Electrochemical Kinetics of Corrosion and Passivity

The basis of a rate expression for an electrochemical process is Faraday's law:

$$m = \frac{Ita}{nF}$$

Where m is the mass reacted, I is the measured current in ampere, t is the time, a is the atomic weight, n the number of electrons transferred and F is the Faraday constant (96500 $Cmol^{-1}$). Dividing Faraday's law by the surface area A and the time t leads to an expression for the corrosion rate r:

$$r = \frac{m}{tA} = \frac{ia}{nF}$$

With the current density i defined as i = I/A.

<u>Exchange current density:</u>

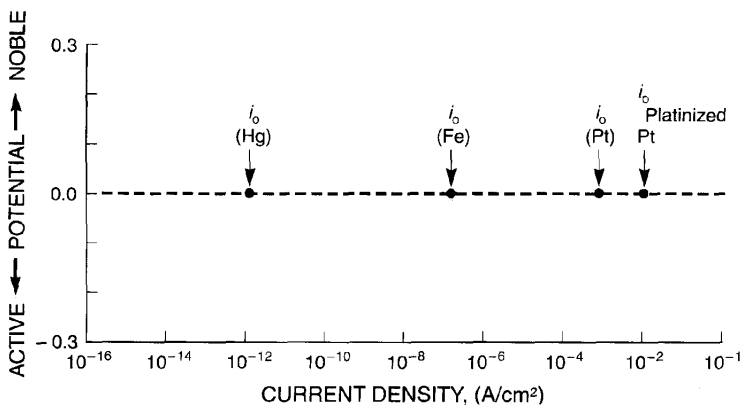
We consider the reaction for the oxidation/reduction of hydrogen:

$$2H^+ + 2e^- \underset{r_r}{\overset{r_f}{\rightleftharpoons}} H_2$$

This reaction is in the equilibrium state at the standard half cell potential $e^0(H^+/H_2)$. This means that the forward reaction rate r_f and the reverse reaction rate r_r have the same magnitude. This can be written as:

$$r_f = r_r = \frac{i_0 a}{nF}$$

In this case is i_0 the exchange current density equivalent to the reversible rate at equilibrium. In other words, while the standard half cell potential e^0 is the universal thermodynamic parameter, i_0 is the fundamental kinetic parameter of an electrochemical reaction. The exchange current density cannot be calculated. It has to be measured for each system. The following figure shows that the exchange current density for the hydrogen reaction depends strongly on the electrode material, whereas the standard half cell potential remains the same.



Electrochemical Polarization:

Polarization η is the change in the standard half cell potential e caused by a net surface reaction rate. Cathodic polarization η_c means that electrons are supplied to the surface and they build up a negative potential in the metal. Therefore η_c is negative by definition. Anodic polarization η_a is the opposite process. There are two different kinds of polarization (sometimes also known as overpotential) namely activation and concentration polarization.

Activation Polarization:

In this case a step in the half cell reaction controls the rate of electron (charge) flow. For example the hydrogen evolution reaction

$$2H^+ + 2e^- \rightarrow H_2$$

proceeds at a metal surface in three major steps. In the first step H+ reacts with an electron from the metal to form an adsorbed hydrogen atom at the surface.

$$H^+ + e^- \rightarrow H_{ads}$$

In the second steps the reaction of two adsorbed hydrogen atoms forms a hydrogen molecule.

$$H_{ads} + H_{ads} \rightarrow H_{2ads}$$

In the third step enough adsorbed hydrogen molecules combine and nucleate a hydrogen bubble on the surface. Any of these steps can be the rate limiting step and therefore cause the activation polarization. The activation polarization can be calculated using the current densities, which represent the reaction rates. For cathodic η_c and anodic η_a polarization one can write:

$$\eta_c = \beta_c \log \frac{i_c}{i_0}$$

$$\eta_a = \beta_a \log \frac{i_a}{i_0}$$

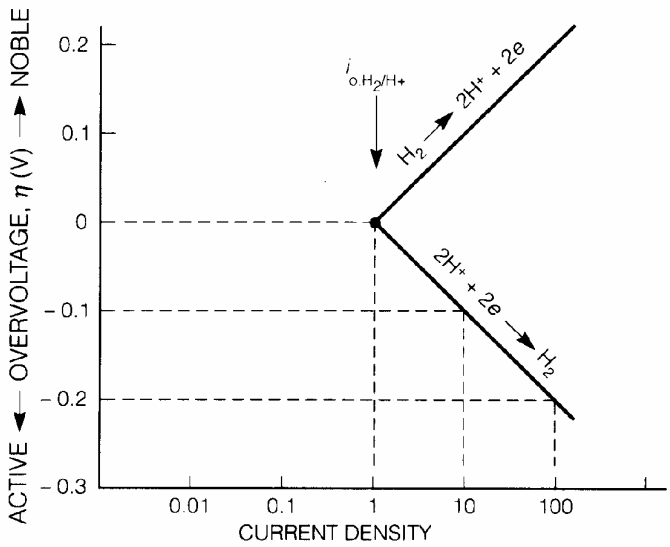
For zero η both equations reduce to $i = i_0$. For polarization potentials below the equilibrium half cell potential the reduction or forward reaction is favored:

$$2H^+ + 2e^- \rightarrow H_2$$

while above the half cell potential the reverse reaction is favored.

$$H_2 \rightarrow 2H^+ + 2e^-$$

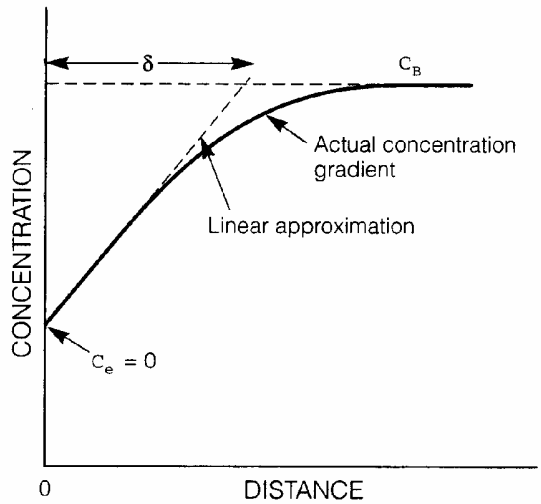
In the figure the so called Tafel plot is shown. It depicts the change in the polarization potential with the current density.



The activation polarization is related to the activation energy of the rate limiting step. Therefore a thermodynamical derivation of β is possible.

Concentration Polarization:

If the reaction on the metal surface is fast it can lead to a depletion of the adjacent solution of the dissolved species that reacts on the surface. This is shown for the H^+ concentration in the next figure. c_B is the H+ concentration in the bulk of the solution.



From the Nernst equation it is clear that the half cell potential is dependent on the H^+ concentration, in the form that the potential decreases with decreasing concentration.

$$e_{H^+/H_2} = e^0_{H^+/H_2} + \frac{2.3RT}{nF}\log\frac{(H^+)^2}{p_{H_2}}$$

The decrease in the half cell potential is the concentration polarization η_{conc}, which can be written in terms of current density using the Nernst equation as:

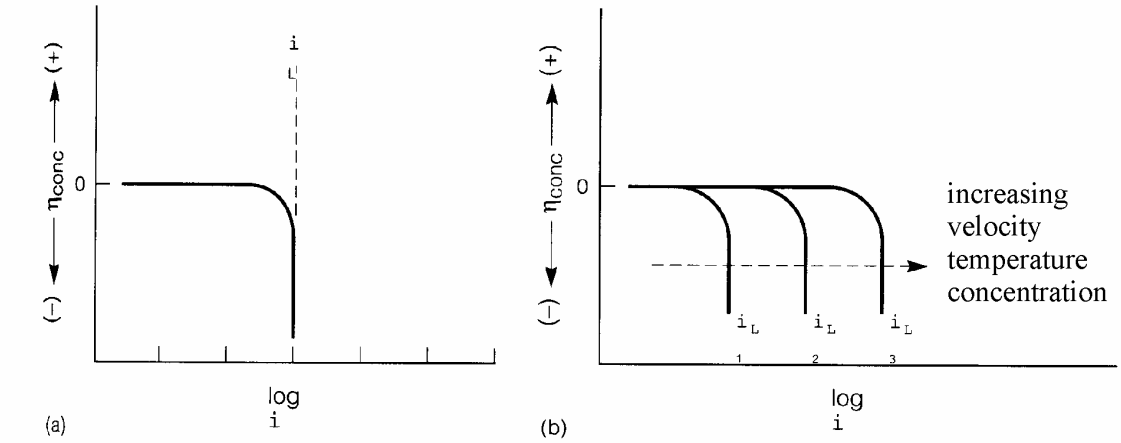
$$\eta_{conc} = \frac{2.3RT}{nF}\log\left[1 - \frac{i_c}{i_L}\right]$$

A plot of this equation can be seen in the next figure. One can see that η_{conc} is low until a limiting current density i_L is reached. This current density is the measure of a maximum reaction rate that cannot be exceeded because of a limited diffusion rate of H^+ within the solution. The limiting current density can be calculated as follows:

$$i_L = \frac{D_Z nFC_B}{\delta}$$

D_Z is the diffusivity of the reacting species Z, C_B is the concentration in the bulk of the solution and δ is the thickness of the depleted zone. i_L is increased with increasing concentration, with increasing diffusivity (temperature) and higher solution agitation, which

decreases δ.



Concentration polarization is only significant for cathodic reduction processes, as for anodic oxidation one usually has an unlimited supply of metal atoms at the interface. Only at very high corrosion rates or during intentional anodic dissolution by an impressed current one can find concentration polarization due to limited rates of transport of soluble oxidation products away from the surface.

<u>Mixed Potential Theory:</u>

Charge conservation is required to apply the equations derived for polarization potentials. This means that the sum of anodic oxidation currents must equal the sum of cathodic reduction currents. For anodic oxidation there is one reaction of the general form:

$$M \rightarrow M^{n+} + ne^-$$

There are basically three different kinds of cathodic reactions:

1. Evolution of Hydrogen from acid or neutral solutions:

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(acid solutions)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(neutral and alkaline solutions)}$$

2. Reduction of dissolved oxygen in acid or neutral solutions:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(acid solutions)}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(neutral and alkaline solutions)}$$

3. Reduction of a dissolved oxidizer in a redox reaction (e.g.):