Experiment 18 Cyclic Voltammetry

Cyclic voltammetry (CV) has become increasingly popular in all fields of chemistry as a means of studying redox states. The electrode potential at which a drug, a metal ion or complex, or some other compound undergoes reduction or oxidation can be rapidly located by CV. Furthermore, information regarding the stability of the product of the electrode reaction is revealed by the cyclic voltammogram. Such information can be useful in subsequent experiments involving liquid chromatography/electrochemistry (LCEC), anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), electrosynthesis, corrosion, and coulometry.

The effectiveness of CV results from its capability for rapidly observing redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan. A very important aspect of CV is its ability to generate a new redox species during the first potential scan and then probe the species' fate on the second and subsequent scans. CV is therefore a powerful kinetic probe for monitoring reactive species. Since the rate of potential scan is variable, both fast and slow reactions can be followed.

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode is controlled relative to a **reference electrode such as a saturated calomel electrode (SCE) or a silver-silver chloride electrode (Ag/AgCl)**. The controlling potential can be considered an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform, as shown in Fig.1. This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the switching potentials.

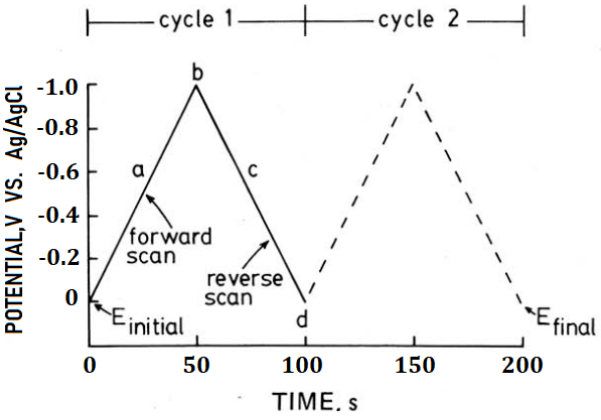


Fig.1 Typical excitation signal for CV triangular potential wave-form with switching potentials at 0 and -1.0 V vs Ag/AgCl

The excitation signal in Fig.1 causes the potential to first scan negatively from 0.00 to -1.00 V vs Ag/AgCl, at which point the scan

direction is reversed, causing a positive scan back to the original potential of 0.00 V. The scan rate, reflected by the slope, is 20 mV/sec. A second cycle is indicated by the dashed line. Single or multiple cycles can be used. Modern instrumentation enables switching potentials and scan rates to be easily varied.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis), as shown in Fig. 2. Because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This is helpful in understanding the fundamentals of the technique. The reducing or oxidizing strength of the electrode is precisely controlled by the applied potential. As shown in Fig. 2, scanning the potential in the negative direction makes the electrode a stronger reductant, whereas scanning the potential in the positive direction makes it a better oxidant.

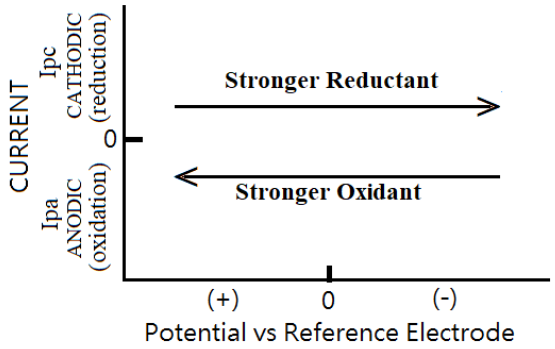
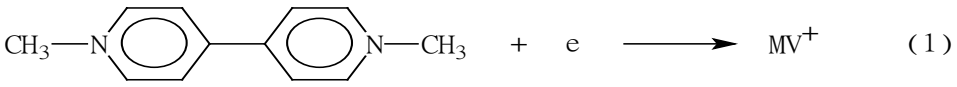


Fig. 2 Potential-current axes for CV

A typical cyclic voltammogram is shown in Fig. 3 for a tin oxide film working electrode in a solution containing 0.5 mM methyl viologen di-cation (MV^{2+}) as the electroactive species in aqueous 0.1M phosphate buffer pH 7.0 as the supporting electrolyte. (Methyl viologen, also known as paraquat, is an effective defoliant of plants.)

The excitation signal used to obtain this voltammogram is that shown in Fig. l, but with a negative switching potential of -0.92 V. Thus, the vertical axis in Fig. l is now the horizontal axis for Fig. 3. The initial potential (Ei) of 0.00 V applied at *a* is chosen to avoid any electrolysis of $MV^{2+}$when the electrode is switched on. The potential is then scanned negatively ("forward scan"), as indicated by the arrow. When the potential is sufficiently negative to reduce MV^{2+} , cathodic current is indicated at *b* due to the electrode process:



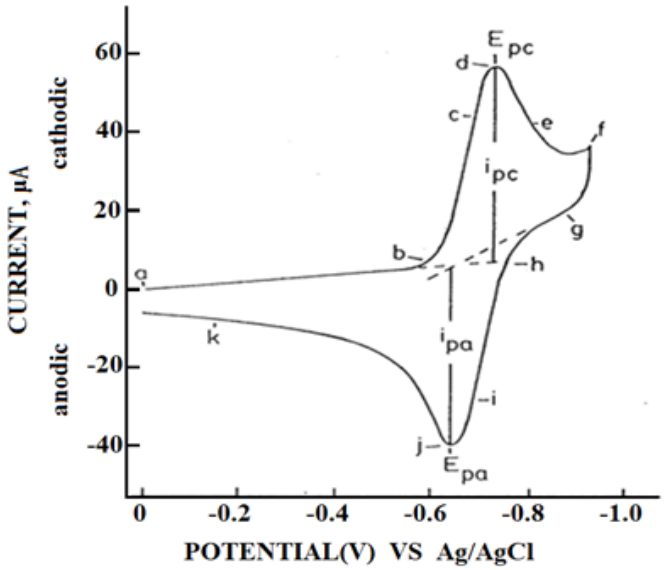


Fig. 3 Cyclic voltammogram of 0.5mM methyl viologen in 0.1 M phosphate buffer,pH7.0. Scan initiated at 0.0 V vs Ag/AgCl in negative direction at 20mV/sec. Tin oxide electrode: area=0.6 cm^2

The electrode is now a sufficiently strong reductant to reduce MV^{2+} to the radical cation. The cathodic current increases rapidly (*b-d*) until the concentration of MV^{2+} at the electrode surface approaches zero, causing the current to peak (*d*). The current then decays at a $t^{-1/2}$ rate as the solution surrounding the electrode is depleted of MV^{2+} due to its electrolytic conversion to MV^{+}. The scan direction is switched to positive at -0.92 V (*f*) for the reverse scan. The potential is still sufficiently negative to reduce MV^{2+} , and so cathodic current continues even though the potential is now scanning in the positive direction. When the electrode becomes a sufficiently strong oxidant, MV^{+}, which has been accumulating adjacent to the electrode, can now be oxidized by the electrode process:

$$MV^{+} \rightarrow MV^{2+} + e^{-} \qquad (2)$$

This causes anodic current (*i-k*). The anodic current rapidly increases until the surface concentration of MV^{+} approaches zero, at which point the current peaks (*j*). The current then decays (*j,k*) as the solution surrounding the electrode is depleted of MV^{+}. The first cycle is completed when the potential reaches 0.00 V. Now that the cyclic voltammogram is obtained, it is apparent that any potential positive of about -0.5 V would be suitable as an initial potential in that reduction of MV^{2+} would not occur when the potential is applied. This procedure avoids inadvertent electrolysis as a result of applying the wrong initial potential.

Simply stated, in the forward scan MV^+ is electrochemically generated from MV^{2+} as indicated by the cathodic current. In the reverse scan this MV^+ is oxidized back to MV^{2+} as indicated by the anodic current. Thus, CV is capable of rapidly generating a new oxidation state during the forward scan and then probing its fate on the reverse scan.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}), and the cathodic peak potential (E_{pc}). These parameters are labeled in Fig. 3. One method for measuring i_p involves extrapolation of a baseline current, as shown in the figure. The establishment of a correct baseline is essential for the accurate measurement of peak currents. This is not always easy, particularly for more complicated systems.

A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal reduction potential ($E^{0\prime}$) for a reversible couple is centered between E_{pa} and E_{pc} :

$$E^{0\prime}=(E_{pa}+E_{pc})/2 \qquad (3)$$

The number of electrons transferred in the electrode reaction (n) for a **reversible couple** can be determined from the separation between the peak potentials:

$$\Delta E_p=E_{pa}-E_{pc}=0.059/n \qquad (4)$$

Thus, a one-electron process such as the reduction of MV^{2+} to MV^+ should ideally exhibit a ΔE_p of 0.059 V.

The peak current for a **reversible system** is described by the Randles-Sevcik equation for the forward sweep of the first cycle:

$$i_p=269n^{3/2}AD^{1/2}C\nu^{1/2} \qquad (5)$$

where i_p is the peak current (amperes), n is the electron stoichiometry, A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/sec), C is the concentration (mol/L), andvis the scan rate (V/sec) Accordingly, i_p increases with $\nu^{1/2}$ and is directly proportional to concentration. The relationship to concentration is particularly important in analytical

applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} should be identical for a simple reversible (fast) couple. However, the ratio of peak currents can be significantly influenced by chemical reactions coupled to the electrode process.

Electrochemical irreversibility is caused by slow electron change of the redox species with the working electrode. In this case, Eqs. (3), (4), and (5) are not strictly applicable. Electrochemical irreversibility is characterized by a separation of peak potentials greater than indicated by Eq. (4). This is a very common situation.

Interpreting complex cyclic voltammograms is often a challenge best met by the combination of chemical intuition with the study of model compounds, exactly in the same manner used by many spectroscopists to interpret optical, magnetic resonance, or mass spectra.

Apparatus:

Potentiostat
Corning magnetic stirrer
Pt working electrode
Ag/AgCl reference electrode
Pt auxiliary electrode

Procedure

1. Polish the surface of the Pt electrode with 0.05μm alumina powder on a polishing pad. Rinse the electrode with distilled deion water thoroughly.
2. Prepare 1 M KCl solution in a 25 ml volumetric flask. (助教已製備)
3. Assemble the electrolytic cell and fill the cell with 10 ml 1M KCl solution. Be sure the ends of the three electrodes are immersed in the solution. The system is deoxygenated by purging with N_2(g) for 10 minutes.
4. While the system is being deoxygenated, set the following scan parameters on the potentiostat :

   Initial potential: +0.7 V
   Final potential: -0.1 V
5. When deoxygenation is complete, the working electrode is switched on.
6. After obtaining the first cyclic voltammogram, add 10.0 μl of 0.4 M $Fe(CN)_6^{3-}$ solution into the electrolytic cell using a micropipette. Turn on the stirrer for 1minute, then turn

it off. Start another CV scan.

7. Use a solution of 0.4 mM $Fe(CN)_6^{3-}$ in 1 M KCl to investigate the effect of the scan rate on the voltammograms. CVs are performed at the following scan rate: 20, 50, 100, 200 mV/s. Be sure that same initial conditions of solution and electrode are met before each scan. Record i_p and E_p under different scan rates; examine their relationship with scan rate.
8. Repeat the procedure in step (6) three more times at a fixed scan rate of **100 mV/s**.
9. Measure the magnitude of i_{pc} and i_{pa}, and E_{pc} and E_{pa} in each voltammogram. Examine the relationship between i_p and [$Fe(CN)_6^{3-}$]. Check the reversibility of electrochemical reaction of $Fe(CN)_6^{3-}$.

Reference

1. W. R. Heineman and P. T. Kissinger, Current Separation, 1989, 9 (1/2), 15
2. J. J. Van Benschoten, J. Y. Lewis, W, R. Heineman, D, A. Roston and P. T. Kissinger, J. Chem. Edu., 1983, 60 (9), 772.

儀器設定:

Working electrode :

Reference electrode :

counter (auxiliary) electrode :

結果:

(1) 在循環伏安圖(CV 圖)上**標明濃度**並畫上基準線(baseline)，同時將還原峰電流(i_{pc})、氧化峰電流(i_{pa})、還原峰電位（E_{pc}）與氧化峰電位（E_{pa}）標示清楚。並由CV圖中，量測以下實驗參數，包括： E_{pa}、E_{pc}、i_{pa}、i_{pc}。

(a) 固定濃度 (0.4 mM)，改變掃描速率

scan rate (mv/sec)	log(scan rate)	i_{pc} (μA)	i_{pa} (μA)	log(ipc)	log(ipa)	E_{pc} (v)	E_{pa} (v)	ΔE (v)
20								
50								
100								
200								

(b) 固定掃描速率(　　mv/sec)，改變濃度

concentration (mM)	i_{pc} (μA)	i_{pc} (μA)	E_{pc} (v)	E_{pa} (v)

(2)求*ipa*和scan rate的關係以及*ipc*和scan rate的關係？

$\because$ $i_p = \underline{269n^{3/2}AD^{1/2}C}\nu^{1/2}$

↓

常數(k)

$\therefore i_p = k\nu^{1/2}$

$\log (i_p) = \log (k\nu^{1/2})$

$\log (i_p) = \log k + 1/2 \log(\nu)$

i_p : peak current (A)
n : electron stoichiometry
A : electrode area (cm^2)
D: diffusion coefficient
C : concentration (mol/L)
ν: scan rate (V/sec)

$\therefore$ A plot of log (i_p) *versus* log (ν) will yield a straight line with the *slope of* 1/2

理論值是 1/2；你的實驗值是多少呢！(最後結論請寫成**$i_p \propto \nu^{***}$**)

(3)求E_{pa}和scan rate的關係以及E_{pc}和scan rate的關係？

(4)求i_{pa}和$[Fe(CN)_6^{3-}]$的關係以及i_{pc}和$[Fe(CN)_6^{3-}]$的關係？

(5) Check the reversibility of electrochemical reaction of $Fe(CN)_6^{3-}$.