Analysis of Cyclic Voltammetric Traces- Part 1

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Let us start with what does one means by a cyclic voltammetric trace. It is a simple graphical representation of current-voltage variation when the potential of an electrochemical system is varied in a cyclic manner. This implies that one will be able to obtain in the trace the anodic and cathodic components of current in an electro-chemical reaction. A typical cyclic voltammogram is shown in Fig.1.

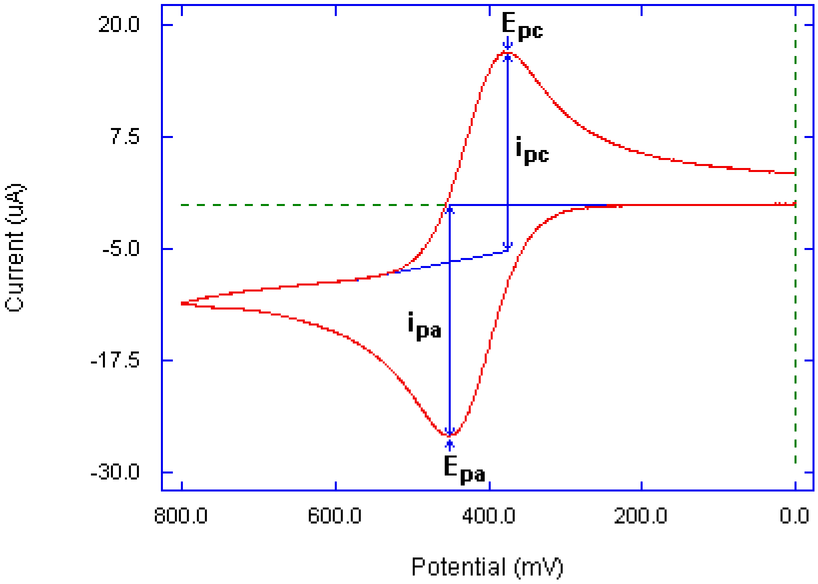

Fig 1 Typical cyclic voltammogram – Points to note are the base lines for both cathodic (i_{pc}) and anodic(i_{pa}) current measurements the corresponding peak potentials (E_{pc} and E_{pa} and and the difference between the two peak potentials (ΔE). All are marked clearly for easy comprehension.

In a redox system remains in equilibrium throughout the potential scan, then the redox process is said to be reversible (example any redox system involving M/M^+ like ferric/ferrous). The criterion of reversibility is easily discernible by the computation of the surface concentration of oxidized and redox forms and they should be maintained at the value required by the famous Nernst

Equation. In addition the following parameters are used to characterize the reversible nature of the cyclic voltammetric trace. They are in the order

1. The separation between the two peak potentials (ΔE) [$=E_{pc} - E_{pc}$] = 58/n mV at 298 K for all scan rates.
2. The ratio of the peak currents = [i_{pa}/i_{pc}] = 1 at all scan rates.
3. The peak current function defined as $i_p/\nu^{1/2}$ [ν is the scan rate] is independent of the scan rate. This situation arises because of the equation connection peak current and scan rate which is given by

   $I_p = 2.69 \text{ X } 10^5 n^{3/2} ACD^{1/2}\nu^{1/2}$

   Where n is the numberof electrons transferred/molecule

   A is the area of the electrode in cm^2

   C is theconcentraion (mol cm^{-3}

   D is the diffusion coefficient in cm^2s^{-1}.

   For a reversible process E^o is given as the mean of the peak potentials.

   The variation of the parameters as shown above indicates departure from reversible behavior.

   Let us consider two important irreversible behavior in electrochemical sense.

   1. Slow electron Transfer Kinetics

      Reversibility automatically implies that the electron transfer kinetics are fast enough to maintain the surface concentration of O and R species at the values required by the Nernst equation. Therefore reversibility depends on the relative values of the standard heterogeneous electron transfer rate constants (k_s) and the rate of change ofpotential – the scan rate ν. If the ratio of (k_s/ν) is sufficiently small that concentrations demanded by Nernst equation cannot be maintained, then the process is called quasi-reversible. Note the terminology of quasi reversible. This process is characterized by $\Delta E > (58/n)$ mV the value increasing with increasing ν. Note for reversible process it has different dependence on ν.

      It is therefore possible a quasi-reversible process to become reversible process if sufficient time is allowed for the surface to

adjust the concentrations to the required value by the Nernst equation by the changing potential.

Another criterion is that ΔE_p depends on the value of (k_s/ν) and k_s can be calculated from the variation of $\Delta E_p$with ν.

However, increase in ΔE_p with increasing ν can also be due to uncompensated solution resistance R. The effect of solution resistance can be minimized by careful experimental design or by feedback compensation or post data manipulation. The two effects can be differentiated by varying the analyte concentration (the potential drop due to uncompensated solution resistance and hence the resulting ΔE_pincreases with increasing current, where ask_s is independent of analyte concentration.

2. **Chemical reactions of O and R**

Equilibrium concentrations of O and R can be maintained only if these two species are stable on the experimental time scale. For example if the reduction of O to R is followed by the conversion of R to products then more R must be generated to compensate for the loss of R. Therefore the rate of reduction increases and E_{pc} moves to more positive value. In addition (i_{pa}/i_{pc}) is less than unity (since only a fraction of the molecules that were reduced on the forward scan are available for reoxidation on the reverse scan). The value of the current function can also be affected by chemical reactions following electron transfer.

The effect of a chemical reaction depends on the value of the ratio (k/ν) (where k is the rateofthe chemical reaction). If this value is large, then the chemical reaction has a significant effect while any effect is less if this ratio is small. Therefore it may be possible to eliminate the effect of the chemical reaction(thereby restoring reversibility) by increasing ν. The value of "k" can be calculated either by simulation studies or by investigating the effect of ν on (I_{pa}/i_{pc}).

In spite of the positive (so called advantages in employing CV) there are a few disadvantages in employing this technique.

They are:

1. **The effects of slow heterogeneous electron transfer and chemical reactions cannot be separated. If both of these effects are present, then the rate constants for these processes can only be calculated using simulation methods.**
2. **There is a background charging current throughout the experiment of magnitude νC_{dl}(whereC_{dl} is the capacitance of the interface at the working electrode). This restricts the detection limit to about 10^{-5}M. In addition the ratio of peak Faradaic current to the charging current decreases with increasing ν (since i_p is proportional to $\nu^{1/2}$) and this places an upper limit on the value of ν that can be used.**

   However CV is a suited technique for the study of a variety of applications. In fact it is emerging as one of the standard techniques in Elecctrochemistry.