

Studies on iron-chromium redox storage system

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Abstract. The performance of the redox storage battery based on the Fe-Cr redox couple is studied in charging and discharging modes of the system. The stability of each charged species is determined by measuring the variation of half-cell potential with time. The spectra of the electrolytes are recorded before and after charging of the system. The effect of atmosphere on the charged species has also been investigated.

Keywords. Photochemical storage system; iron-chromium redox couples.

1. Introduction

In recent years redox battery systems have generated interest as an energy storage system. A redox flow cell (or battery) (Giner *et al* 1976; Beccu and Crespy 1976; Ciprois *et al* 1977; Thaller 1977, 1979; Butler *et al* 1979; Savinelli *et al* 1979; Warshay and Wright 1977) is one in which the chemical species participate in storing electrical energy and regenerate the energy when needed. The cell is charged with the input of electrical energy to drive the overall cell reaction. The oxidized species are produced in one half-cell (anodic compartment) and the reduced species are formed in another half-cell (cathodic compartment).

A number of redox couples have been proposed for such systems. These include Fe(III)/Fe(II) (HCl) (Thaller 1977, 1979); Cr(III)/Cr(II) (HCl) (Beccu and Crespy 1976; Thaller 1977, 1979); Ti(IV)/Ti(III) (Savinelli *et al* 1979); Br₂/Br⁻ (Gileadi *et al* 1977; Yeo and McBreen 1979) and for PEC cells, S₂²⁻, S_x²⁻ and Se²⁻, Se₂²⁻ (Ellis *et al* 1976; Miller and Heller 1976). Out of these couples, Fe-Cr redox system (Thaller 1979; Thaller 1979) seems to be promising due to its high value of electrochemical potential ($E^0 = 1.18$ V).

Chen *et al* (1981) studied iron (III), and iron (II) complexes with O-phenanthroline and related ligands as solution redox couples for electrochemical energy storage. They found that the complexation with O-phenanthroline or bipyridyl-type ligands results in significant positive shifts in the potential of the redox couple. Liu *et al* (1981) revealed that the approach of using a chelating agent in the anolyte for an Fe-Ti redox system shows only marginal improvement in cell discharge performance. However, the application of a solid reducing agent in the anolyte, particularly lead, enhanced the performance of the redox system.

In recent years solar energy is converted into electrical energy by photochemical conversion with semiconductor liquid junction cells. The efficiencies achieved with these cells are comparable to that of solid state junction cells. Energy can be stored with semiconductor liquid junction cells by using photoelectrochemical redox storage cells. The oxide semiconductors are stable and suitable for photoelectrochemical redox storage cells. The α -Fe₂O₃ semiconductor electrode is attracted in the PEC cell due to its comparatively low band gap energy than that of TiO₂ and SrTiO₃. K₄Fe(CN)₆ is the most suitable redox electrolyte in PEC cells formed with α -Fe₂O₃ electrode.

In the present investigation, an attempt was made to form a redox storage cell

with $\text{K}_4\text{Fe}(\text{CN})_6$ and CrCl_3 . The electrode potential of the solutions before and after charging was measured and it is found that the formal potential of the couple is sufficiently shifted towards the desired direction. Spectrophotometric studies reveal the charging of the system. Moreover this system shows improved characteristics with respect to stability when it is air-tight.

2. Experimental

The schematic diagram of the redox storage cell is shown in figure 1. Two beakers are connected by the conducting bridge, 19 cm in length, formed with agar-agar gel. The first compartment of the cell consists of $\text{K}_4\text{Fe}(\text{CN})_6$ solution in which oxidation takes place. The other compartment consists of CrCl_3 solution in which reduction takes place.

The cell was charged with external electricity. The electrical characteristics of the mode of charging and discharging were studied with circuits shown in figures 1a and 1b respectively.

Spectrophotometric studies have been carried out by using a spectrophotometer (Hitachi 330) in the ultraviolet and visible wavelength. The spectra of the redox solutions before and after charging were recorded in the wavelength range of 350 to 600 nm. The studies were carried out using 0.1 M concentration of the electrolytes. The durability of the system is greater when the system is air-tight.

3. Results and discussion

In order to study the mode of changing, the flow of electrons in terms of current is

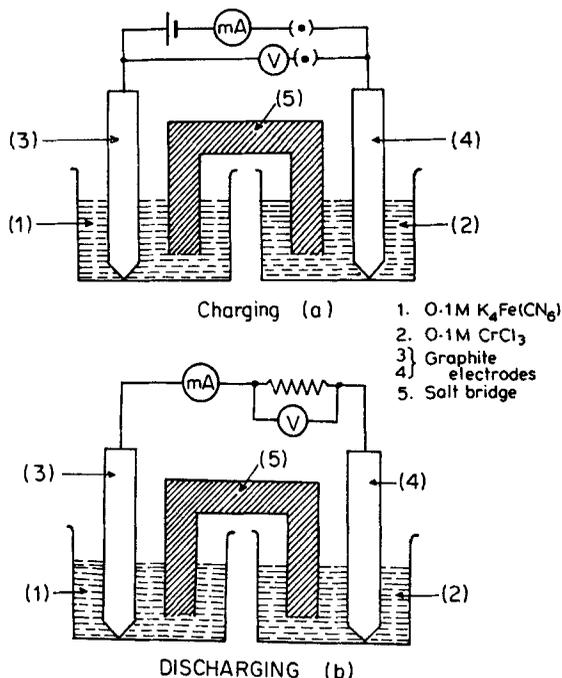
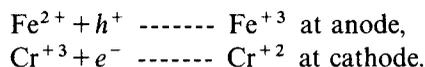


Figure 1. Redox storage cell.

measured with time. The variation of current with time is shown in figure 2. The current decreases with charging time attaining a steady state value. The open circuit voltage of the system is also found to change from 0.2 V to 0.8 V as shown in figure 2. The associated electrode reactions during charging are



Thus electrical energy is stored in the form of chemical species. The nature of plots in figure 2 shows that the rate of charging of the redox storage cell is not constant but decreases exponentially. The plot of $\ln I$ versus time is linear (figure 3).

When electricity is cut off the cell is allowed to discharge through load resistance $RL = 33 \text{ K}\Omega$. The voltage is measured across RL and the current is measured in the series of the circuit (figure 1b). The variations of discharging current and voltage with time are shown in figure 4. It is seen that both the voltage and current decrease with time and attain the original values after 90 min of discharge. In the discharge mode

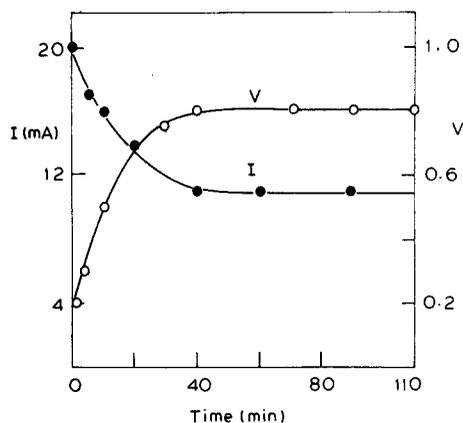


Figure 2. Current-voltage characteristics of redox storage cell formed with $\text{K}_4\text{Fe}(\text{CN})_6$ and CrCl_3 during charging.

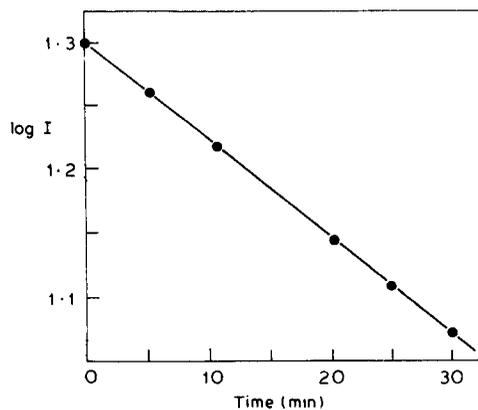


Figure 3. Variation of $\log I$ versus time.

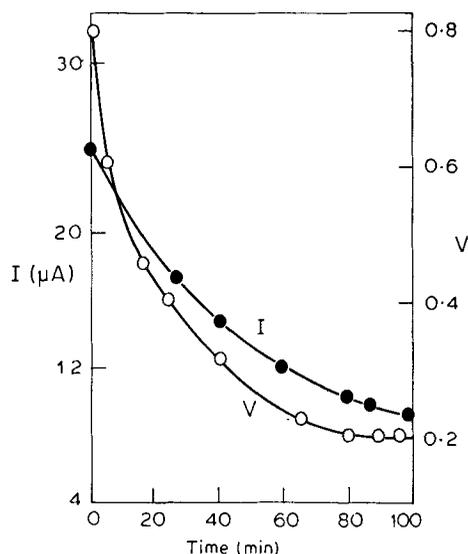
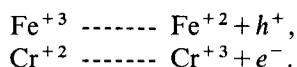


Figure 4. Variation of discharging current and voltage with time formed with $K_4Fe(CN)_6$ and $CrCl_3$.

Table 1. Half cell potentials.

System	Before charging <i>V</i> vs SCE	After charging <i>V</i> vs SCE
0.1 M $K_4Fe(CN)_6$ in water	-0.092 V	-0.203 V
0.1 M $CrCl_3$ in 2N HCl	-0.488 V	+0.467 V

the following reactions take place:



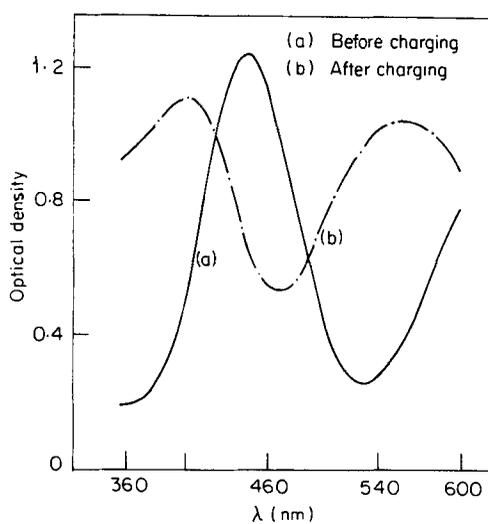
The life-time of the charged species was studied by measuring the potential of the redox cell. The cell voltage decreases with time and about 8 to 10 hours are required for redox species to get its original voltage and about 105 minutes for Fe^{+3} species to get its original voltage measured with respect to SCE before charging.

In order to understand the mechanism of charging and discharging of redox storage cell, we have measured the half-cell potentials of the two compartments with respect to SCE (table 1). It is seen that the values of both compartments change remarkably. This is attributed to the change in state of the chemical species.

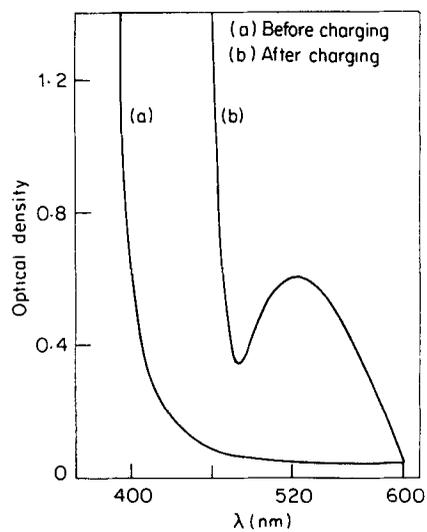
The qualitative test of the charged species is carried out to confirm the change in the original species. The charged solution of $K_4Fe(CN)_6$ is tested by adding $AgNO_3$ solution to it. An orange stuff is formed which indicates that the $K_4Fe(CN)_6$ containing Fe^{+2} species has changed into $K_4Fe(CN)_6$ containing Fe^{+3} species. In the case of $CrCl_3$ solution it is tested with liquor ammonia as also with the solution of $(NH_4)_2S$,

which is the test for Cr^{+3} species. However, the charged CrCl_3 solution forms precipitate with the above solutions. This indicates that the charging of the solution is due not merely to Cr^{+2} species but also to some other forms.

Further analysis was made with spectrophotometric measurements. It is observed that during charging the chromium solution changes from green to deep blue in colour. Johnson and Reid (1985) demonstrated spectrophotometrically that in aqueous solutions containing (Cr(III) and chloride ions, three inner sphere complex ions are present: $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}^{+1}$ (green), $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$ (blue-green) and $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ (blue)). These ions are relatively 'inert' i.e. they are very slow to exchange ligands in their coordination sphere. The $(\text{K}_4\text{Fe}(\text{CN})_6)$ solution changes from pale yellow to yellow.

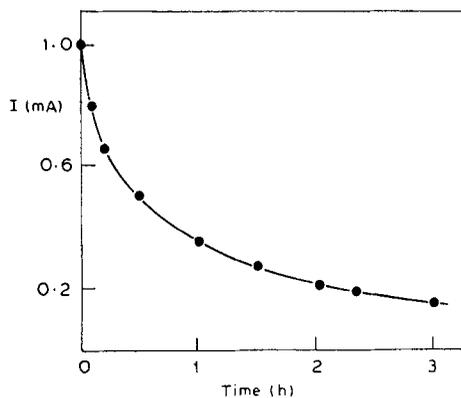


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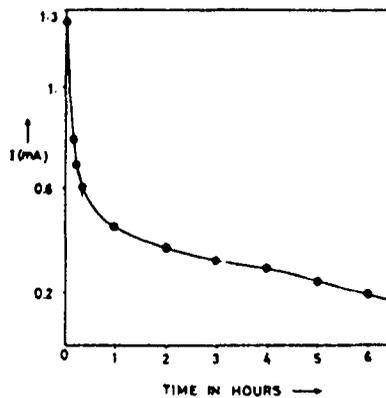


(6)

Figures 5 and 6. Spectra in the wavelength range of 360 nm to 600 nm before and after charging. 5. CrCl_3 solution. 6. $\text{K}_4\text{Fe}(\text{CN})_6$ solution.



(7)



(8)

Figures 7 and 8. Variation of current with time when the system is 7. open. 8. air-tight.

The spectra of the chromium solutions of the redox cell were characterized by two broad absorption bands with a maxima of 408–430 nm and 575–610 nm. The spectra of the cell solutions are recorded before and immediately after charging in the wavelength range of 350 to 600 nm. In CrCl_3 , for the first peak the λ_{max} changes from 445 nm to 405 nm, and for the second peak, the λ_{max} changes from 610 to 570 nm. $\text{K}_4\text{Fe}(\text{CN})_6$ gives a stepline with λ_{max} 410 nm before charging and an additional peak is obtained with λ_{max} 520 nm. The graphs are shown in figures 5 and 6. The shifting in the λ_{max} after charging indicates that the species are charged.

Results with air-tight system show longer stability as compared to the open system. The graphs show that the current is extracted at least up to 3 hours when the system is open and for 6 hours when the system is air-tight (figures 7 and 8). Thus the stability of the system is enhanced when the system is air-tight.

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