SHORT COMMUNICATION

Hexacyanoferrate layers as electrodes for secondary cells

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1. Introduction

It is known that intercalation compounds represent highly reversible electroactive materials in secondary cells, as the change of structure of the host lattice is negligibly small during cycling. Thus inorganic materials such as TiS_2 [1] and graphite salts [2] are successfully used as positives in secondary cells.

The zeolite-like hexacyanoferrates, which intercalate cations such as K^+ and NH_4^+, have been investigated recently with regard to their application to electrochromic displays [3, 4], electrocatalysts [5] and ion-selective electrodes [6, 7]. Their suitability for use as electrodes in secondary cells, however, has not been described so far. This preliminary report shows that thin layers of hexacyanoferrates of iron and copper are promising electrodes for reversible charging in secondary cells.
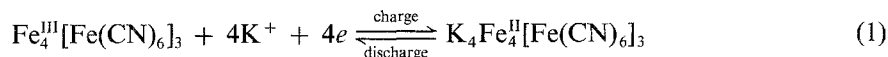
2. Experimental procedure

Thin layers of hexacyanoferrates of iron (FeHCF) and of copper (CuHCF) on platinum were prepared electrochemically as reported in the literature [3, 4, 6, 7]. The layers were 50–150 nm thick and the charge density was $3-9 \, mC \, cm^{-2}$. Cyclic voltammograms of FeHCF or CuHCF electrodes were taken in a conventional three-electrode cell with a saturated calomel electrode (SCE) as reference electrode. Charge–discharge curves were obtained by using a galvanostat (Amel Model 545), the individual electrodes being located in a three-electrode cell. A simple secondary cell has been built with a CuHCF layer as positive and a FeHCF layer as negative. The distance between the electrodes was 0.4 cm. The electrolyte was an aqueous solution of K_2SO_4 of variable concentration. All experiments were performed at room temperature (22° C).
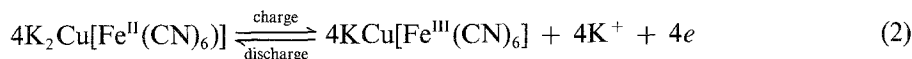
3. Results and discussion

3.1. *Cyclic voltammetry*

Fig. 1 shows typical cyclic voltammograms of layers of FeHCF (left curve) and of CuHCF (right curve). The voltammograms were taken separately and combined in Fig. 1 for comparison.

Starting at a potential of about 500 mV versus SCE, where the FeHCF layer is in its oxidized state (prussian blue, PB), a potential scan in the negative direction converts the layer to the reduced state (Everitt's salt, ES) according to [8]

$$Fe_4^{III}[Fe(CN)_6]_3 + 4K^+ + 4e \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} K_4 Fe_4^{II}[Fe(CN)_6]_3 \tag{1}$$

Similarly, the CuHCF layer is oxidized upon scanning the potential from 500 to 900 mV versus SCE [4]

$$4K_2 Cu[Fe^{II}(CN)_6] \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 4K Cu[Fe^{III}(CN)_6] + 4K^+ + 4e \tag{2}$$
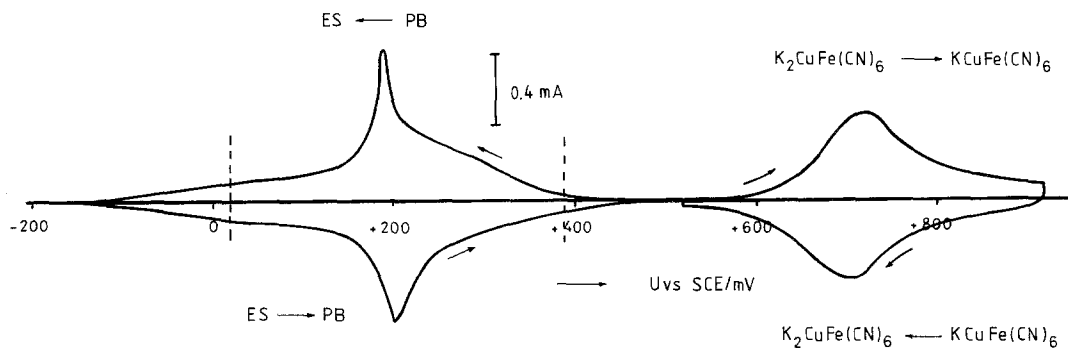
Fig. 1. Cyclic voltammograms of layers of FeHCF (left curve; $v = 20\,mV\,s^{-1}$) and of CuHCF (right curve; $v = 10\,mV\,s^{-1}$). Electrolyte, $0.5\,M\ K_2SO_4$; charge density, $9.4\,mC\,cm^{-2}$; electrode area, $0.5\,cm^2$. Dashed lines show potential limits for cycling of FeHCF.

According to Equations 1 and 2, charging of the FeHCF layer is associated with uptake of K^+ whereas charging of the CuHCF is associated with release of K^+; the reverse processes occur upon discharging.

From cyclic voltammograms the charge of the layers is obtained simply by integration of the curve. Thus it can be seen that cycling of the FeHCF electrode between 20 and 390 mV versus SCE (dashed lines in Fig. 1) embraces only 91% of the total charge of the layer. The symmetry of the voltammograms with respect to the potential axis indicates the highly reversible character of the redox reactions and of the associated intercalation processes. The cyclovoltammograms show that in a cell with a CuHCF layer as positive and a FeHCF layer as negative, a maximum cell voltage of 0.9 V will be obtained at full charge; the mean voltage would be equal to the peak potential difference ($\sim 0.5\,V$).
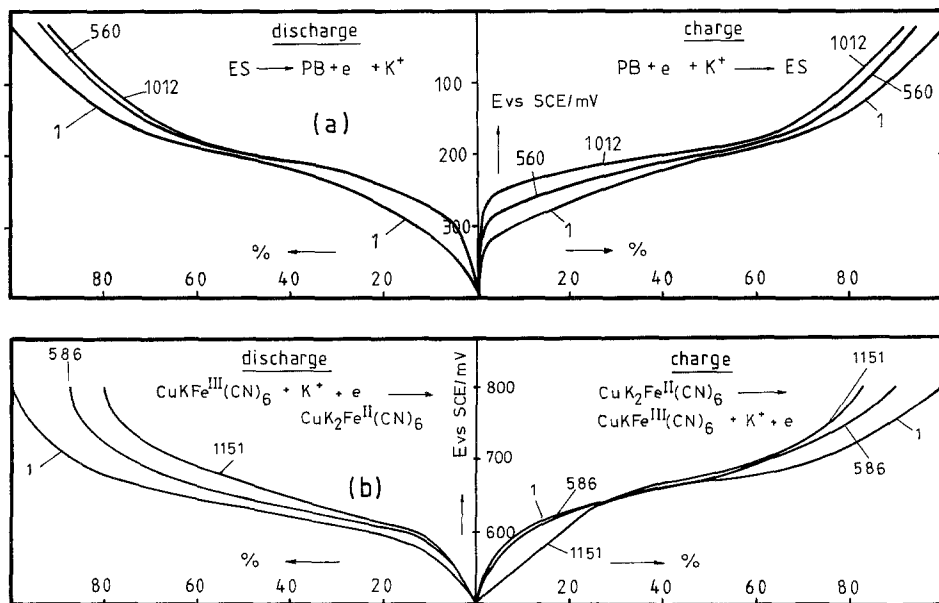

Fig. 2. Charge–discharge curves of FeHCF (a) and CuHCF (b). Electrolyte: (a) 0.5 M; (b) $0.05\,M\,K_2SO_4$. Charge density: (a) $8.6\,mC\,cm^{-2}$; (b) $3.2\,mC\,cm^{-2}$. Electrode area, $0.5\,cm^2$; current density, $1\,mA\,cm^{-2}$. Potential limits (a) 0.02–0.39 V versus SCE; (b) 0.5–0.8 V versus SCE. Numbers indicate the cycle number.
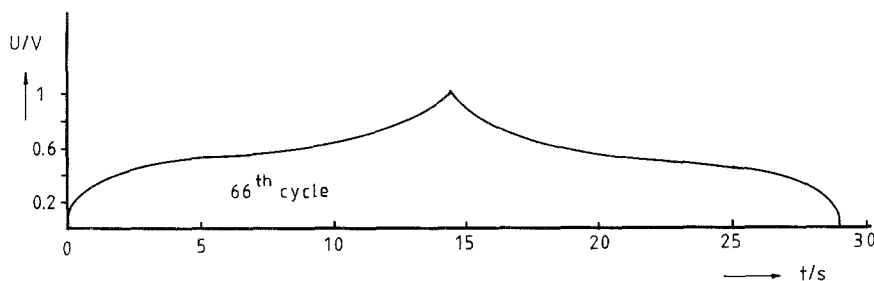
Fig 3. Typical charge–discharge curve of the cell Pt/CuHCF/0.05 M K$_2$SO$_4$ (pH 4)/FeHCF/Pt (66th cycle). Charge density: 2.6 mC cm^{-2} (CuHCF); 3.4 mC cm^{-2} (FeHCF). Electrode area, 0.5 cm^2; potential limits, 0.1–1 V; current density, 0.2 mA cm^{-2}.

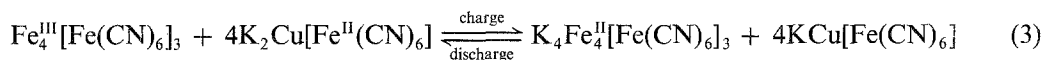### 3.2. *Charge and discharge of FeHCF and CuHCF layers*

Charge–discharge curves obtained from cycling of FeHCF or CuHCF layers are shown in Fig. 2. During more than 1000 cycles the shape of the charge–discharge curve does not change substantially, thus indicating that the mean charge and discharge voltage are nearly constant. In addition, the current efficiency, defined as proportion of discharge time to charge time at constant current, is about 100% at all cycles. Only the coulombic capacity of the layers varies upon cycling: it decreases by about 10% (FeHCF) and 20% (CuHCF) with respect to the coulombic capacity of the first cycle during 1012 and 1151 cycles, respectively.

Cyclic voltammograms taken after cycling indicate that the loss of coulombic capacity can be attributed to a decrease of layer thickness caused by some corrosion process or by gradual dissolution of the layer.

3.3. *Cycling of a hexacyanoferrate secondary cell*

A simple secondary cell has been built by placing a FeHCF and a CuHCF layer electrode in a glass tube filled with 0.05 M K$_2$SO$_4$ at pH 4 (H$_2$SO$_4$). A total of 766 cycles were performed in the cell; a typical charge–discharge curve is shown in Fig. 3.

According to Equations 1 and 2 the cell reaction is given by

$$Fe_4^{III}[Fe(CN)_6]_3 + 4K_2Cu[Fe^{II}(CN)_6] \xrightleftharpoons[\text{discharge}]{\text{charge}} K_4Fe_4^{II}[Fe(CN)_6]_3 + 4KCu[Fe(CN)_6] \qquad (3)$$

With a mean cell voltage of 0.5 V a theoretical energy density of about 50 W h kg^{-1} is obtained. The theoretical capacity is 124 A h kg^{-1} for FeHCF and 85 A h kg^{-1} for CuHCF.

As with the individual FeHCF and CuHCF electrodes, the shape of the charge–discharge curves of the cell and the current efficiency, which is nearly 100%, do not change during cycling. This points to the highly reversible character of cell operation. On the other hand, the coulombic capacity decreases over 766 cycles by about 70%. This can be explained by the fact that the charge density of the CuHCF electrode (2.6 mC cm^{-2}) was substantially smaller than that of the FeHCF electrode (3.4 mC cm^{-2}). Hence the CuHCF layer was permanently overcharged which apparently led to strong oxidative degradation or dissolution.

Despite this CuHCF corrosion and the low theoretical energy density and charge capacity of hexacyanoferrate layers the high reversibility of such systems is attractive and study will continue.

References

[1]   R. Schöllhorn, *Angew. Chem.* **92** (1980) 1015.

[2]   F. Beck and H. Krohn, *Dechema-Monographie* **92** (1982) 57.
[3]   K. Itaya, K. Shibayama, H. Akahoshi and S. Toshima, *J. Appl. Phys.* **53** (1982) 804.
[4]   L. M. Siperko and T. Kuwana, *J. Electrochem. Soc.* **130** (1983) 396.
[5]   K. Itaya, N. Shoji and I. Uchida, *J. Amer. Chem. Soc.* **106** (1984) 3423.
[6]   D. Engel and E. W. Grabner, *Ber. Bunsenges. Phys. Chem.* **89** (1985) 982.
[7]   E. W. Grabner and D. Engel, *Dechema-Monographie* **102** (1986) 575.
[8]   K. Itaya, T. Ataka, S. Toshima and T. Shinohara, *J. Phys. Chem.* **86** (1982) 2415.