Cyclic Voltammetric Study of ferrocyanide/ferricyanide Redox Couple

Background:

Cyclic voltammetry (CV) is a versatile electroanalytical technique for the study of electroactive species. CV monitors redox behavior of chemical species within a wide potential range. The current at the working electrode is monitored as a triangular excitation potential is applied to the electrode. The resulting voltammogram can be analyzed for fundamental information regarding the redox reaction. Cyclic voltammograms are the electrochemical equivalent to the spectra in optical spectroscopy.

The potential at the working electrode (WE) is controlled vs a reference electrode (RE), Ag/AgCl(s)/(satd. KCl) electrode. The controlling potential that is applied across the WE and the auxiliary electrodes is the excitation signal. The excitation signal is varied linearly with time; first scan positively (-100 mV vs. RE to 500 mV vs. RE). Then the potential is scanned in reverse, causing a negative scan back to the original potential to complete the cycle. Single or multiple cycles can be used on the same surface. A cyclic voltammogram is the plot of the response current at the working electrode to the applied excitation potential.

As the potential is scanned positively (forward scan, here) and is sufficiently positive to oxidize Fe(CN)$_6$-$^{4}$, the anodic current is due to the electrode process

$$\text{Fe(CN)}_6^{4-} \rightarrow \text{Fe(CN)}_6^{3-} + e^-$$

The electrode acts as an oxidant and the oxidation current increases to a peak. The concentration of Fe(CN)$_6$-$^{4}$ at the electrode surface depletes and the current then decays. As the scan direction is switched to negative, for the reverse scan the potential is still sufficiently positive to oxidize Fe(CN)$_6$-$^{4}$, so anodic current continues even though the potential is now scanning in the negative direction. When the electrode becomes a sufficiently strong reductant, Fe(CN)$_6$-$^{3}$, which has been forming adjacent to the electrode surface, will be reduced by the electrode process,

$$\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}$$

resulting in a cathodic current which peaks and then decays as Fe(CN)$_6$-$^{3}$ in the solution adjacent to the electrode is consumed.

In the forward scan Fe(CN)$_6$-$^{3}$ is electrochemically generated from Fe(CN)$_6$-$^{4}$ (anodic process) and in the reverse scan this Fe(CN)$_6$-$^{3}$ is reduced back to Fe(CN)$_6$-$^{4}$ (cathodic process). Note that the technique of CV rapidly generates various oxidation states.

The quantities of note a CV plot are the anodic peak current $i_{pa}$, cathodic peak current $i_{pc}$, anodic peak potential $E_{pa}$, and cathodic peak potential $E_{pc}$. Measuring $i_p$ does involve the extrapolation of the base-line current.
A redox couple in which half reactions rapidly exchange electrons at the working electrode are said to be electrochemically reversible couples. The formal reduction potential $E^{\circ}$ (different from $E^{\circ}$, strictly speaking) for such a reversible couple is the mean of $E_{pa}$ and $E_{pc}$ and the $i_{pa}$ and $i_{pc}$ are very close in magnitude.

$$
E^{\circ} = \frac{E_{pa} + E_{pc}}{2}
$$

The number of electrons involved in the redox reaction for a reversible couple is related to the difference of peak potentials by:

$$
E_{pa} - E_{pc} = \frac{59mV}{n}
$$

For slow electron transfers at the electrode surface, i.e. irreversible processes, the difference of peak potentials widen. The peak current in reversible systems for the forward scan is given by Randles-Sevcik equation,

$$
i_{pc} = 2.69 \times 10^8 n^{3/2} A D^{1/2} v^{1/2} C
$$

where, $i_{pc} =$ peak current, A; $n =$ # electrons involved, ; $A =$ electrode area, m$^2$; $D =$ diffusion coefficient, m$^2$/s; $C =$ concentration, mol/L and $v =$ scan rate, V/s.

Thus $i_{pc}$ increases with square root of $v$ and is directly proportional to concentration of the species. The values of $i_{pa}$ and $i_{pc}$ are very similar for a one step reversible couple leading to their ratio to be unity. Ratio of peak currents may differ from unity if the reactions coupled to other electrode process.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Potentiostat, glassy carbon working electrode (diameter 1mm), platinum auxiliary electrode, Ag/AgCl reference electrode, nitrogen cylinder, oxygen absorber, polishing material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals</td>
<td>10 mM $K_4Fe(CN)_6$ in 1.0 M potassium nitrate solution, 1.0 M KNO$_3$ (matrix), Unknown: $K_4Fe(CN)_6$ in 1.0 M KNO$_3$, 1000ppm $K_4Fe(CN)_6$ in 1.0 M potassium nitrate solution</td>
</tr>
</tbody>
</table>

**Procedure:**

Polish the electrode surface to a mirror finish with alumina slurry and rinse well with DI water and dry it. Fill the cell with 10 mL 10 mM $K_4Fe(CN)_6$ in 1.0 M KNO$_3$.

Turn on the computer, cell stand and the controlling unit.

Double click Epsilon Icon. Open an ‘old’ CV experiment to get a feel of the output.

Open the Setup/Manual Settings window.
Make sure Under the Cell Stand accessories - C3-Cell Stand is checked.
Under Line freq – 50 Hz Checked.
Under Purge/Stir/RDE-2 – Purge (as needed), Stir (as needed).

Deoxygenate the solution by purging with oxygen free nitrogen for approximately 5 min. Turn off the purging but maintain an envelope of nitrogen over the solution. Set the scan parameters suggested below, they may be changed appropriately from the Cyclic Voltammetry Parameter window.

CV Parameters:

<table>
<thead>
<tr>
<th>Initial Potential (mV)</th>
<th>0</th>
<th># of Segments</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switching Potential (mV)</td>
<td>750</td>
<td>Scan rate (mV/s), (v)</td>
<td>100</td>
</tr>
<tr>
<td>Reverse E Limit (mV)</td>
<td>0</td>
<td>Quiet Time (sec)</td>
<td>15</td>
</tr>
<tr>
<td>Final E (mV)</td>
<td>0</td>
<td>Full Scale</td>
<td>100 uA</td>
</tr>
</tbody>
</table>

Activate [IR-COMP]. To keep the Parameters entered above [Apply].

Excite the working electrode with the potential scan and obtain the background CV of the supporting electrolyte solution by RUNning the experiment. (Save all data in named files.)

Using the same solution and obtain CV's at the following scan rates (\(v\)): 20, 50, 75, 125, 150, 175, and 200 mV/s. Between each scan, stir the solution in the cell to restore initial conditions and allow the system to acquire quiescence before applying the excitation potential scan.

Determine the concentration of the unknown by standard addition method, start with a fresh solution of 10.00mL the ferricyanide unknown solution and proceed as before with a scan rate of 100mV/s. (Use 100uL aliquots of stock standard solution at each addition of the standard addition routine.)

**Treatment of Results:**

1. Plot \(i_{pc}\), vs \(v^{1/2}\), \(i_{pa}\) vs \(v^{1/2}\).
2. Plot \(E_p\) values vs \(v\) for the above runs - comment on the reversibility of the redox reaction.
3. Verify the formal standard electrode potential of Fe(II)/Fe(III) system and number of electrons involved in the half reaction, \(n\), from appropriate plots.
4. Determine the diffusion coefficient ratio of the two species.
5. Present voltammograms of appropriate ‘sets’ overlapped on the same paper.
6. Using the standard addition method determine the concentration of the unknown solution.