Electrochemical Techniques: Cyclic Voltammetry

Cyclic Voltammetry of Ferrocene Carboxylic Acid

1. Aims

To use cyclic voltammetry to investigate the solution electrochemistry of a simple redox couple.

2. Background

Cyclic voltammetry is a powerful analytical technique that provides information about the characteristic electrochemical processes an analyte undergoes in solution.

To perform cyclic voltammetry, typically a potentiostat and a three electrode cell is used to first apply a linear potential sweep from E1 to E2, followed by a reverse sweep back to E1. The triangular voltage-time wave form used for cyclic voltammetry measurements is represented in **Figure 2.1a**.

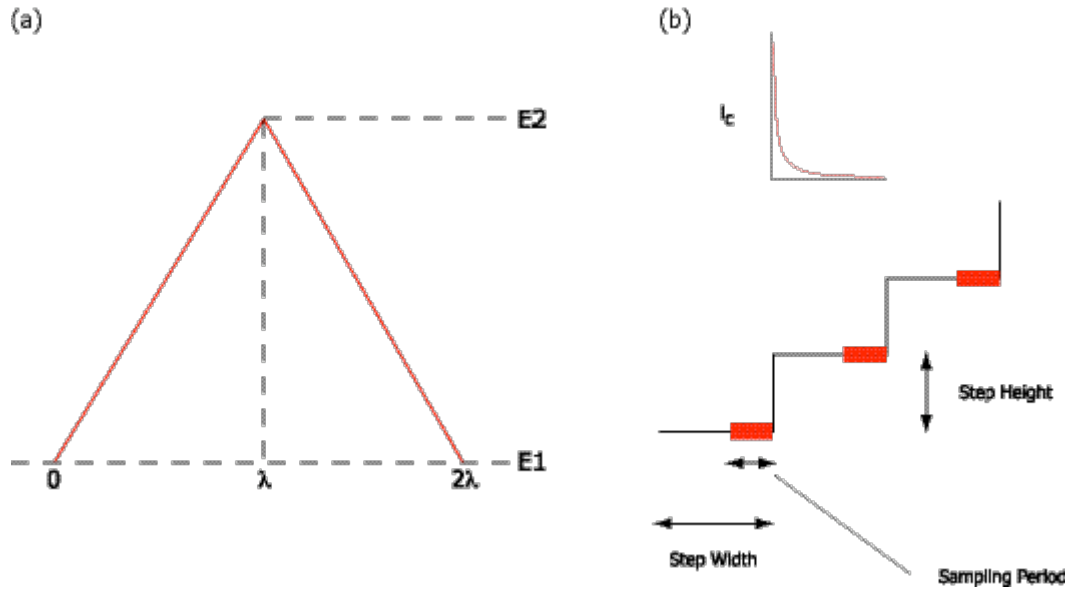

Figure 2.1 (a) Voltage-time profile for cyclic voltammetry measurements where λ is the switching time and *E* the applied potential. (b) Staircase ramp used by digital potentiostats. Sampling is restricted to the final 1/4 of the step width to give time for capacitive current, i_c, to decay when the potential is changed.

The potential applied, E, will control the concentration of the two redox forms in accordance with the Nernst equation:

$$E = E_0 + \left(RT/nF\right)\ln\left[\text{Ox}\right]/\left[\text{Red}\right] \qquad \ldots\ldots (2.1)$$

where Ox = oxidised species; Red = reduced species.

With digital instruments, a staircase potential ramp is used, as represented in **Figure 2.1b**. This is because digital to analog converters output discrete voltage values. To reduce the influence of the capacitive current, i_c, which forms when the voltage is changed, current sampling is generally restricted to the final 1/4 of the step width, where i_c has decayed.

The Faradaic current (i_f) will depend on the concentration gradient of Ox at the electrode surface (Nernst diffusion layer) according to:

$$i_f = nFAD_a\left(\text{d}\left[\text{Ox}\right]/\text{d}x\right) \qquad \ldots\ldots (2.2)$$

Where D_a is the diffusion coefficient for the electroactive species and A is the area of the electrode. During the reducing scan, the surface concentration of species Ox progressively decreases, resulting in an increased concentration gradient and a larger current. As reduction continues, the concentration of Ox at the electrode surface is depleted, and the current peak will decay if fresh Ox from the bulk solution does not have enough time to diffuse to the electrode surface. When the direction of the potential scan is reversed, a peak resulting from the re-oxidation of reduced Red is observed.

Currents generated by the oxidation and reduction reactions at the working electrode are measured and plotted against applied potential on a cyclic voltammogram (CV). **Figure 2.2** shows the shape of typical CV for a single electron transfer process. Cyclic voltammograms are characterised by peak potentials, E_p, at which the current reaches a local maximum or minimum and the value of the peak current, i_p, at these points.

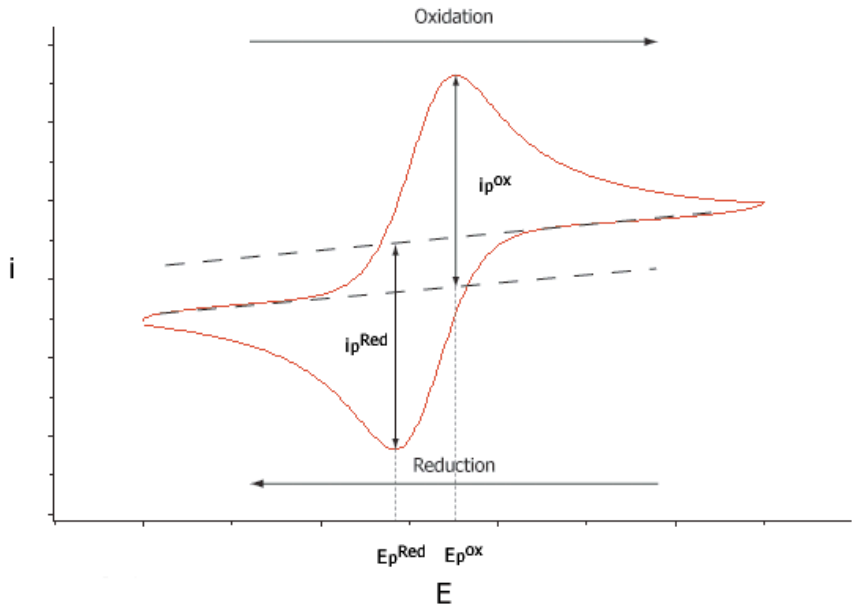

Figure 2.2 A typical cyclic voltammogram for a reversible single electron transfer

When a redox reaction is 100% reversible, the oxidation and reduction peak currents are equivalent, and the peak current is given by the relation:

$$i_p = 0.4463nF\left(nF/RT\right)^{\frac{1}{2}}\left(D_a\right)^{\frac{1}{2}}\left(V\right)^{\frac{1}{2}}C_aA \qquad \ldots\ldots (2.3)$$

where V is the potential scan rate in V/s and C_a is analyte concentration in mol/cm^3.

Hence, reversible reactions may be diagnosed using the following criteria:

- Peak separation $\Delta E_p = E_p^{Red} - E_p^{Ox} = 59$ mV ($59 \cong 2.303\ nF/RT$ at 298 K)
- $i_p^{Ox}/i_p^{Red} = 1$
- i_p^{Ox} and $i_p^{Red} \propto V^{1/2}$
- E_p^{Ox} and E_p^{Red} independent of V

In this practical, the potential scan rate (V) in **Equation 2.3** is adjusted to see its influence on the shape of a CV and the magnitude of the peak current. Observations made are then related to processes occurring at the surface of the working electrode and the properties of the analyte and solution.

Ferrocene Carboxylic Acid (FCA) is investigated, which undergoes a reversible single electron oxidation to ferricene as follows:

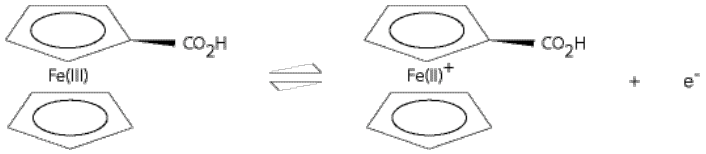

Figure 2.3 Single electron transfer between FCA and FCA$^+$.

In an electrochemical cell, the forward (oxidation) reaction is favoured at potentials positive of the E^0 for the couple and gives a positive current. The reverse (reduction) reaction is favoured at potentials negative of the E^0 for the couple and gives a negative current.

3. Equipment Required

Per Group:

- Computer with EChem installed
- e-corder
- EA160 Potentiostat
- From the ET014 EChem Electrode Kit

  1.5 mm Glassy Carbon Disk Electrode (working electrode)

  mini Ag/AgCl Reference Electrode

  Pt Auxiliary Electrode

  3 mL Mini Cell

  Cell Stand
- Nitrogen gas cylinder with a needle valve and a hose terminating in Teflon tubing drawn down to a 1mm OD at the tip
- A role of electrical tape

4. Reagents Required

- 0.002 M Ferrocene Carboxylic Acid Solution in Sodium Citrate Buffer with pH adjusted to 7.

5. Procedure

5.1 Electrode Set-up

5.1.1 Set up the e-corder and Potentiostat using instructions in their respective manuals on the eDAQ Software Installer CD.

5.1.2 Place 2 mL of ferrocene carboxylic acid solution into the cell provided and place into the cell stand. Secure the lid and place the working electrode into the largest hole, adjusting the rubber O-ring into a position so that the tip of the electrode is submerged in solution.

5.1.3 Insert the reference and auxiliary electrodes through two of the other holes, and tape to the working electrode. The tips of the electrodes should all be in the same plane.

5.1.4 Make sure that needle valve of the nitrogen supply is closed and insert the fine Teflon tube end of the gas line through the remaining hole in the lid. Adjust the cylinder regulator to give a pressure reading of not more than 0.5 bar. (0.1 bar ideal). Slowly open the needle valve, adjusting the flow to give a steady stream of small gas bubbles.

5.1.5 Connect the Red alligator clip from the potentiostat cable to the Auxiliary Electrode, the Green to the Working Electrode and the Yellow to the Reference Electrode.

5.2 Familiarisation with EChem software

5.2.1 Double-Click the EChem icon on your computers desktop to launch EChem. The screen shows an X-Y graph of potential applied to the working electrode (V) against the current passed by the working electrode in µA

5.2.2 Double-Click on the Potentiostat button to the right of the main window to open the potentiostat dialog box. Change the radio button from Standby to dummy, which internally connects a resistor between the electrodes. Set the current range to 10 µA and alter the applied potential using either the slider control or by typing a value into the potential display. Increase the potential in 0.1 V jumps, the current trace should vary as you change the potential. The relationship between should be linear as expected from Ohm's law. Finally reset the potential to 0 V.

5.2.3 Change the radio button from dummy to cell. The potential will now be applied across the electrodes. Repeat the procedure in Step **5.2.2**, keeping the potentials between –0.2 V and +1.0 V. Do NOT exceed these limits. It will be necessary to change the current range (try 50 µA) to see the current responses. Notice that there is a small range of potentials over which the current is very sensitive to applied potential.

5.2.4 Reset the potential to 0 V and click OK to close the potentiostat dialog box. The potentistat will automatically switch to standby mode.

5.3 Cyclic Voltammetry of Ferrocene Carboxylic Acid

5.3.1 Switch the current range to 10 µA.

5.3.2 From the techniques menu select Cyclic Voltammetry. This opens the Staircase Cyclic Voltammetry dialog box, which is used to set the limits and ramp rate of the voltage waveform applied to the working electrode. In the dialog box, select the following parameters:

Initial = 0 mV
Final = 0 mV
Upper Limit = 700 mV
Lower Limit = 0 mV
Rest Time = 5 s
Ramp Rate = 100 mV/s
Step Width = 20 ms
Step Height = 2 mV
Sampling Period = 5 ms
Number of Cycles = 3

Click on View to preview the waveform defined. It should look like **Figure 5.1**.

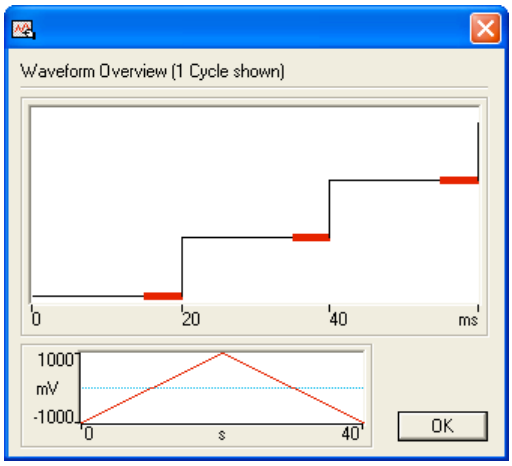

Figure 5.1 Waveform Overview Window

5.3.3 Select the Notebook under the Windows menu. Write some general notes on the experiment including your name, Date, time and solution details. Close the window and save the file using a suitable filename.

5.3.4 Lift the nitrogen line out of the solution. Check that there are no bubbles trapped on the surface of the electrode. If there are, lightly tap the cell to dislodge them.

5.3.5 Click on Start to begin the potential scans. Voltammograms similar to that shown in **Figure 5.3** should be recorded on pages 1, 2 and 3. After the scans, place the nitrogen line back into the solution.

5.3.6 If you are happy with the scans, click on the Page comment button (bottom left of screen) and enter a comment for the middle scan (solution, scan rate etc.).

5.3.7 In the Staircase Cyclic Voltammetry dialog box, change the Ramp Rate to 200 mV/s, the Step Width to 10 ms and the Sampling Period to 2.5 ms. Repeat Steps **5.3.4** to **5.3.6** to obtain a new set of three voltammograms. If the current reading goes off scale, adjust the current range, and repeat the scans.

5.3.8. Repeat **5.3.7**, with a Ramp Rate of 500 mV/s, Step Width of 4 ms and a Sampling Period of 1 ms, adjusting the current range if necessary.

5.3.9 Switch the current range to 5 µA and obtain scans at 10 mV/s, Step Width of 200 ms and a Sampling Period of 50 ms.

6. Data Analysis

6.1 Overlay the middle CV of the three obtained for straight FCA at the different scan rates, by highlighting the corresponding page tabs and selecting **Overlay All** in the **Display Menu**. Print and label the overlain CVs for inclusion in your report. Annotate a single CV on the printout with the peak potentials (E_p^{Ox} and E_p^{Red}) and peak currents (i_p^{Ox} and i_p^{Red}).

6.2 Tabulate the E_p^{Ox} and E_p^{Red} values obtained for each of the CVs in **Table 7.1**.

6.3 As with many electrochemical techniques, cyclic votammograms often have sloping baselines, and the peak currents can not be read directly. In EChem, two marker

points can be used to define an estimated baseline from which the peak currents can be determined.

To set the two marker points, switch to the view of current and applied potential against time view by selecting IE v t in the Display pop-up menu.

The CVs should now look similar to **Figure 6.1**.

6.3.1 To measure the peak oxidation current (i_p^{Ox}), drag the marker onto current (I) channel to t=0. Press Control-Alt (Command-Option for Macintosh) and drag a second marker onto the CV that is independent of the waveform. Adjust the second marker so the tie line forms a tangent with the initial current slope during the oxidising sweep. See **Figure 6.1** for an example. Use the cursor to measure the peak current relative to the baseline and tabulate in **Table 7.1**. Repeat for each CV.

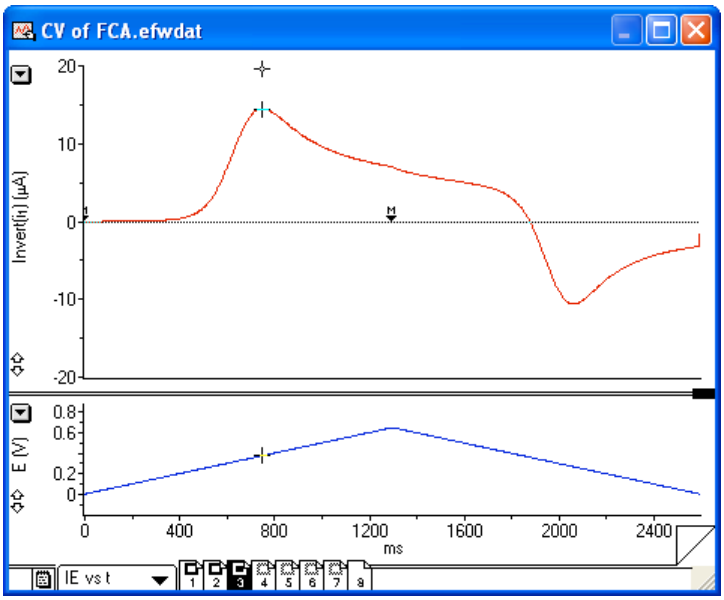

Figure 6.1 Setting the baseline for i_p^{Ox} in IE v t view

6.3.2 To measure the peak reduction current (i_p^{Red}) drag an initial marker onto the current channel at the time where the reduction scan starts. Press Control-Alt (Command-Option for Macintosh) and drag a second marker onto the CV that is independent of the waveform. Adjust the second marker so the tie line forms a tangent with the initial current slope during the oxidising sweep. See **Figure 6.2** for an example. Use the cursor to measure the peak current relative to the baseline and tabulate in **Table 7.1.** Repeat for each CV.

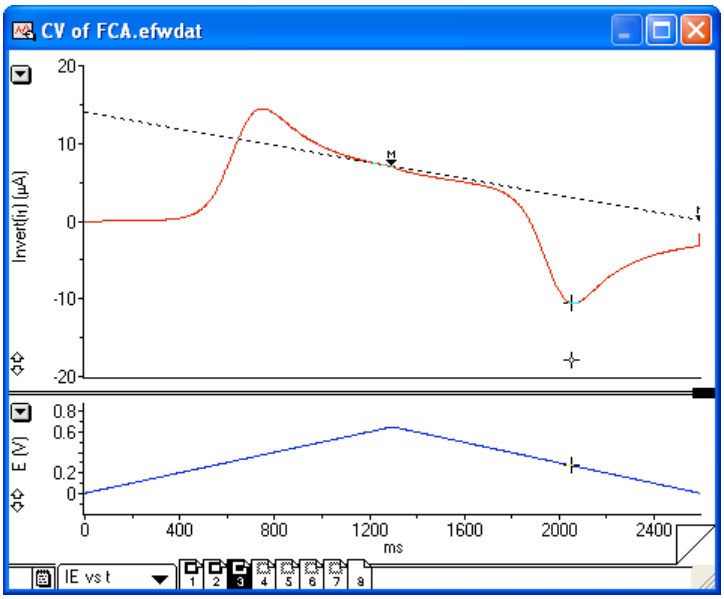

Figure 6.2 Setting the baseline for i_p^{Red} in IE v t view

7. Results

7.1 CV Parameters

	E_p^{Ox} (mV)	i_p^{Ox} (µA)	E_p^{Red} (mV)	i_p^{Red} (µA)	ΔE_p (mV)
100 mV/s scan 1					
100 mV/s scan 2					
100 mV/s scan 3					
200 mV/s scan 1					
200 mV/s scan 2					
300 mV/s scan 3					
500 mV/s scan 1					
500 mV/s scan 2					
500 mV/s scan 3					
10 mV/s scan 1					
10 mV/s scan 2					
10 mV/s scan 3					

8. Questions

8.1

Do the results obtained support the electron transfer between ferrocene and ferricene being reversible? What evidence is there to support this?

The observations made should indicate that the electron transfer is reversible:

ΔE_p should be approximately 59 mV, however this can vary with laboratory temperature and the positioning of the electrodes in the cell.

$I_p^{Ox} \approx |I_p^{Red}|$ However there may be errors associated with defining the baseline of the CV.

8.2

What happens to the peak current (i_p) as the potential scan rate (V) changes? Explain why this occurs?

The peak current increases at fast scan rates, and decreases at slower scan rates. This occurs because Faradaic current is proportional to the concentration gradient of the oxidised species at the working electrode surface. Larger concentration gradients are produced at fast scan rates as there is reduced time for the bulk solution to diffuse into the layer of product that forms locally at the surface of the working electrode.

8.3

Why do current signals decay after the peak currents (i_p) are reached, even though oxidising or reducing potentials are still being applied to the working electrode? Why is this more pronounced at faster scan rates?

With time, the analyte at the electrode surface is consumed and the concentration gradients at the electrode surface decrease, causing a decrease in Faradaic current if fresh analyte does not have sufficient time to diffuse through the product produced to the electrode surface.

8.4

What do you predict will occur if a working electrodes with a smaller surface area is used to perform cyclic voltammetry? What would be the advantages and disadvantages of using the smaller electrode?

At equivalent potential scan rates, the peak current will be reduced because less analyte can transfer electrons with the electrode surface. In addition the peak currents will not decay as much because the volume of the diffusion layer is not as great and bulk analyte diffuses to the electrode surface faster.

The advantage of using a smaller electrode is that flatter more stable peak currents are obtained at faster scan rates. The disadvantage is that noise may become a problem when small currents are being measured.

9. Instructors Notes

9.1 Computer System and Software Required

A PC (running Windows 98 or later) or Mac (running OS 9 or later) computer with USB support is required per group. EChem must be installed for this experiment.

9.2 Reagents

Use a sonicating bath to help prepare the ferrocene carboxylic acid solution, as the ferrocene derivative is only sparingly soluble in water. For the citrate buffer, prepare a combined 0.1 M Sodium Citrate and 0.5 M NaCl solution with pH adjusted to 7 with HCL.

9.3 Microelectrodes extension

If an EA162 Picostat and some microelectrodes are available, this experiment can be extended to investigate cyclic voltammetry with microelectrodes. The file microelectrodes.efwdat that is included in this experiment's resources folder, shows some examples of cyclic voltammograms obtained using Pt microelectrodes with diameters ranging between 1 and 100 µm.

As the currents obtained using these electrodes are in the pA range, noise can severely interfere with the signals obtained, hence the experiments are best performed inside a faraday cage.

10. Bibliography

P.W. Atkins, *Chapter 29 – Dynamic Electrochemistry*, in Physical Chemistry – 5th ed., Oxford University Press 1994.

H.A.O. Hill & G.S. Sanghera, *Mediated amperometric enzyme electrodes,* in Biosensors A Practical Approach (A.E.G. Cass), Oxford University Press 1990.