanoferrate samples was determined from AC impedance measurements, which were performed using PAR M273 Potentiostat/Galvanostat equipped with 5208 Lock-in (EG&G, PARC, USA) in the frequency range of 0.1 Hz to  $1 \times 10^5$  Hz with a bias of 5 mV employing a home-made two-electrode cell. To conduct the AC impedance measurements, the sample of hexacyanoferrates prepared chemically was pressed to a disk pellet (1.3-cm in diameter) using a hydraulic pump (Shimadzu). The thickness of hexacyanoferrate disk was measured with a vernier caliper. The electric contact between the DyHCF sample disk and two electrodes was made by two copper wafers. Because the copper wafers and the electrodes are good conductors, the contribution of the electric contact to the measured values of conductivity of samples is very small, if it is not zero, and can be neglected. To rule out the possible effects of the water vapor in air on the conductivity, the sample disk was stored in a desiccator before experiments. FTIR spectrum of DyHCF, which was electrodeposited on the surface of a Pt sheet (2 cm $\times$ 2 cm), was obtained with a Nexus 670 FT-IR spectrophotometer (Nicolet Instrumental Co., USA). The resolution is 4 cm $^{-1}$ . SEM images of DyHCF were obtained with JEOL JSM-561 V Scanning Electron Microscope (Japan). XPS experiments were carried out on ESCALab MK2 using monochromatic Mg K $_{\alpha}$  line at 1253.6 eV. The values of binding energy were calibrated with that of C1s (284.6 eV). The iron, dysprosium and potassium content of chemically prepared DyHCF were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (PS-I, Leeman) of the digested samples. Digestion was achieved by hydrochloric acid. The

UV-Vis spectra of DyHCF were obtained using a Hitachi U-3400 spectrophotometer (Japan).

### Procedures

Prior to depositing DyHCF, the GC electrode (3-mm in diameter) was polished sequentially with metallographic abrasive paper (no. 6), slurries of 0.3 and 0.05- $\mu$ m alumina to a mirror finish. After being rinsed with doubly distilled water, it was ultrasonicated in ethanol and then in doubly distilled water for about 1 min. Finally, it was cyclically scanned between the potential range of  $-0.2$ – $0.8$  V in a 0.2 mol/L KCl solution at a scan rate of 50 mV/s until a stable cyclic voltammogram was obtained.

The solution for preparation of the DyHCF with the electrodeposition method was a  $1.0 \times 10^{-2}$  mol/L DyCl $_3$  and  $1.0 \times 10^{-2}$  mol/L K $_3$ Fe(CN) $_6$  solution containing 0.2 mol/L MeCl (Me = Na, K or Li, respectively) and freshly prepared each time. The DyHCF was deposited on the surface of GC electrode by potential cycling from +0.8 V to  $-0.2$  V at a sweep rate of 100 mV/s for 20 cycles in the above solutions. The DyHCF was found to grow on the surface of GC electrode with each potential cycle, as revealed by the change of peak currents. No further growth was observed after that time, thus, 20 cycles were adopted in all cases. Finally, the electrode was rinsed thoroughly with distilled water and transferred into other solutions to study its electrochemical characteristics.

The DyHCF samples were also prepared chemically by precipitation via dropwise addition of 100 mL of  $2.0 \times 10^{-2}$  mol/L (or  $2.0 \times 10^{-3}$ , 0.2 mol/L) DyCl $_3$  into a stirring solution of 100 mL of  $2.0 \times 10^{-2}$  mol/L K $_4$ Fe(CN) $_6$  (containing KCl at 1 mol/L level). The resulting precipitates were collected by filtration, and washed: first, with KCl electrolyte, and later, with distilled water. The prepared samples have a similar color of green and the maximum absorption peaks locate at 310 nm in UV-Vis spectra. Atomic absorption analysis was employed to determine the stoichiometry of the prepared sample. The results indicated that the calculated stoichiometry of the samples is very close to the theoretical one. All the solid samples were dried overnight in vacuum at ambient temperature and then stored in a desiccator.

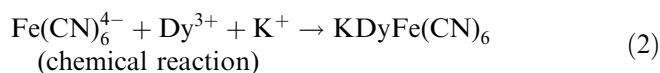
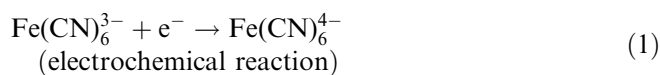
Before the electrochemical experiments, high-purity nitrogen was purged into the solution for 15 min and a continuous flow of the gas was maintained over the solution during the experiments, which were performed at room temperature ( $22 \pm 2$  °C).

## Results and discussion

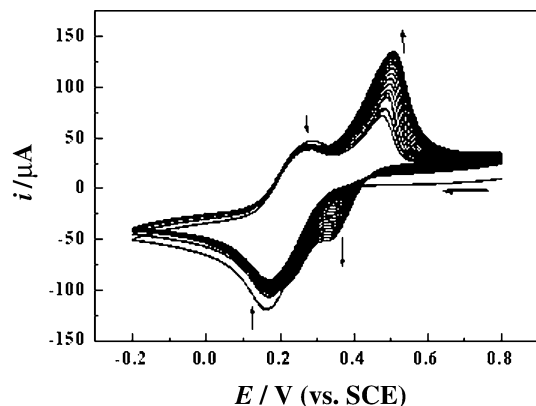
### Electrochemical deposition of DyHCF on GC electrode surface

Figure 1 shows a typical cyclic voltammogram of the deposition process of DyHCF on the surface of GC

electrode in a solution of  $1 \times 10^{-2}$  mol/L  $\text{DyCl}_3$  and  $1 \times 10^{-2}$  mol/L  $\text{K}_3\text{Fe}(\text{CN})_6$  containing 0.2 mol/L KCl as supporting electrolyte. When the potential was scanned from +0.8 V to -0.2 V, a cathodic peak, which corresponded to the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$ , appeared at +163 mV. The anodic peak corresponding to the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  to  $\text{Fe}(\text{CN})_6^{3-}$  appeared at +284 mV when the potential was scanned back to +0.8 V. It can be seen that the peak currents corresponding to the reaction of  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple decrease gradually with the increase of the scan cycles, which indicates the formation of DyHCF on the electrode surface. It could be concluded that the formation of the DyHCF started at the potential that the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  occurred, then  $\text{Dy}^{3+}$  ion reacted instantaneously with  $\text{Fe}(\text{CN})_6^{4-}$  to form DyHCF deposited on the electrode surface. The formation mechanism is supported by the following controlled experimental results, which indicated that DyHCF can be produced chemically in the mixed solution of  $1 \times 10^{-2}$  mol/L  $\text{DyCl}_3$  and  $1 \times 10^{-2}$  mol/L  $\text{K}_4\text{Fe}(\text{CN})_6$  containing 0.2 mol/L KCl, and cannot be produced in the same solution but with  $\text{K}_3\text{Fe}(\text{CN})_6$  instead of  $\text{K}_4\text{Fe}(\text{CN})_6$ . Thus, the formation process of DyHCF on the electrode surface can be expressed as the following EC reaction mechanism:



This formation mechanism can be further supported by determination of the oxidation state of iron in DyHCF as prepared electrochemically by XPS technique. Figure 2a represents the XPS spectrum of the Fe2p region. The peak of Fe2p appears at 708.2 eV, which is the characteristic of Fe(II) [37]. There is no evidence of Fe(III) existing in DyHCF samples, because the XPS

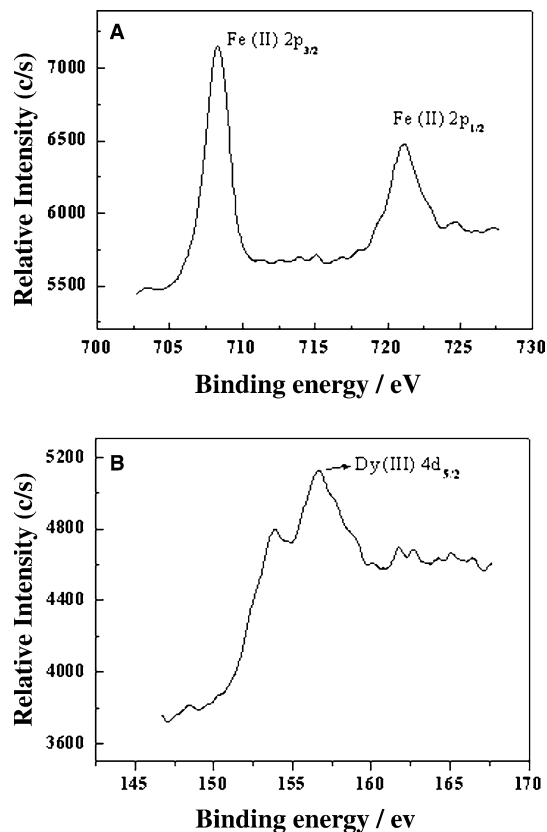


**Fig. 1** A typical cyclic voltammograms of DyHCF deposition process on a GC electrode surface in a solution of  $1.0 \times 10^{-2}$  mol/L  $\text{DyCl}_3$  and  $1.0 \times 10^{-2}$  mol/L  $\text{K}_3\text{Fe}(\text{CN})_6$  containing 0.2 mol/L KCl as supporting electrolyte. The scan rate is 100 mV/s

peak corresponding to Fe(III) should appear at 710 eV [37]. The peak of Dy4d appears at 156.2 eV (Fig. 2b), which corresponds to the characteristic peak of the Dy(III) [38].

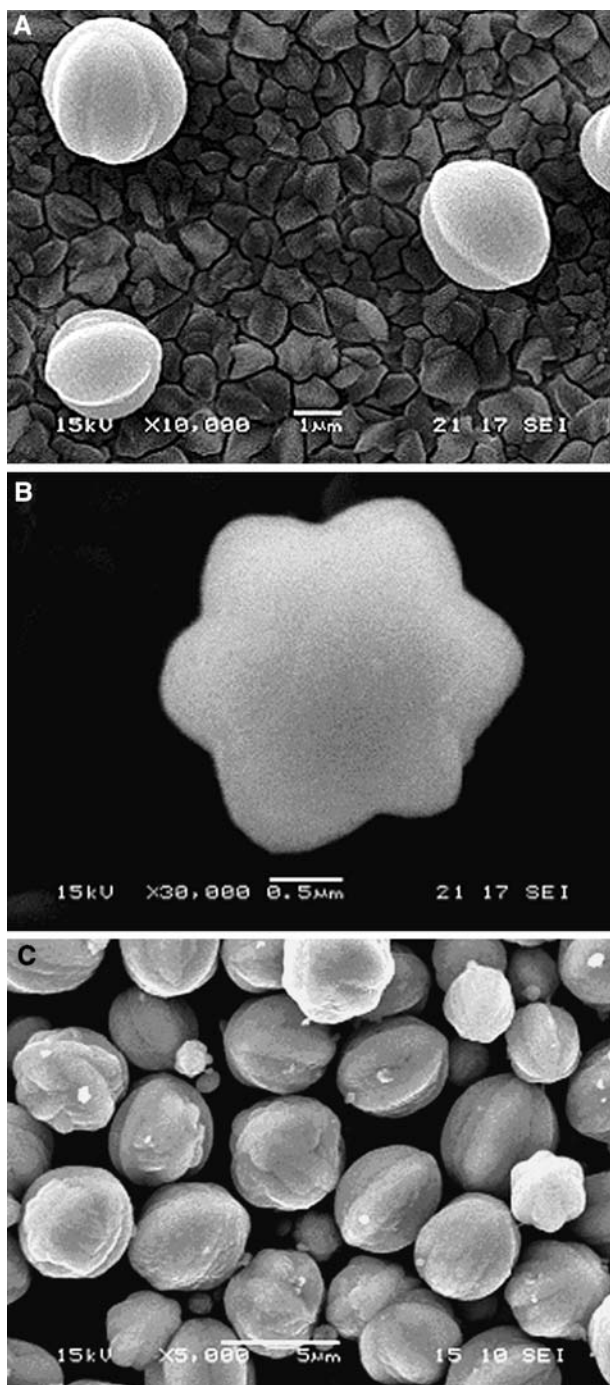
Besides the redox couple of  $\text{Fe}(\text{CN})_6^{3-/4-}$ , there was a new redox couple appearing in Fig. 1, as compared with the formation process of lanthanum hexacyanoferrate (LaHCF) [30] and samarium hexacyanoferrate (SmHCF) [10]. The anodic and cathodic peak potential of this new redox couple was +508 mV and +342 mV, respectively, and the anodic peak potential moved to the positive direction and the cathodic peak potential almost remained unchanged with continuous scans; however, the peaks currents increased. It should also be noticed that the cathodic peak did not appear at the first cycle; it appeared only at the second cycle and thereafter. Although the characteristics of this new redox couple cannot be clarified clearly at present time (see infra), there is no evidence to show it comes from the redox reaction of  $\text{Dy}^{3+}$  since the cyclic voltammogram (not shown here) of  $\text{DyCl}_3$  solution do not show such a pair of redox couple.

The deposition of DyHCF on the surface of GC electrode can also be verified by SEM and FTIR spectroscopy. The SEM images presented in Fig. 3a showed that the electrochemically deposited DyHCF is in form of particles adhered on the surface of the electrode.



**Fig. 2** XPS spectra of the Fe2p region (a) and Dy4d region (b) of electrochemically prepared DyHCF

There are two kinds of particles, the smaller (less than 1  $\mu\text{m}$ ) and irregular particles in the lower layer contact each other, the bigger particles ( $2.7 \pm 0.3 \mu\text{m}$ ) in the upper layer have a regular shape (see Fig. 3b, taken from top) and separate each other. The population of the bigger particles is small as compared with that of the smaller ones in the lower layer. The EDX analysis showed that the bigger and smaller particles have a



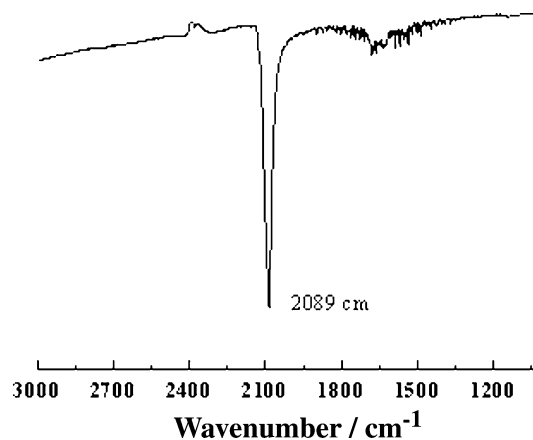
**Fig. 3** SEM images of DyHCF electrochemically deposited on the surface of Pt sheet (a, 10000 $\times$ , b, 30000 $\times$ , taken from top) and chemically prepared (c, 5000 $\times$ )

similar atomic content in terms of Dy, Fe and K. The SEM image of electrochemically prepared DyHCF is different from that of SmHCF [10] and LaHCF [30]. In both latter cases, only one size of particles, which were also separated from each other, was observed. For comparison, the chemically prepared DyHCF was also shown in Fig. 3c. It can be concluded that chemically prepared DyHCF particles have a size of  $4.5 \pm 0.6 \mu\text{m}$  and almost the same shape as that of the bigger particles of electrochemically prepared DyHCF. DyHCF was also characterized by IR spectrum, which was recorded by means of the reflection technique. The resulting reflection FTIR spectrum of DyHCF prepared on a Pt sheet is shown in Fig. 4. A very strong and sharp peak, which is located at  $2089 \text{ cm}^{-1}$ , appears on the FTIR spectrum. This peak can be assigned to the stretching vibration of the  $\text{C} \equiv \text{N}$  group in the DyHCF, because metal hexacyanoferrates, such as Prussian blue and its analogs, have a common characteristic absorption peak around  $2100 \text{ cm}^{-1}$ , which corresponds to the stretching vibration of the  $\text{C} \equiv \text{N}$  group [39]. The results of SEM and FTIR spectrum further confirm that DyHCF has deposited on the surface of GC electrode.

The electronic conductivity ( $\kappa$ ) of DyHCF was calculated from AC impedance measurements by adopting the Eq. 3. The values of  $\kappa$  were list in Table 1.

$$\kappa = \frac{1}{R} \cdot \frac{l}{A} \quad (3)$$

where  $A$  is the surface area of the hexacyanoferrate samples' disk (1.3-cm in diameter),  $l$  is the thickness of samples (see Table 1) and  $R$  is the resistance of samples, which was taken as the value of intercept at real axis in AC spectrum (also see Table 1). For comparison, Table 1 also shows a list of the values of electronic conductivity of two transition hexacyanoferrates, NiHCF and CoHCF, and two other rare earth hexacyanoferrates, LaHCF and SmHCF. They are all semiconductors with conductivity between  $10^{-5} \text{ cm}^{-1}$  and  $10^{-3} (\Omega \text{ cm})^{-1}$  [40].



**Fig. 4** The reflection FTIR spectrum of DyHCF deposited on the surface of Pt sheet at wavenumbers between  $1000 \text{ cm}^{-1}$  and  $3000 \text{ cm}^{-1}$

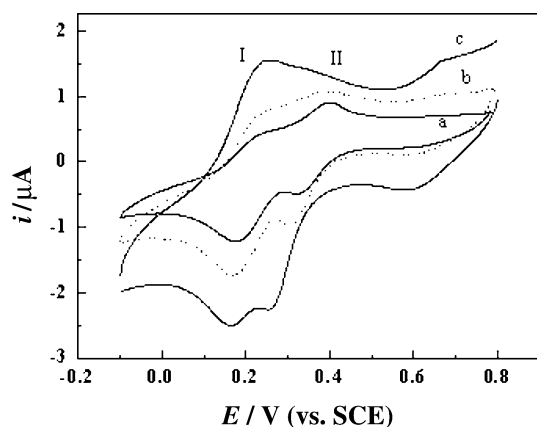
**Table 1** Electric conductivity of some hexacyanoferrates\*

Hexacyanoferrates	$R / \Omega$	$10^2 l/cm$	$10^3 \kappa/(\Omega^{-1} \cdot cm^{-1})$
LaHCF	51020	4.96	0.073
SmHCF	56842	1.65	0.022
DyHCF	6250	2.14	0.26
CoHCF	480	2.14	3.36
NiHCF	410	3.46	6.36

\*The values of the electric conductivity ( $\kappa$ ) were calculated using equation of  $\kappa=1/R \cdot l/A$ , where  $A$  is the surface area (1.3-cm in diameter) and  $l$  the thickness of hexacyanoferrate samples

### Voltammetric characteristics of the DyHCF/GC electrode

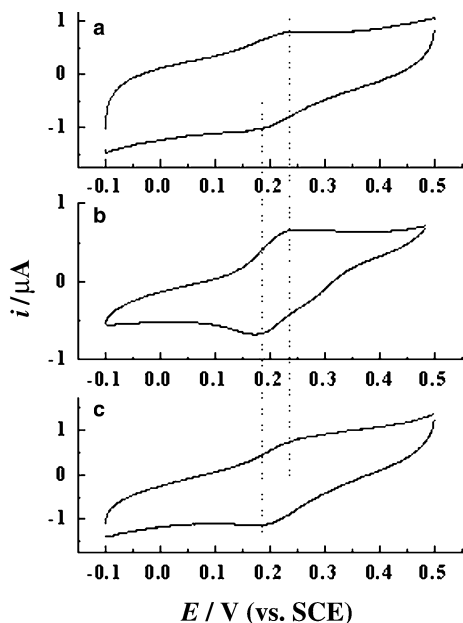
Figure 5, curve a shows a cyclic voltammogram of a DyHCF/GC electrode obtained in a solution of 0.2 mol/L KCl at a scan rate of 10 mV/s. There are two pairs of redox peaks, namely redox couple I and redox couple II, appearing in the curve. The anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials are +244 and +176 mV, respectively, and the formal potential  $E^{0'}$ , which was defined as the mid-point potential of the anodic and cathodic peak potentials, is +210 mV at a scan rate of 10 mV/s for redox couple I. The separation of the anodic and cathodic peak potentials,  $\Delta E_p$ , is 68 mV. For redox couple II, the value of  $E_{pa}$ ,  $E_{pc}$ ,  $E^{0'}$  and  $\Delta E_p$  is +401, +323, +362 and 78 mV, respectively. If the GC electrode was scanned 20 cycles in a solution of  $1.0 \times 10^{-2}$  mol/L  $K_3Fe(CN)_6$  containing 0.2 mol/L KCl as supporting electrolyte in the potential range of +0.8 to -0.2 V at a scan rate of 100 mV/s, and then taken out and performed the cyclic voltammetric experiments in 0.2 mol/L KCl solution. The results indicated that no redox peaks could be observed in the cyclic voltammogram (not shown here). These results indicate that the redox peaks in a curve originate from the electrochemical reaction of DyHCF deposited electrochemically on the surface of GC electrode not from the redox reaction of  $Fe(CN)_6^{3-}$ , which may be adsorbed on the GC electrode surface when the electrode was cycled in the



**Fig. 5** Cyclic voltammograms of DyHCF/GC electrode in 0.2 mol/L KCl solution at a scan rate of 10 (a), 20 (b) and 100 (c) mV/s

preparation solution. As the scan rate increases, the anodic and cathodic peak potential for redox couple I shift to the positive and negative direction, respectively, the values of  $\Delta E_p$  increase; however, the values of  $E^{0'}$ , are almost independent of the scan rates. For redox couple II, both the anodic and cathodic peak potentials move towards the negative direction, and the  $\Delta E_p$  increases with the increase of the scan rates. It can also be noticed from Fig. 5 that the cathodic peak of redox couple II disappeared gradually with the increase of scan rate.

It was reported in the previous works that there was only one pair of redox peak in the cyclic voltammograms of LaHCF and SmHCF-modified electrode [9, 10, 30, 31]. To clarify the characteristics of the two couple of redox peaks of Fig. 5, DyHCF samples were prepared chemically in the solution of  $1 \times 10^{-2}$  mol/L  $K_4Fe(CN)_6$  containing  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$  and 0.1 mol/L, respectively,  $DyCl_3$  (each containing 1 mol/L KCl as electrolyte). The atomic absorption analysis showed that the stoichiometry of the samples was almost independent of the concentration of  $DyCl_3$  in preparation solution. EDX analysis also showed a similar result. The composition of the samples was determined to be  $KDyFe(CN)_6$ . The XPS results showed that chemically prepared DyHCF has almost the same features as that for electrochemically prepared DyHCF, as shown in Fig. 2, in terms of peak position. The experimental results indicated that no precipitate of DyHCF can be formed if the concentration of  $DyCl_3$  in preparation solution decreases further, for example,  $1 \times 10^{-4}$  mol/L. The solid sample of DyHCF was attached to a paraffin-impregnated graphite electrode, which was prepared and impregnated using commercial graphite rods (spectroscopically pure) in this laboratory, using a method of solid-state electrochemistry [9, 31, 41, 42], and then performed the cyclic voltammetric experiments in 0.2 mol/L KCl solution. The cyclic voltammograms are presented in Fig. 6, which indicated that only one pair of redox peak for chemically prepared DyHCF and also the redox peak potential is independent of the concentration of  $DyCl_3$  in prepared solution. Even if 1 mol/L KCl was not included in preparation solution, the formed DyHCF also resulted in a similar cyclic voltammogram to that shown in Fig. 6. For comparison, the cyclic voltammograms of electrochemically and chemically prepared DyHCF were shown together in Fig. 7. One can conclude that the redox peak of chemically prepared DyHCF corresponds to the redox couple I of electrochemically prepared DyHCF. Thus, we propose that the redox potential is dependent on the particle size; the redox couple I in Fig. 5 originates from the electrochemical reaction of bigger particles of DyHCF and the redox couple II originates from the smaller particles since the chemically prepared DyHCF has similar size and shape to that of bigger particles of electrochemically prepared DyHCF (see Fig. 3). According to the results of LaHCF [30] and SmHCF [9, 10, 31], the electrochemical reaction process can be expressed as following:



**Fig. 6** Cyclic voltammograms of a graphite electrode attached chemically prepared  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.2 mol/L KCl solution at a scan rate of 10 mV/s. DyHCF was prepared from the solution of  $1 \times 10^{-2}$  mol/L  $\text{K}_4\text{Fe}(\text{CN})_6$  containing  $1 \times 10^{-3}$  (a),  $1 \times 10^{-2}$  (b) and 0.1 mol/L (c)  $\text{DyCl}_3$

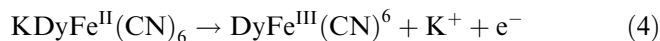
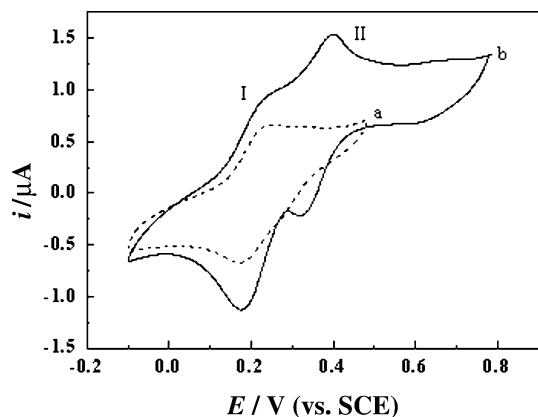
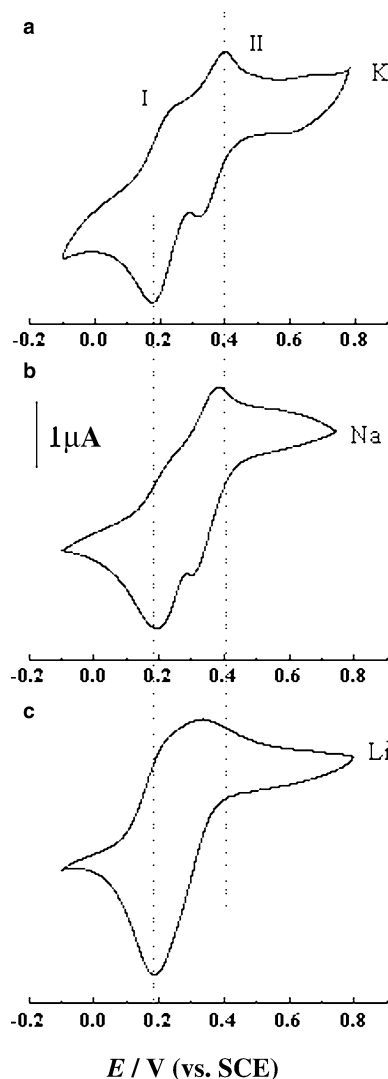


Figure 8 shows the cyclic voltammograms of DyHCF/GC electrode in 0.2 mol/L supporting electrolyte solution with different alkali metal cations. The DyHCF/GC electrode was prepared in  $1.0 \times 10^{-2}$  mol/L  $\text{DyCl}_3$  and  $1.0 \times 10^{-2}$  mol/L  $\text{K}_3\text{Fe}(\text{CN})_6$  solution containing 0.2 mol/L MeCl (Me = Na, K or Li, respectively). From the cyclic voltammograms, one can see that the cathodic peak of redox couple II disappears in LiCl solution, and the redox peak potentials of redox couple I remain unchanged in different supporting electrolyte. The anodic peak potentials of redox couple II, however,



**Fig. 7** Cyclic voltammograms of a graphite electrode attached chemically prepared  $\text{K}_4\text{Fe}(\text{CN})_6$  (a) and a DyHCF/GC electrode prepared electrochemically (b) in 0.2 mol/L KCl solution at a scan rate of 10 mV/s



**Fig. 8** Cyclic voltammograms of the DyHCF/GC electrode in 0.2 mol/L KCl (a), NaCl (b) and LiCl (c) solution at a scan rate of 10 mV/s

shift towards the negative direction in the order of KCl, NaCl and LiCl. For example, the anodic peak potential of redox couple II is +401, +381 and +336 mV, respectively, in KCl, NaCl and LiCl solution.

The stability of DyHCF/GC was checked by repetitive scanning. The height of redox peak decreased with the continuously cycles, this may be due to the gradually dissolution of DyHCF from electrode surface because DyHCF was oxidized and correspondingly iron in sample was changed to high spin state, which may be soluble, when the potential was scanned to the positive direction.

## Conclusions

A rare earth metal hexacyanoferrate, dysprosium hexacyanoferrate (DyHCF), was prepared by electrochemi

cal deposition on the surface of GC electrode (DyHCF/GC) in a solution of  $\text{DyCl}_3$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  containing NaCl, LiCl or KCl as supporting electrolyte, respectively, and was characterized by cyclic voltammetry, FTIR, SEM, XPS, etc. techniques. The DyHCF/GC electrode exhibits two pairs of redox peaks with the formal potential of +210 and +362 mV (vs. SCE), respectively, at a scan rate of 10 mV/s in 0.2 mol/L KCl solution. The effects of supporting electrolyte solution with different alkali metal cations on the electrochemical characteristics of DyHCF/GC electrode were also studied by cyclic voltammetry.

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