

# Cyclic Voltammetry

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January 22, 2008

Literature:

1. Allen J. Bard, Larry R. Faulkner "Electrochemical Methods: Fundamentals and Applications"
  2. <http://www.cheng.cam.ac.uk/research/groups/electrochem/teaching.html>
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# Chapter 1

## Cyclic Voltammetry

### 1.1 Background

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. It offers a rapid location of *redox potentials* of the electroactive species.

A few concepts have to be introduced before talking about this method.

#### 1.1.1 Electronegativity

Electronegativity is the affinity for electrons. The atoms of the various elements differ in their affinity for electrons. The term was first proposed by Linus Pauling in 1932 as a development of valence bond theory. The table for all elements can be looked up on Wikipedia: <http://en.wikipedia.org/wiki/Electronegativity>.

Some facts to remember:

- Fluorine (F) is the most electronegative element.  $\chi_F = 3.98$ .
- The electronegativity of oxygen (O)  $\chi_O = 3.44$  is exploited by life, via shuttling of electrons between carbon (C,  $\chi_C = 2.55$ ) and oxygen (O): Moving electrons against the gradient (O to C) - as occurs in photosynthesis - requires energy (and stores it). Moving electrons down the gradient (C to O) - as occurs in cellular respiration - releases energy.
- The relative electronegativity of two interacting atoms plays a major part in determining what kind of chemical bond forms between them.

Examples:

- Sodium ( $\chi_{Na} = 0.93$ ) and Chlorine ( $\chi_{Cl} = 3.16$ ) = Ionic Bond: There is a large difference in electronegativity, so the chlorine atom takes an electron from the sodium atom converting the atoms into ions ( $Na^+$ ) and ( $Cl^-$ ). These are held together by their opposite electrical charge forming ionic bonds. Each sodium ion is held by 6 chloride ions while each chloride ion is, in turn, held by 6 sodium ions. Result: a crystal lattice (not molecules) of common table salt ( $NaCl$ ).
- Carbon (C) and Oxygen (O) = Covalent Bond. There is only a small difference in electronegativity, so the two atoms share the electrons. A covalent bond (depicted as C:H or C-H) is formed, where atoms are held together by the mutual affinity for their shared electrons. An array of atoms held together by covalent bonds forms a true molecule.
- Hydrogen (H) and Oxygen (O) = Polar Covalent Bond. Moderate difference in electronegativity, oxygen atom pulls the electron of the hydrogen atom closer to itself. Result: a polar covalent bond. Oxygen does this with 2 hydrogen atoms to form a molecule of water.

Molecules, like water, with polar covalent bonds are themselves polar; that is, have partial electrical charges across the molecule; may be attracted to each other (as occurs with water molecules); are good solvents for polar and/or hydrophilic compounds. May form hydrogen bonds.

## 1.2 Electrode Reactions

A typical electrode reaction involves the transfer of charge between an electrode and a species in solution. The electrode reaction usually referred to as electrolysis, typically involves a series of steps:

1. Reactant (O) moves to the interface: this is termed mass transport
2. Electron transfer can then occur via quantum mechanical tunnelling between the electrode and reactant close to the electrode (typical tunnelling distances are less than 2 nm)
3. The product (R) moves away from the electrode to allow fresh reactant to the surface

The 'simplest' example of an electrode reaction is a single electron transfer reaction, e.g.  $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$ . Several examples are shown in Fig. 1.1

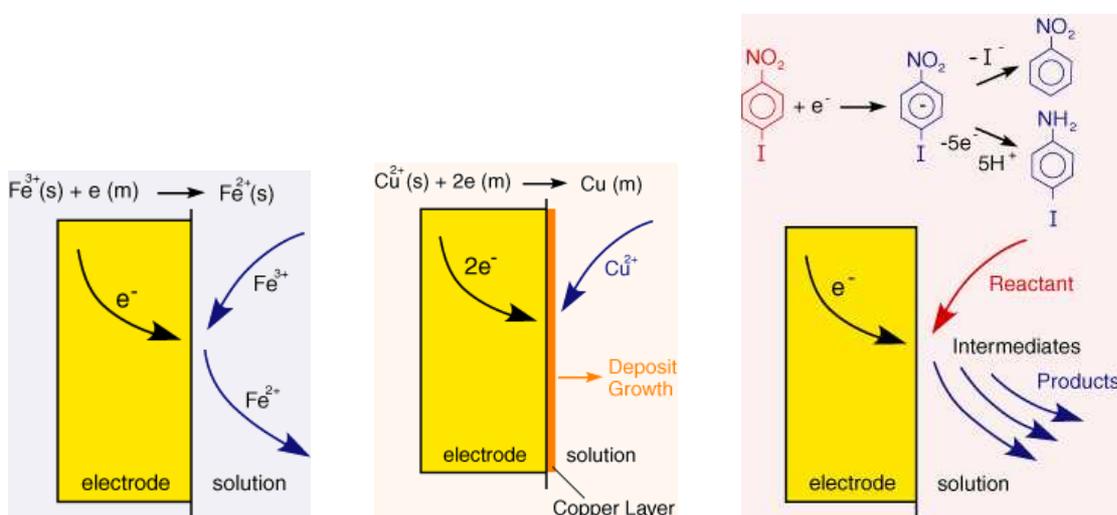


Figure 1.1: Simple electrode reactions: (left) A single electron transfer reaction. Here the reactant  $\text{Fe}^{3+}$  moves to the interface where it undergoes a one electron reduction to form  $\text{Fe}^{2+}$ . The electron is supplied via the electrode which is part of a more elaborate electrical circuit. For every  $\text{Fe}^{3+}$  reduced a single electron must flow. By keeping track of the number of electrons flowing (ie the current) it is possible to say exactly how many  $\text{Fe}^{3+}$  molecules have been reduced. (middle) Copper deposition at a Cu electrode. In this case the electrode reaction results in the formation of a thin film on the original surface. It is possible to build up multiple layers of thin metal films simply by passing current through appropriate reactant solutions. (right) Electron transfer followed by chemical reaction. In this case an organic molecule is reduced at the electrode forming the radical anion. This species however is unstable and undergoes further electrode and chemical reactions.

## 1.3 Electron Transfer and Energy levels

The key to driving an electrode reaction is the application of a voltage. If we consider the units of volts

$$V = \text{Joule/Coulomb} \quad (1.1)$$

we can see that a volt is simply the energy required to move charge. Application of a voltage to an electrode therefore supplies electrical energy. Since electrons possess charge an applied voltage can alter the 'energy' of the electrons within a metal electrode. The behaviour of electrons in a metal can be partly understood by considering the Fermi-level. Metals are comprised of closely packed atoms which have strong overlap between one another. A piece of metal therefore does not possess individual well defined electron energy levels that would be found in a single atom of the same material. Instead a continuum of levels are created with the available electrons filling the states from the bottom upwards. The Fermi-level corresponds to the energy at which the 'top' electrons sit.

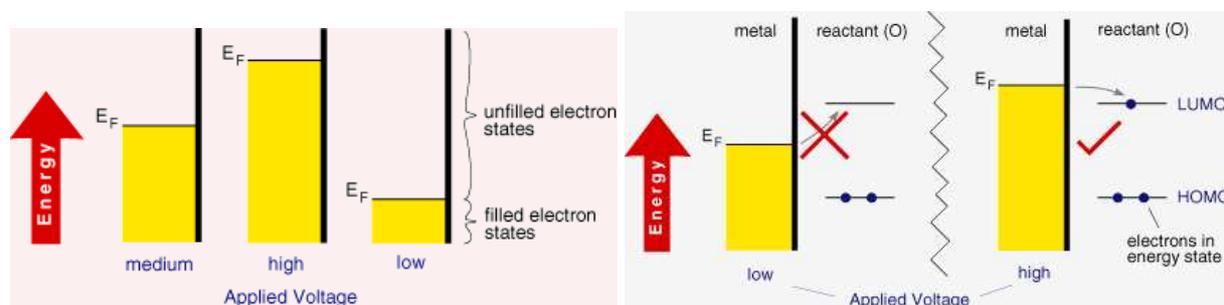


Figure 1.2: Representation of the Fermi-Level in a metal at three different applied voltages (left). Schematic representation of the reduction of a species (O) in solution (right).

This level is not fixed and can be moved by supplying electrical energy. Electrochemists are therefore able to alter the energy of the Fermi-level by applying a voltage to an electrode.

Figure 1.2 shows the Fermi-level within a metal along with the orbital energies (HOMO and LUMO) of a molecule (O) in solution. On the left hand side the Fermi-level has a lower value than the LUMO of (O). It is therefore thermodynamically unfavourable for an electron to jump from the electrode to the molecule. However on the right hand side, the Fermi-level is above the LUMO of (O), now it is thermodynamically favourable for the electron transfer to occur, ie the reduction of O.

Whether the process occurs depends upon the rate (kinetics) of the electron transfer reaction and the next document describes a model which explains this behavior.

## 1.4 Kinetics of Electron Transfer

In this section we will develop a quantitative model for the influence of the electrode voltage on the rate of electron transfer. For simplicity we will consider a single electron transfer reaction between two species (O) and (R)



The current flowing in either the reductive or oxidative steps can be predicted using the following expressions

$$i_O = F A k_{\text{ox}} c_R \quad (1.4)$$

$$i_R = -F A k_{\text{red}} c_O \quad (1.5)$$

For the reduction reaction the current  $i_R$  is related to the electrode area  $A$ , the surface concentration of the reactant  $c_O$ , the rate constant for the electron transfer  $k_{\text{red}}$  and Faraday's constant  $F$ . A similar expression is valid for the oxidation, now the current is labelled  $i_O$ , with the surface concentration that of the species  $R$ . Similarly the rate constant for electron transfer corresponds to that of the oxidation process. Note that by definition the reductive current is negative and the oxidative positive, the difference in sign simply tells us that current flows in opposite directions across the interface depending upon whether we are studying an oxidation or reduction. To establish how the rate constants  $k_{\text{ox}}$  and  $k_{\text{red}}$  are influenced by the applied voltage we will use transition state theory.

In this theory the reaction is considered to proceed via an energy barrier, as shown in Fig 1.3. The summit of this barrier is referred to as the transition state. Using this picture the corresponding reaction rates are given by

$$k_{\text{red,ox}} = Z \exp\left(\frac{-\Delta G_{\text{red,ox}}}{k_B T}\right) \quad (1.6)$$

If we plot a series of the free energy profiles as a function of voltage the free energy of R will be invariant with voltage, whereas the right handside (O + e) shows a strong dependence.

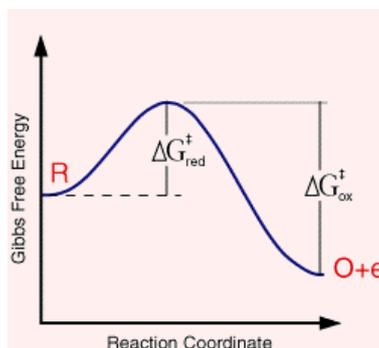


Figure 1.3: Transition occurs via a barrier  $\Delta G$ .

This can be explained in terms of the Fermi level diagrams noted earlier: as the voltage is altered the Fermi level is raised (or lowered) changing the energy state of the electrons.

However it is not just the thermodynamic aspects of the reaction that can be influenced by this voltage change as the overall barrier height (ie activation energy) can also be seen to alter as a function of the applied voltage. We might therefore predict that the rate constants for the forward and reverse reactions will be altered by the applied voltage. In order to formulate a model we will assume that the effect of voltage on the free energy change will follow a linear relationship (this is undoubtedly an over simplification). Using this linear relationship the activation free energies for reduction and oxidation will vary as a function of the applied voltage as follows (Buttler-Volmer model)

$$\Delta G_{\text{red}} = \Delta G_{\text{red}}(V = 0) + \alpha FV \quad (1.7)$$

$$\Delta G_{\text{ox}} = \Delta G_{\text{ox}}(V = 0) - (1 - \alpha)FV \quad (1.8)$$

The parameter  $\alpha$  is called the transfer coefficient and typically is found to have a value of 0.5. Physically it provides an insight into the way the transition state is influenced by the voltage. A value of one half means that the transition state behaves mid way between the reactants and products response to applied voltage. The free energy on the right hand side of both of the above equations can be considered as the chemical component of the activation free energy change, ie it is only dependent upon the chemical species and not the applied voltage. We can now substitute the activation free energy terms above into the expressions for the oxidation and reduction rate constants, which gives

$$k_{\text{red}} = Z \exp \frac{-\Delta G_{\text{red}}^{V=0}}{k_B T} \exp \frac{-\alpha FV}{k_B T} \quad (1.9)$$

$$k_{\text{ox}} = Z \exp \frac{-\Delta G_{\text{ox}}^{V=0}}{k_B T} \exp \frac{(1 - \alpha)FV}{k_B T} \quad (1.10)$$

These results show us that the rate constants for the electron transfer steps are proportional to the exponential of the applied voltage. So the rate of electrolysis can be changed simply by varying the applied voltage. This result provides the fundamental basis of the experimental technique called voltammetry which we will look at more closely later.

In conclusion we have seen that the rate of electron transfer can be influenced by the applied voltage and it is found experimentally that this behaviour can be quantified well using the simple model presented above. However the kinetics of the electron transfer is not the only process which can control the electrolysis reaction. In many circumstances it is the rate of transport to the electrode which controls the overall reaction.

## 1.5 Mass transport

In the electrode kinetics section we have seen that the rate of reaction can be influenced by the cell potential difference. However, the rate of transport to the surface can also effect or even dominate the overall reaction rate and in this section we look at the different forms of mass transport that can influence electrolysis reactions.

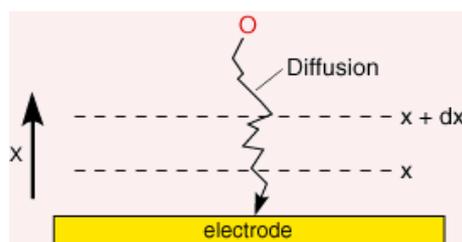


Figure 1.4: Diffusion of the reactants to the electrode

We have already seen that a typical electrolysis reaction involves the transfer of charge between an electrode and a species in solution. This whole process due to the interfacial nature of the electron transfer reactions typically involves a series of steps.

In the section on electrode kinetics we saw how the electrode voltage can effect the rate of the electron transfer. This is an exponential relationship, so we would predict from the electron transfer model that as the voltage is increased the reaction rate and therefore the current will increase exponentially. This would mean that it is possible to pass unlimited quantities of current. Of course in reality this does not arise and this can be rationalized by considering the expression for the current that we encountered in the electrode kinetics section

Clearly for a fixed electrode area ( $A$ ) the reaction can be controlled by two factors. First the rate constant  $k_{\text{red}}$  and second the surface concentration of the reactant ( $C_O^{\text{surf}}$ ). If the rate constant is large, such that any reactant close to the interface is immediately converted into products then the current will be controlled by the amount of fresh reactant reaching the interface from the bulk solution above. Thus movement of reactant in and out of the interface is important in predicting the current flowing. In this section we look at the various ways in which material can move within solution - so called mass transport.

There are three forms of mass transport which can influence an electrolysis reaction

- Diffusion
- Convection
- Migration

In order to predict the current flowing at any particular time in an electrolysis measurement we will need to have a quantitative model for each of these processes to complement the model for the electron transfer step(s).

Diffusion occurs in all solutions and arises from local uneven concentrations of reagents. Entropic forces act to smooth out these uneven distributions of concentration and are therefore the main driving force for this process. One example of this can be seen in the animation below. Two materials are held separately in a single container separated by a barrier. When the barrier is removed the two reagents can mix and this processes on the microscopic scale is essentially random. For a large enough sample statistics can be used to predict how far material will move in a certain time - and this is often referred to as a random walk model. Diffusion is particularly significant in an electrolysis experiment since the conversion reaction only occurs at the electrode surface. Consequently there will be a lower reactant concentration at the electrode than in bulk solution. Similarly a higher concentration of product will exist near the electrode than further out into solution.

The rate of movement of material by diffusion can be predicted mathematically and Fick proposed two laws to quantify the processes. The first law

$$J_O = -D_O \frac{\partial c_O}{\partial x} \quad (1.11)$$

relates the diffusional flux  $J_O$  (ie the rate of movement of material by diffusion) to the concentration gradient and the diffusion coefficient  $D_O$ . The negative sign simply signifies that material moves down a concentration gradient i. e. from regions of high to low concentration. However, in many measurements we need to know how the concentration of material varies as a function of time and this can be predicted from the first law. The result is Fick's second law

$$\frac{\partial c_O}{\partial t} = -\frac{\partial J_O}{\partial x} \quad (1.12)$$

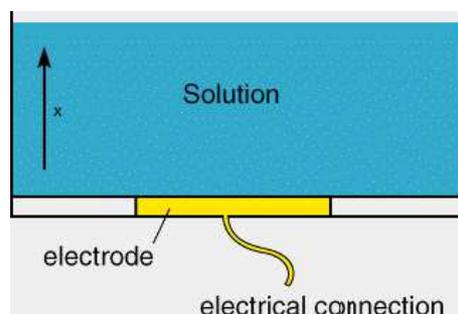


Figure 1.5: Schematic of the setup.

In this case we consider diffusion normal to an electrode surface ( $x$  direction). The rate of change of the concentration  $c_O$  as a function of time  $t$  can be seen to be related to the change in the concentration gradient. So the steeper the change in concentration the greater the rate of diffusion. In practice diffusion is often found to be the most significant transport process for many electrolysis reactions.

Fick's second law is an important relationship since it permits the prediction of the variation of concentration of different species as a function of time within the electrochemical cell. In order to solve these expressions analytical or computational models are usually employed.

## 1.6 Voltammetry

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry

- Potential Step
- Linear sweep
- Cyclic Voltammetry

For each of these cases a voltage or series of voltages are applied to the electrode and the corresponding current that flows monitored. In this section we will examine potential step voltammetry, the other forms are described on separate pages

For the moment we will focus on voltammetry in stagnant solution. The figure below shows a schematic of an electrolysis cell. There is a working electrode which is hooked up to an external electrical circuit. For our purposes at the moment we will not worry about the remainder of the circuit, obviously there must be more than one electrode for current to flow. But as we shall see later it is only the so called working electrode that controls the flow of current flow in the electrochemical measurement. The essential elements needed for an electrolysis measurement are as follows:

- The electrode: This is usually made of an inert metal (such as Gold or Platinum)
- The solvent: This usually has a high dielectric constant (eg water or acetonitrile) to enable the electrolyte to dissolve and help aid the passage of current.
- A background electrolyte: This is an electrochemically inert salt (eg NaCl or Tetra butylammonium perchlorate, TBAP) and is usually added in high concentration (0.1 M) to allow the current to pass.
- The reactant: Typically in low concentration  $10^{-3}$  M.

### 1.6.1 Potential Step Voltammetry

In the potential step measurement the applied voltage is instantaneously jumped from one value  $V_1$  to another  $V_2$  The resulting current is then measured as a function time. If we consider the reaction



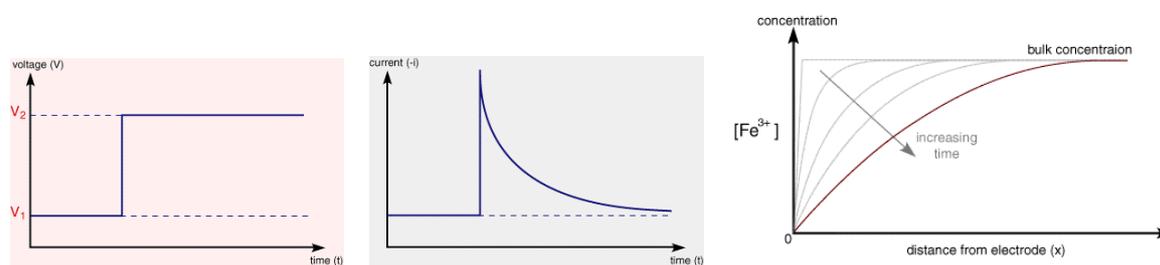


Figure 1.6: Potential step voltammetry: voltage vs time, current versus voltage, and concentration versus distance from the electrode plotted for several times.

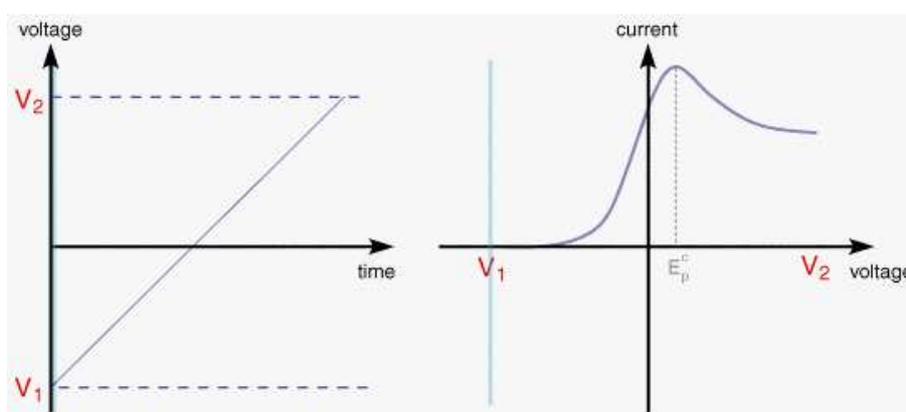


Figure 1.7: Linear increase of the potential vs time.

Usually the voltage range is set such that at  $V_1$  the reduction of  $(\text{Fe}^{3+})$  is thermodynamically unfavorable. The second value of voltage ( $V_2$ ) is selected so that any  $\text{Fe}^{3+}$  close to the electrode surface is converted to product ( $\text{Fe}^{2+}$ ). Under these conditions the current response is in Fig. 1.6.1

The current rises instantaneously after the change in voltage and then begins to drop as a function of time. This occurs since the instant before the voltage step the surface of the electrode is completely covered in the reactant and the solution has a constant composition below

Once the step occurs reactant ( $\text{Fe}^{3+}$  is converted to product  $\text{Fe}^{2+}$  and a large current begins to flow. However now for the reaction to continue we need a supply of fresh reactant to approach the electrode surface. This happens in stagnant solution via diffusion. As we noted in a previous section the rate of diffusion is controlled by the concentration gradient. So the supply of fresh  $\text{Fe}^{3+}$  to the surface (and therefore the current flowing) depends upon the diffusional flux. At short times the diffusional flux of  $\text{Fe}^{3+}$  is high, as the change in concentration between the bulk value and that at the surface occurs over a short distance

As the electrolysis continues material can diffuse further from the electrode and therefore the concentration gradient drops. As the concentration gradient drops (see concentration profiles below) so does the supply of fresh reactant to the surface and therefore the current also decreases.

Solving the mass transport equation in 1D case we obtain

$$i = nFAk_{\text{red}}c_{\text{O}}^{\text{bulk}}\sqrt{\frac{D}{\pi t}} \propto t^{-1/2} \quad (1.14)$$

Here the current is related to the bulk reactant concentration. Step voltammetry allows the estimation of the diffusion coefficients of the species to be obtained.

## 1.7 Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown below. The characteristics of the linear sweep voltammogram depend on a number of factors including:

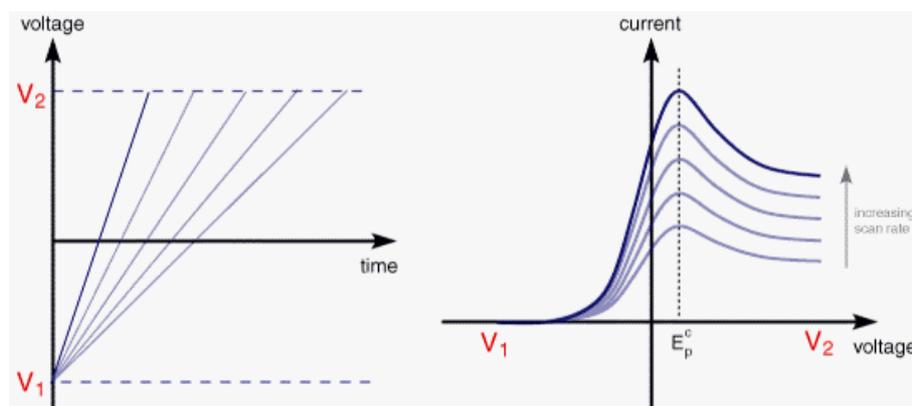


Figure 1.8: Linear increase of the potential vs time.

- The rate of the electron transfer reaction(s)
- The chemical reactivity of the electroactive species
- The voltage scan rate

In LSV measurements the current response is plotted as a function of voltage rather than time, unlike potential step measurements.

The scan begins from the left hand side of the current/voltage plot where no current flows. As the voltage is swept further to the left (to more reductive values) a current begins to flow and eventually reaches a peak before dropping. To rationalise this behaviour we need to consider the influence of voltage on the equilibrium established at the electrode surface. Here the rate of electron transfer is fast in comparison to the voltage sweep rate. Therefore at the electrode surface an equilibrium is established identical to that predicted by thermodynamics. You may recall from equilibrium electrochemistry that the Nernst equation

The exact form of the voltammogram can be rationalised by considering the voltage and mass transport effects. As the voltage is initially swept from  $V_1$  the equilibrium at the surface begins to alter and the current begins to flow. The current rises as the voltage is swept further from its initial value as the equilibrium position is shifted further to the right hand side, thus converting more reactant. The peak occurs, since at some point the diffusion layer has grown sufficiently above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation. In this situation the current begins to drop just as it did in the potential step measurements. In fact the drop in current follows the same behaviour as that predicted by the Cottrell equation.

The above voltammogram was recorded at a single scan rate. If the scan rate is altered the current response also changes. The figure 1.8 shows a series of linear sweep voltammograms recorded at different scan rates. Each curve has the same form but it is apparent that the total current increases with increasing scan rate. This again can be rationalised by considering the size of the diffusion layer and the time taken to record the scan. Clearly the linear sweep voltammogram will take longer to record as the scan rate is decreased. Therefore the size of the diffusion layer above the electrode surface will be different depending upon the voltage scan rate used. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode the magnitude of the current will be lower at slow scan rates and higher at high rates. This highlights an important point when examining LSV (and cyclic voltammograms), although there is no time axis on the graph the voltage scan rate (and therefore the time taken to record the voltammogram) do strongly effect the behaviour seen. A final point to note from the figure is the position of the current maximum, it is clear that the peak occurs at the same voltage and this is a characteristic of electrode reactions which have rapid electron transfer kinetics. These rapid processes are often referred to as reversible electron transfer reactions.

This leaves the question as to what would happen if the electron transfer processes were ‘slow’ (relative to the voltage scan rate). For these cases the reactions are referred to as quasi-reversible or irreversible

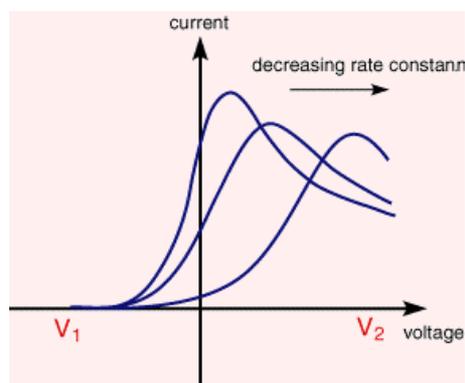


Figure 1.9: Change of the rate constant.

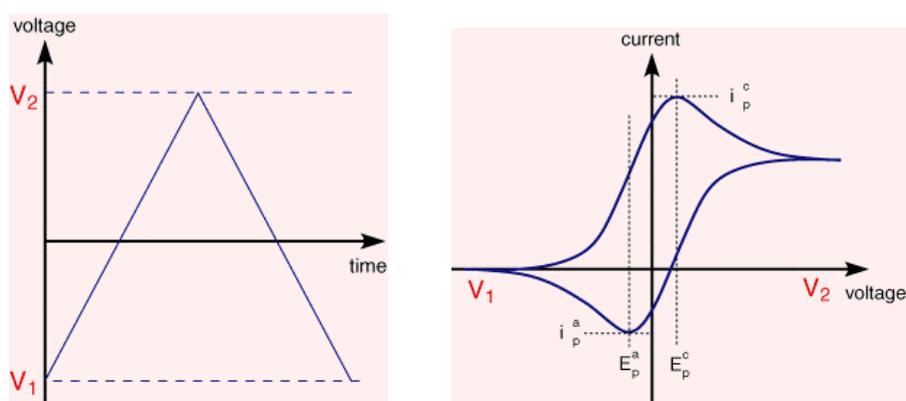


Figure 1.10: Voltage as a function of time and current as a function of voltage for CV

electron transfer reactions. The figure below shows a series of voltammograms recorded at a single voltage sweep rate for different values of the reduction rate constant  $k_{\text{red}}$

In this situation the voltage applied will not result in the generation of the concentrations at the electrode surface predicted by the Nernst equation. This happens because the kinetics of the reaction are 'slow' and thus the equilibria are not established rapidly (in comparison to the voltage scan rate). In this situation the overall form of the voltammogram recorded is similar to that above, but unlike the reversible reaction now the position of the current maximum shifts depending upon the reduction rate constant (and also the voltage scan rate). This occurs because the current takes more time to respond to the the applied voltage than the reversible case.

### 1.7.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is very similar to LSV. In this case the voltage is swept between two values (see below) at a fixed rate, however now when the voltage reaches  $V_2$  the scan is reversed and the voltage is swept back to  $V_1$

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in below. Again the solution contains only a single electrochemical reactant

The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product ( $\text{Fe}^{2+}$  back to reactant ( $\text{Fe}^{3+}$ ). The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward seep but otherwise the behaviour can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

1. The voltage separation between the current peaks is
2. The positions of peak voltage do not alter as a function of voltage scan rate

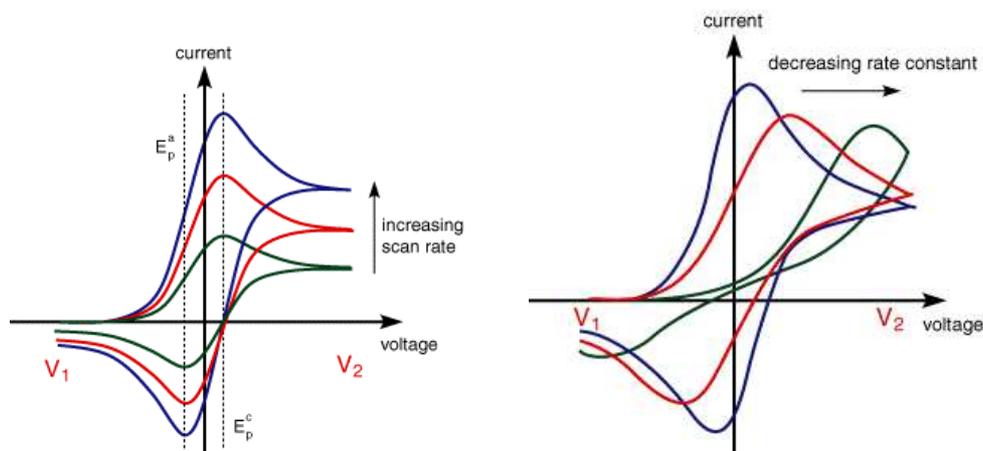


Figure 1.11: Scan rate and rate constant dependence of the I-V curves.

3. The ratio of the peak currents is equal to one
4. The peak currents are proportional to the square root of the scan rate

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen in Fig. 1.11. As with LSV the influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. The CV for cases where the electron transfer is not reversible show considerably different behaviour from their reversible counterparts.

By analysing the variation of peak position as a function of scan rate it is possible to gain an estimate for the electron transfer rate constants.