

Analysis of Electrochemical Reactions Part 2

Electrochemical irreversible reaction- characteristic features

In part 1 of this series, it has been shown how the current versus potential measurement can be used to differentiate an electrochemical process is reversible or quasi reversible. However, it is necessary to carefully what does one mean quasi reversible? Where does it cross over to an irreversible process. These are questions which are relevant for the study of electrochemical process taking place at the electrode surface. It is necessary that these questions are answered adequately for us to understand the nature of electrochemical processes from the current voltage measurements, which is usually the majority of measurements made in electrochemistry.

To understand a irreversible electrochemical process one has to consider the general mechanism of electron transfer at an electrode. Before one proceeds to understand an irreversible process, it is necessary to comprehend the potential current measurement that has to be made in a typical electrochemical cell. Essentially this type of measurement is made using a three electrode system, the electrode where the electron transfer takes place is termed as working electrode (WE). One is considering the concentration of oxidized or reduced species around this noble electrode in the electrolyte, the electrolyte normally contains an inert electrolyte (so called supporting electrolyte) which is employed to reduce or minimize internal IR drop. Along with this WE an reference electrode is also kept immersed to form the electrochemical cell.

The potential of the reference electrode (RE) is constant, variation in cell emf is the variation in the working electrode only. At the thermodynamic equilibrium of the system no net current flows across the reference electrode and working electrode, no chemical reaction takes place and hence the composition of the solution remains unchanged. The potential of the working electrode will be its equilibrium potential E_e , which according to Nernst equation is,

$$E_e = E_e^\circ + (RT/nF) \ln C_O / C_R$$

Where C_O and C_R are the activities of the oxidized and reduced species. E_e° is the standard or formal reversible potential and is a constant. The equilibrium state that is referred is a dynamic state. Though no net current flows across the electrodes, both reduction and oxidation takes place at equal rate so that the composition of the electrolyte does not change. This dynamic flow of electrons or charges in both directions can be shown in terms of current densities. That is $I_A = -I_C = I_0$, where I_A and I_C are the respective current densities and it is convention that the cathode current density is given negative sign while the anode current density is given positive sign. This is a convention and it should be marked in mind. I_0 is usually termed as exchange current density. It may be defined, as "the flow of charge or electrons across an electrochemical system in equilibrium is known as exchange current density". Its value normally is low, of the order 10^{-8} A. It refers to the extent of both oxidation and reduction that occurs.

The equilibrium situation at an electrode is characterised by equilibrium potential and exchange current density.

For the reaction to have practical significance, a net current should flow and a net reaction either oxidation or reduction should occur. That means the system should not be at equilibrium. For this situation the kinetic aspect of the system must be considered. It is to be recalled that thermodynamics fixes the direction and kinetics determines the rate. This is an axiom for chemical reactions.

For this let us apply an external potential to the working electrode, more negative than E_e . This will cause an increase in cathodic current and a net quantity of oxidized form will be reduced to reduced form. The value of the ratio C_O/C_R at the electrode surface will diminish. The magnitude of net cathodic current and the time for the new value of C_O/C_R to be achieved depend on the rate or the kinetics of the electron transfer reaction. The net cathodic current will be due to the increase in partial cathodic current (I_C) and a decrease in partial anodic current (I_A) at this new potential. Hence reversible condition changes to irreversible condition. One can consider that the situation where I_C is not equal to I_A as the indication of irreversible nature of the electrochemical process. This is achieved by applying a more negative potential or excess potential than E_e , which is known as conventionally termed as over potential. Conversely it can be argued that if working electrode is made more positive than E_e (by applying external potential more positive than E_e) a net anodic current will flow through the cell.

Equilibrium state	$-I_C + I_A = 0$	Exchange current density; no net current
Cathodic current	$-I_C + I_A < 0$	Net cathodic current
Anodic current	$-I_C + I_A > 0$	Net Anodic Current

The Butler-Volmer equation is expressed as:

$$I = I_0 \exp([\alpha_A n F \eta] / RT) + \exp([- \alpha_C n F \eta] / RT)$$

From this equation, it can be understood that the measured current density is a function of (i) over potential (η), (ii) exchange current density (I_0) and (iii) anodic and cathodic transfer coefficients ($\alpha_A + \alpha_C$)

Transfer coefficients are not independent variables. In general, $\alpha_A + \alpha_C = 1$. In general, the current density at any overpotential is the sum of cathodic and anodic current densities. If the over potential is highly negative, cathodic current density increases while anodic current density becomes negligible. Under this condition the first term of the Butler-Volmer equation becomes negligible. Under these conditions

$$\log -I_C = \log I_0 - ([\alpha_C n F \eta] / 2.303 RT)$$

This equation can be regarded as the cathodic Tafel equation.

The corresponding anodic Tafel equation can be written as

$$\log I_A = \log I_0 + \left\{ \alpha_A n F \eta_A / 2.303 RT \right\}$$

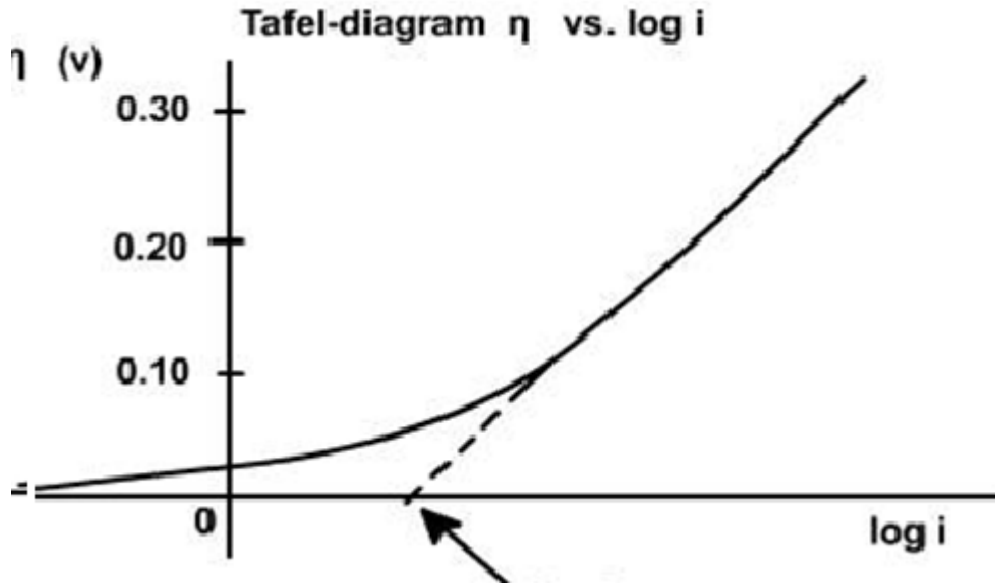
Experimental Determination of I and Tafel Plot

The test electrode is kept immersed in its salt solution (supporting electrolyte). The solution should be dilute so that the concentration near the surface of the electrode does not differ much from the bulk concentration. A calomel electrode(reference electrode) is kept close to the test (working electrode) electrode. An inert electrode is also taken which serves as the counter electrode. A DC potential is applied across the test and the counter electrodes, making the test electrode negative. This establishes a potential across the test and the reference electrodes which is read by a very sensitive voltmeter connected in the circuit. From this value the rest potential is subtracted to get the applied potential component on the test electrode. An ammeter connected in series reads the current passing through the circuit. The applied potential is increased which increases the over potential on the cathode (test electrode is made more negative) and the corresponding current value is measured (ammeter reading). In this way the current values are taken for several over potential values making test electrode more and more negative. The log values of these current values are then plotted against the over potential (computed from the measured potential values).

In the next step the test electrode is connected to the positive terminal and the counter to negative. As done earlier the current is measured for various over potential values and



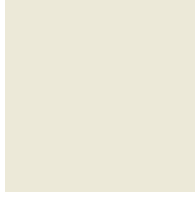
plotted against them on the other side of the graph.



Significance of Tafel Plots

1. The point of intersection on the Y axis of the extrapolated graph gives the value of I_0 , the exchange current density, which is otherwise difficult to determine. It the current passing at equilibrium conditions and a very low value. [Note at equilibrium both the anode and cathode current have definite value and the net current alone is zero]
2. The transfer coefficients can be determined; from the anodic slope, α_A and from cathodic slope α_C can be determined. This value is very important in industrial practice of electrochemical reactions. This determines the potential that is to be applied to affect the desired rate of reduction or oxidation.
3. Knowing the value of transfer coefficient for a reaction the number of electrons, n , for an unknown reaction can be determined. This reflects on the mechanism of the reaction; that is how many electrons are involved in that step. Whether the reaction is single step or multi step is revealed by this value.
4. The fact that the experimental data fit to Tafel equation itself is an indication of the possibility of irreversible reaction.

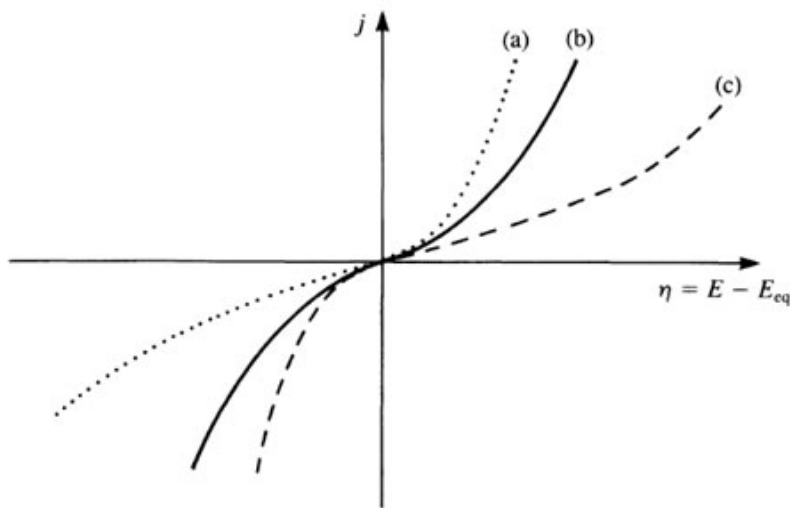
The effect of α_C on current density is shown in the following plot. The following points may have to be kept from this plot.



- (a) All three curves pass through one point
- (b) When the value of alpha is less than 0.5, it means oxidation is favoured while if it is greater than 0.5 reduction is favoured.
[This is only a text book knowledge and the material can be available in various sources in the net or text books and nothing original is claimed]

When $\alpha_c = 0.25$ oxidation is usually favoured, whereas $\alpha_c = 0.5$ indicate symmetry of the reaction while $\alpha_c = 0.75$ indicates that reduction is favoured.

As cathodic transfer coefficient value increases reduction is favoured and oxidation is not favoured and vice versa for anodic transfer coefficient. The transfer coefficients depend on the pH of the medium; in acidic conditions (low pH) reduction is favoured which is revealed by an increase in α_c .



The effect of the value of α_c on the current density, j . (a) $\alpha_c = 0.25$: oxidation favoured; (b) $\alpha_c = 0.50$: symmetric; (c) $\alpha_c = 0.75$: reduction favoured.