Analysis of Mixtures of Ferrocyanide and Ferricyanide using UV-Visible Spectroscopy for Characterisation of a Novel Redox Flow Battery

MOHAMMED HARUN CHAKRABARTI and EDWARD PELHAM LINDFIELD ROBERTS

1Department of Environmental Engineering,
NED University of Engineering and Technology, Karachi, Pakistan.
2School of Chemical Engineering and Analytical Sciences, University of Manchester, UK.

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Summary: A novel Redox Flow Battery (RFB) was designed and developed at the University of Manchester. This system eliminated the ion-exchange membrane altogether by employing porous flow through electrodes. This system was characterised [1] using the ferrocyanide/ferricyanide [hexacyanoferrate (II)/hexacyanoferrate (III)] redox couple which had relatively fast electrochemical kinetics at several electrode surfaces. In this study an accurate method had been developed to determine the concentrations of the ferrocyanide/ferricyanide species from samples obtained from the battery. UV/Visible spectroscopy was chosen as the analytical tool for this purpose. Analysis of a range of standard solutions showed that by measuring the absorbance at 260 nm and 420 nm it was possible to determine the concentration of both ferrocyanide and ferricyanide ions in a mixture of the two active species. Using the correlations developed, it was possible to determine the concentrations of ferrocyanide and ferricyanide ions to an accuracy of ± 4% in mixtures with concentrations in the range 0.01 to 0.1 mM. In work reported elsewhere [1] this analytical method was used to characterise the Redox Flow Battery and it was found that high conversion (>90%) could be achieved at relatively high concentrations (0.1 M) of the active species.

Introduction

Under growing pressure from high oil prices, the governments in developing countries are encouraging research in renewable energy technologies. Among them, the most notable are solar, wind, geothermal, tidal, biogas, biodiesel and others. Pakistan being located in a very hot and sunny region of the world can capitalize mainly from solar energy.

Several technologies have emerged over the years for the efficient storage of solar energy. These include flywheel energy storage, hydrogen based storage, capacitors, electrochemical and others [2]. The electrochemical technology has been used successfully for energy storage for a long time and various different systems have been researched upon [3, 4]. One possible system with a huge potential for efficient storage of solar energy is the Redox Flow Battery [5]. As opposed to conventional lead-acid type batteries, negative and positive electrolytes in the Redox Flow Battery are pumped from storage tanks or reservoirs to a cell composed of electrodes separated by an ion exchange membrane [5]. The redox reactions occur at electrodes during charging and discharging, converting electrical energy into chemical energy and vice versa.

Several different types of electrolytes have been tested in the past [5] but problems of electrolyte cross-contamination and high costs of ion exchange separators have always plagued the system. One possible solution to the problem of cross contamination was the use of a single species with different oxidation states as active electrolytes. This was how the concept of an all-vanadium Redox Flow Battery was born [6]. This system, since its conception in 1985, has already been commercialized due to its high charge/discharge efficiency [7]. However, problems still remain due to high costs and technical issues associated with the ion exchange membrane [8]. This problem has been addressed in new research endeavours conducted at the University of Manchester for several years [1, 9-11]. A novel Redox Flow Battery system was developed that eliminated the ion exchange separator altogether in response to the general problems being faced by the redox flow battery technology. Its electrochemical characteristics needed to be ascertained, however and this research work was conducted as a result.

In general, electrochemical cells have been characterised in various research works using the reversible ferrocyanide/ferricyanide redox couple [12, 13].
Concentrations of the ferrocyanide and ferricyanide ions in solution were determined using UV-Visible spectroscopy in most cases [14-16]. UV-Vis spectroscopy has had applications in various other research areas as well [17-20] and was considered as an ideal analytical tool for the characterisation of the novel Redox Flow Battery employed in this work.

Results and Discussion

The results were obtained for standard samples of potassium ferrocyanide [K₃Fe(CN)₆] and potassium ferricyanide [K₄Fe(CN)₆] at a range of concentrations as shown in Tables 1 and 2. Fig. 1 shows the absorption spectra for 0.025 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 2 shows the absorption spectra for 0.050 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 3 shows the absorption spectra for 0.075 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 4 shows the absorption spectra for 0.100 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. These figures suggest that when the concentration of K₄Fe(CN)₆ was fixed while that of K₃Fe(CN)₆ was increased, a linear increase in the absorbance with concentration of K₃Fe(CN)₆ occurred at wavelengths, λ = 420, 317, 303 and 260 nm, as expected from the Beer-Lambert law. For these purposes of work, it was decided to investigate the effect of concentration on UV/Vis absorbance at wavelengths of 420 and 260 nm (at 420 nm, absorbance was more towards the visible range of the electromagnetic spectrum whereas at 260 nm, absorbance was in the UV range). Fig. 5 shows the relationship between absorbance at 260 nm and standard concentrations of 0.025 mM K₄Fe(CN)₆ for a range of concentrations of K₃Fe(CN)₆. Similarly, Fig. 6 shows the relationship between absorbance at 420 nm and standard concentrations of 0.050 mM K₄Fe(CN)₆ for a range of concentrations of K₃Fe(CN)₆. Both Fig. 5 and Fig. 6 show a linear relationship between absorbance at 260 and 420 nm and concentrations of K₃Fe(CN)₆ thus confirming the original observations from Figs. 1-4.

Fig. 7 shows the absorption spectra for 0.025 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 8 shows the absorption spectra for 0.050 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 9 shows the absorption spectra for 0.075 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. Fig. 10 shows the absorption spectra for 0.100 mM K₄Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆. As can be seen from these figures, when the concentration of

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<tr>
<th>Concentration of K₃Fe(CN)₆ (mM)</th>
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Table-1: Composition of standard samples for characterising the absorbance of UV and visible light against the concentrations of Fe(CN)₆³⁻ ions.

<table>
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<th>Concentration of K₃Fe(CN)₆ (mM)</th>
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Table-2: Composition of standard samples for characterising the absorbance of UV and visible light against the concentrations of Fe(CN)₆³⁻ ions.
Fig. 1: UV Spectra for 0.025 mM K₃Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆ [denoted as Fe(III) in the legend above] in 0.25 mM K₂CO₃ solutions.

Fig. 2: UV Spectra for 0.050 mM K₃Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆ [denoted as Fe(III) in the legend above] in 0.50 mM K₂CO₃ solutions.

Fig. 3: UV Spectra for 0.075 mM K₃Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆ [denoted as Fe(III) in the legend above] in 0.75 mM K₂CO₃ solutions.

Fig. 4: UV Spectra for 0.100 mM K₃Fe(CN)₆ and a range of concentrations of K₃Fe(CN)₆ [denoted as Fe(III) in the legend above] in 1.00 mM K₂CO₃ solutions.

Fig. 5: Concentration of K₃Fe(CN)₆ [denoted as Fe(III) above while K₃Fe(CN)₆ is denoted as Fe(II)] against absorbance at 260 nm.

Fig. 6: Concentration of K₃Fe(CN)₆ [denoted as Fe(III) above while K₃Fe(CN)₆ is denoted as Fe(II)] against absorbance at 420 nm.
Fig. 7: UV spectra for 0.025 mM K$_3$Fe(CN)$_6$ and a range of concentrations of K$_4$Fe(CN)$_6$ [denoted as Fe(II) in the legend above] in 0.25 mM K$_2$CO$_3$ solutions.

Fig. 8: UV spectra for 0.050 mM K$_3$Fe(CN)$_6$ and a range of concentrations of K$_4$Fe(CN)$_6$ [denoted as Fe(II) in the legend above] in 0.50 mM K$_2$CO$_3$ solutions.

Fig. 9: UV spectra for 0.075 mM K$_3$Fe(CN)$_6$ and a range of concentrations of K$_4$Fe(CN)$_6$ [denoted as Fe(II) in the legend above] in 0.75 mM K$_2$CO$_3$ solutions.

Fig. 10: UV spectra for 0.100 mM K$_3$Fe(CN)$_6$ and a range of concentrations of K$_4$Fe(CN)$_6$ [denoted as Fe(II) in the legend above] in 1.00 mM K$_2$CO$_3$ solutions.

Fig. 11: Concentration of K$_4$Fe(CN)$_6$ [denoted as Fe(II)] above while K$_3$Fe(CN)$_6$ is denoted as Fe(III)] against absorbance at 260 nm.

K$_3$Fe(CN)$_6$ was fixed and that of K$_4$Fe(CN)$_6$ was varied, the absorbance of UV light appeared to increase linearly with the concentration of K$_4$Fe(CN)$_6$ at wavelengths, $\lambda = 323$, 303 and 260 nm. This was confirmed by plotting absorbance at 260 nm with the concentrations of K$_4$Fe(CN)$_6$ as shown in Fig. 11, which gave a straight line as expected.

The absorbance of UV light by potassium carbonate was not found to interfere with those for ferro/ferricyanide ions [8]. Following Bae [8], absorbance at wavelengths of 420 and 260 nm were used for establishing correlations for the sample concentrations as given below.

If $A_{420}$ and $A_{260}$ refer to the absorbance at 420 and 260 nm respectively, while $K_1$, $K_2$, $K_3$ and $K_4$ refer to proportionality constants with $C_1$ and $C_2$ as...
arbitrary constants, then linear relationships between
the absorbance and concentration of ferro/
ferricyanide can be expressed as Equations 1 and 2.
\([\text{Fe(CN)}_6^{3-}]\) and \([\text{Fe(CN)}_6^{4-}]\) are the concentrations of
\(\text{Fe(CN)}_6^{3-}\) (ferricyanide) and \(\text{Fe(CN)}_6^{4-}\) (ferrocyanide)
ions in the sample, respectively.

\[
A_{420} = K_1[\text{Fe(CN)}_6^{3-}] + K_2[\text{Fe(CN)}_6^{4-}] + C_1 \quad (1)
\]

\[
A_{360} = K_3[\text{Fe(CN)}_6^{3-}] + K_4[\text{Fe(CN)}_6^{4-}] + C_2 \quad (2)
\]

Fig. 5 and Fig. 6 were used for determining
the relationship between absorbance of UV/Vis light
and concentrations of \(K_3\text{Fe(CN)}_6\) using a standard
least squares fit of the data as explained below.
Similarly Fig. 11 was used to determine a relationship
between absorbance and concentrations of \(K_4\text{Fe(CN)}_6\)
using a standard least squares fit of data.

From plots of concentration against
absorbance for standard samples at wavelengths of
420 and 260 nm by using a least squares fit of the
data, the values of \(K_i, K_2, K_3, K_4, C_1\) and \(C_2\) have been
estimated as follows:

\[K_i = 1.058; K_2 = -0.003; K_3 = 1.260\]

\[K_4 = 2.724; C_1 = 0.000925; C_2 = 0.006421\]

The correlations can now be written as shown in Equations 3 and 4:

\[A_{420} = 1.058[\text{Fe(CN)}_6^{3-}] - 0.003[\text{Fe(CN)}_6^{4-}] + 0.000925 \quad (3)\]

\[A_{360} = 1.260[\text{Fe(CN)}_6^{3-}] + 2.724[\text{Fe(CN)}_6^{4-}] + 0.006421 \quad (4)\]

The accuracy of these concentrations
predicted from the above correlations was determined
to be about ± 4% using standard solutions. Thus, it
was verified that the correlations determined in this
research are accurate enough for determining the
concentrations of ferrocyanide and ferricyanide ions
in any samples taken from the novel Redox Flow
Battery described in the literature [1, 9-11].

**Experimental**

UV/Vis Spectroscopy was proposed as the
analytical technique for determining the
concentrations of potassium ferrocyanide
\([K_4\text{Fe(CN)}_6]\) and potassium ferricyanide \([K_3\text{Fe(CN)}_6]\)
ions in samples taken from the novel Redox Flow
Battery described in the literature [1, 9-11]. A brief
schematic representation of the flow reactor is shown in
Fig. 12. As the colour of potassium ferrocyanide
(Merck, Reagent grade) was pale yellow, it was
anticipated that the solution would absorb within the
ultraviolet (UV) region. The colour of potassium
ferricyanide (Merck, Reagent grade) was bright
yellow, indicating that it should absorb solely within
the visible region. However, some interference was

![Fig. 12: Schematic diagram of the electrochemical separation of a mixture of \(K_4\text{Fe(CN)}_6\) and \(K_3\text{Fe(CN)}_6\).](image-url)
observed by Bae [9] and thus experiments were designed in this research to investigate this. It was hypothesized that absorption in the UV region may have been due to the presence of functional groups or bond vibrations, but these were not detailed investigated during this work.

Experiments were conducted to determine the concentrations of Fe(CN)$_6^{3-}$ and Fe(CN)$_5^{4-}$ from a mixture in 0.5 M potassium carbonate (Merck, Reagent grade) using UV/Vis spectroscopy. Due to the possibility of interfering absorbance of UV and visible light by the two different ions, the mixtures were subjected to the lights of continuously changing wavelength while monitoring their absorbances. For this purpose, a range of standard solutions (0 to 0.1 mM ferrocyanide and 0 to 0.1 mM ferricyanide) were made up for determining the relationship between the absorbance of UV and visible light against the concentration of mixtures of Fe(CN)$_6^{3-}$ and Fe(CN)$_5^{4-}$ ions in aqueous solutions of K$_2$CO$_3$ as shown in Tables 1 and 2. In addition, the absorbance of 0.5 M K$_2$CO$_3$ was also determined.

Spectrometric analysis was conducted by means of a Perkin Elmer Lambda 10 UV/Vis spectrometer (double beam) in conjunction with a computer running UV Winlab software. Each scan was performed from 500 nm to 250 nm at a scan rate of 240 nm min$^{-1}$. The absorbance axis was adjusted to read from 0 to 1.5 arbitrary units [9].

In order to perform UV and visible scans on each sample, a quartz cell of dimensions 10 mm x 10 mm x 45 mm (Hellma) was employed. This was initially rinsed with de-ionised water before measuring the absorbance of the samples. A blank sample of de-ionised water was used to autozero the instrument before each set of measurements. The cell was emptied and filled with the sample and scanned between the aforementioned wavelength ranges. Once the scan was complete, the cell was emptied, rinsed and filled with the next sample for analysis.

Conclusions

UV/Vis spectroscopy was selected as the analytical tool for determining the concentrations of potassium ferrocyanide and potassium ferricyanide from experiments conducted on a novel Redox Flow Battery at the University of Manchester (cell design and operation has been described in detail in the literature [1, 9-11]). Suitable correlations were prepared to predict the concentrations from the absorbance spectra of the chemicals in both the visible and ultraviolet ranges. These correlations were tested against standard solutions and their accuracy was determined to be within ± 4%. As a result, an appropriate procedure was formulated using UV/Vis spectroscopy to determine the concentrations of potassium ferrocyanide and potassium ferricyanide from Redox Flow Battery samples accurately.

These correlations were used to evaluate the concentrations of potassium ferrocyanide and potassium ferricyanide in flow hydrodynamic experiments conducted on the novel Redox Flow Battery [1]. It was found from these hydrodynamic experiments that high reactant conversions (in excess of 90%) could be achieved for high concentrations of active redox species at low flow rates. UV-Vis spectroscopy thus proved to be an extremely useful tool in the characterization of the novel Redox Flow Battery as it has been for other types of electrochemical reactors [14-16].

Acknowledgements

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References