

Electrode kinetics

NTT Consultancy
Giel Notten
Senior Corrosion Engineer

Summary

Last year we have been discussing in detail many different forms and cases of corrosion in ammonia and urea plants. To really understand the background and fundamentals of these corrosion problems it is necessary to introduce the modern electrochemical theory of aqueous corrosion.

Although the presentation is necessarily simplified and brief we think this theory will contribute to a better understanding of corrosion phenomena. Our first paper did cover thermodynamic principles while this paper discusses electrode kinetics. The next paper will discuss the application of electrochemical corrosion theory on corrosion reactions in general and in carbamate solutions specific.

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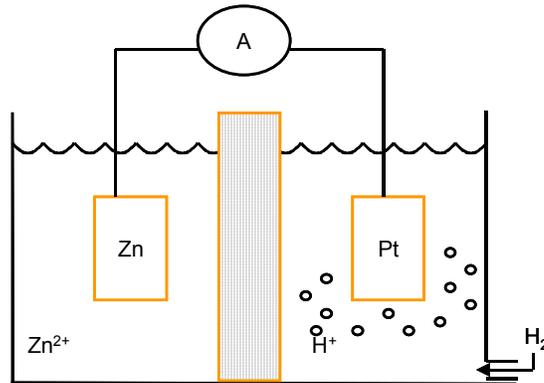
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2.3 Electrode kinetics

2.3.1 Introduction

From an engineering standpoint, the major interest is in the kinetics or rate of corrosion. It is not sufficient to know whether a metal can corrode under given conditions. It is necessary to know the rate of a possible reaction. Corroding systems are not at equilibrium, and therefore thermodynamic calculations cannot be applied. Essentially we are interested in what happens when cells such as have been described before are short-circuited as illustrated in figure 2.3.1.1.

Figure 2.3.1.1
Short-circuited cell containing zinc and hydrogen electrodes.



In this instance a vigorous reaction occurs, the zinc electrode dissolves in the solution and simultaneously a rapid evolution of hydrogen is observed at the platinum electrode. Electrons released from the zinc-dissolution reaction are transferred through the connecting wire to the platinum electrode where they are consumed in the hydrogen-reduction reaction. The process which occurs is the same process that occurs when zinc metal is immersed in an acid solution. In the divided cell as shown in figure 2.3.1.1 the reactions occur on separate electrodes, while at the immersed piece of zinc in an acid solution these reactions occur on the same metal surface.

Before discussing the electrode-kinetics, several useful terms should be defined.

Anode refers to an electrode at which a net oxidation process occurs, and cathode refers to an electrode at which a net reduction reaction occurs. In figure 2.3.1.1 the zinc electrode is the anode, and the platinum or hydrogen electrode is the cathode in this particular cell with short-circuited electrodes.

Anodic reaction is synonymous with an oxidation reaction and cathodic reaction is synonymous with a reduction reaction.

2.3.2 Faraday's law

Electrode reactions are running with transfer of charged particles like ions and electrons. There is a relationship between the current density in the electrochemical cell and the amount of reacting species per time unit (1 Ampere = 1 Coulomb per sec).

By means of an Ampere-meter, installed in the connecting wire between the two electrodes of the electrochemical cell as shown in figure 2.3.1.1, we can measure the current density. The current density is related to the amount of metal which is dissolving, so related with the corrosion rate.

This relationship is given by Faraday's law:

If an electric charge of F coulomb is passed, of each species X , which takes part in the reaction, M_X/n_X g has reacted.

F = Faraday constant = $9.65 \cdot 10^4$ Coulomb per (g)mol

X = symbol for reacting species

M_X = Molecule weight

n_X = number of electrons transferred.

The reaction rate of a species X (v_X) is defined as the amount of species X reacting per surface unit and per time unit. The relationship between the reaction rate v_X and the current density i_X , defined as strength of current per surface unit, is given by:

$$i_X = n_X \cdot F \cdot v_X$$

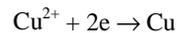
2.3.3 Exchange-current density

Let us consider again for instance the Cu/Zn cell in equilibrium situation as shown in figure 2.2.2.2.

In equilibrium situation at the copper electrode the anodic reaction



is as fast as the cathodic reaction



The reaction rate of both reactions is even in equilibrium situation not zero.

The absolute value of the cathodic current density $I_{C_{Cu}}$ is equal to the anodic current density $I_{A_{Cu}}$. The direction of both currents is opposite which means that there is no net current.

In equilibrium situation the following equation is valid:

$$i_A^{eq} = -i_C^{eq} = i_0$$

The magnitude i_0 is called exchange-current density and is related to the rate at which charged particles are passing through the interface metal/electrolyte.

The relationship between the exchange reaction rate and current density can be directly derived from Faraday's law:

$$v_{oxid} = v_{red} = i_0/nF,$$

where v_{oxid} and v_{red} are the equilibrium oxidation and reduction rates and i_0 is the exchange-current density; n and F have been defined previously.

The exchange-current density depends for instance on kind of metal electrode and on the surface roughness of this metal electrode.

The exchange-current density of hydrogen reaction $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ at platinum is extremely high. For this reason platinum is chosen for the NHE (normal hydrogen reference electrode).

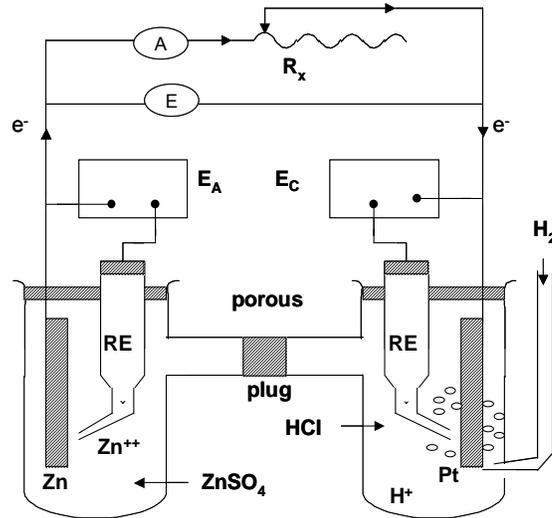
Exchange current densities for the $\text{H}^+ - \text{H}_2$ system are markedly reduced by the presence of trace impurities such as arsenic, sulphur and antimony-containing ions.

2.3.4 Polarization and overvoltage

When a cell as shown in figure 2.3.1.1 is short-circuited, and net oxidation and reduction processes occur at the electrode interfaces, the potentials of these electrodes will no longer be at their equilibrium potential. This deviation from equilibrium potential is called polarization. Polarization can be defined as the displacement of the electrode potential resulting from a net current. The magnitude of polarization is frequently measured in terms of overvoltage. Overvoltage, usually abbreviated as η , is a measure of polarization with respect to the equilibrium potential of an electrode. That is, the equilibrium potential of an electrode is considered as zero, and the overvoltage is stated in terms of volts or millivolts plus or minus with respect to this zero reference.

This polarization phenomenon can be considered by means of the idealized equipment as illustrated in figure 2.3.4.1.

Figure 2.3.4.1
Short-circuited cell containing zinc and hydrogen electrodes.
(L.L. Shreir)



The simplest way of visualizing polarization and overvoltage is to consider the idealized experiment shown in figure 2.3.4.1, in which zinc, in a solution of its own ions, is corroded when an electrical connection is made to platinum in an acid solution. The electrochemical cell may be presented as:



In this corrosion cell, Zn is the anode and its potential E_A is measured by means of a high impedance voltmeter and a reference electrode (R.E). The potential of the Pt electrode, E_C , is similarly monitored. The corrosion rate is controlled by the resistance R_X between Zn and Pt and measured by means of a low impedance ammeter.

Figure 2.3.4.2 shows how E_A , E_C and i (corrosion current) change as R_X varies from ∞ to 0.

When $R_X = \infty$ no current can flow from the anode to the cathode and so $E_A = E_{OA}$, the open circuit potential of the anode. E_C is similarly E_{OC} .

As R_X is reduced, Zn passes into solution as Zn^{2+} and at the cathode H^+ is reduced to H_2 gas. However, the flow of current has increased E_A from E_{OA} to a higher potential, whilst E_C has fallen to a more negative value. The difference between E and E_0 , the open circuit potential, is called the overpotential.

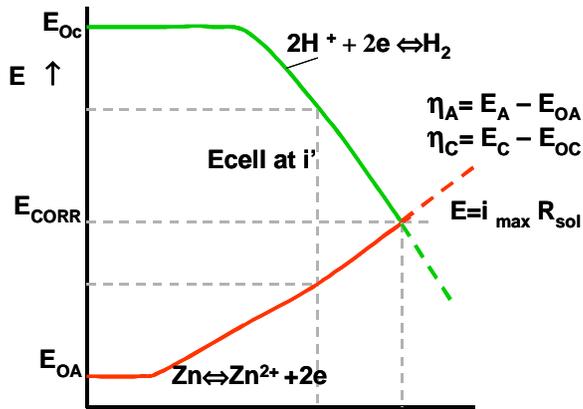
The anodic overpotential η_A is positive: $\eta_A = E_A - E_{OA}$

The cathodic overpotential η_C is negative: $\eta_C = E_C - E_{OC}$

The current flowing through the ammeter i is directly related to the rate at which Zn goes into solution.

When $R_X = 0$, the Zn and Pt are short circuited, (the usual condition during corrosion because the anodic and cathodic reactions are usually occurring on a metal surface in close proximity), and so $E_C = E_A = E_{corr}$. E_{corr} is the corrosion potential, and the corresponding current is the corrosion current.

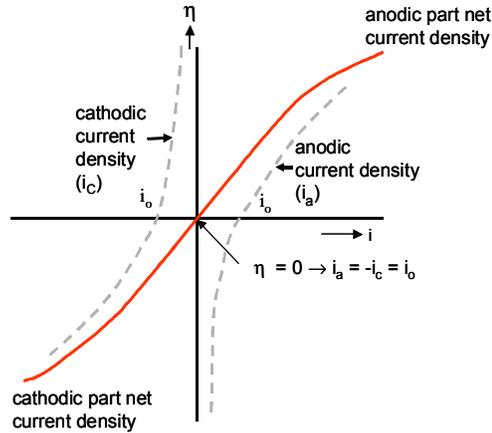
Figure 2.3.4.2
Diagram illustrating polarization and overvoltage of anodic and cathodic electrode reactions.



2.3.5 Polarisation curves; Evans diagrams

Let us consider an electrode reaction, consisting of an anodic and a cathodic reaction, occurring at one single electrode. If we plot the current density i of this reaction against the overvoltage η we get the polarization curve (figure 2.3.5.1).

Figure 2.3.5.1
The liner polarization curve of a single electrode reaction.



The line of net current density is the algebraic sum of the partial current densities i_a and i_c . In the equilibrium situation the polarization $\eta = 0$. This equilibrium potential is indicated as point zero on the vertical axis. On the horizontal axis the linear current density is plotted.

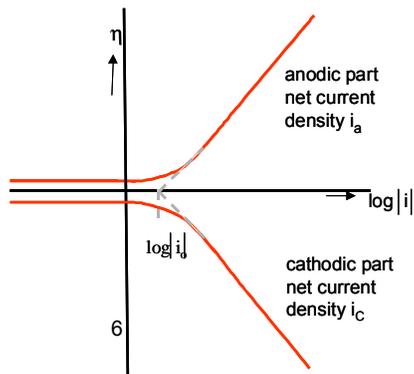
In case the overpotential $\eta = 0$, the net current density is 0. In this situation the anodic and cathodic current densities are equal and opposite in direction. Both current densities equal the exchange-current density i_0 . In case of a large overpotential the net current density is almost equal to one of the partial current densities.

Beside the linear polarization curve one uses the logarithmic polarization curve (Evans diagram), in which the logarithmic current density is plotted horizontally (figure 2.3.5.2)

The anodic and cathodic branch of the polarization curve are located at the same side of the potential axe, which simplifies determining of the corrosion potential and corrosion current density at the intersection of the two polarization curves.

The logarithmic polarization curve also shows that there is a linear relationship between η and $\log |i|$.

Figure 2.3.5.2
Logarithmic polarization curve of a single electrode reaction (Evans diagram).



2.3.6 Polarisation processes, determining the corrosion rate

We have to discuss now more deeply the polarization theory. As mentioned before polarization can be defined as the displacement of electrode potential resulting from a net current. We have to notice that, the greater is the polarization (the larger the slope of the E - i curve) the lower is the corrosion current. Hence polarization is beneficial in reducing the corrosion rate. The most common forms of electrochemical polarization are charge-transfer (chemical or activation) polarization and concentration polarization. A third possibility of polarization is resistance polarization, occurring if the electrolyte has a high resistance, so that migration is slow. The charge-transfer and concentration polarization processes will be discussed in this course.

Charge-transfer polarization

Charge-transfer polarization or activation polarization refers to electrochemical reactions which are controlled by a slow step in the reaction sequence. If the taking-up or giving-off of electrons is rate determining we speak of charge-transfer polarization. As discussed before this slow step during hydrogen evolution might be the electron transfer step or the formation of hydrogen molecules. In figure 2.3.6.1 charge-transfer polarization of an anodic reaction is illustrated. This polarization mechanism is also possible with cathodic reactions.

Figure 2.3.6.1
Charge-transfer polarization at the anode.

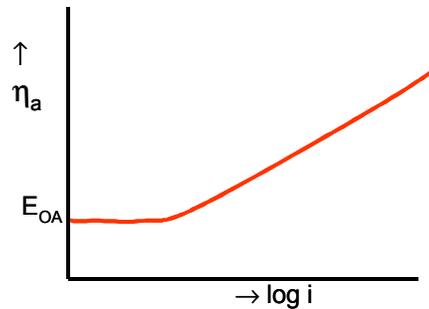
$$\eta_a = \alpha + \beta \log |i|$$

$$\alpha = -\beta \log i_0$$

α = charge transfer coefficient

β = Tafel slope

$$\eta_a = E_A - A_{OA} = \beta \log |i/i_0|$$



If charge transfer is the rate determining step, the overvoltage is indicated as charge transfer overvoltage η_a . In case $|\eta_a| > 0.1$ V the following relationship is valid between the rate of the anodic electrode reaction i , the exchange-current density i_0 and the overvoltage η_a :

$$\eta_a = \alpha + \beta \cdot \log |i| \qquad \alpha = -\beta \cdot \log i_0 \qquad \eta_a = \beta \cdot \log \frac{|i|}{i_0}$$

in which α is the charge transfer coefficient and β is the Tafel slope or Tafel constant.

This equation is called the Tafel equation.

If a logarithmic current scale is used, the relationship between overvoltage or potential and current density is a linear function as shown already in figure 2.3.5.2. The value for β for electrochemical reactions ranges between 0.05 and 0.15 volt and is usually 0.1 volt.

At a very small overvoltage $|\eta_a| < 0.01$ V there is a linear relationship between η_a and i (see figure 2.3.5.1):

$$\eta_a = K \cdot i/i_0 \quad (K = RT/nF)$$

The slope of the polarization curve at equilibrium potential $\eta = 0$ is indicated as polarization resistance R_p . So, previous equation can be written as: $R_p = K/i_0$.

Concentration polarization

When the rate of the charge transfer process is very large (large exchange-current density and/or large overvoltage and high corrosion rate), it is possible for the transport of ions or molecules to or from the electrode to become rate-determining.

If transport of reacting species is limiting the reaction rate, overvoltage is indicated as concentration overvoltage. There are three main mechanisms by which transport can take place:

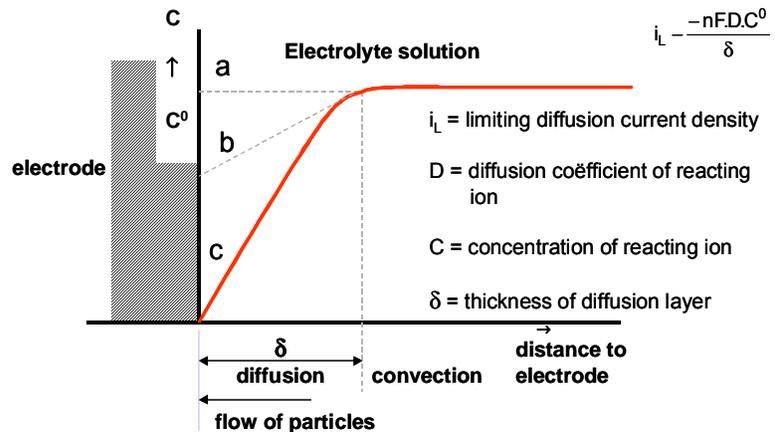
- migration in an electric field,
- convection due to movement of the liquid,
- diffusion caused by concentration differences.

Migration can nearly always be neglected in our case because there usually is an excess of "neutral electrolyte", i.e. ions not taking part in the electrode reaction.

Convection causes homogenization of the solution but, depending on velocity and geometrical factors, concentration differences still exist in a thin boundary layer δ of 0.01 to 0.5 mm thickness. There diffusion will take place.

Nernst introduced a model to calculate the effect of this diffusion. In this model the concentration is assumed to be constant at C^0 in the bulk of the solution. In a boundary layer of thickness δ next to the electrode Nernst assumed a linear concentration gradient from the value C^0 in the bulk of the solution to C at the surface. This is shown in figure 2.3.6.2.

Figure 2.3.6.2
Concentration profile in diffusion layer according to the model of Nernst
(P.J. Gellings)



According to Fick's law the flux of the substance to the electrode is proportional to the concentration gradient with the diffusion coefficient D as the proportionality constant. Combined with Faraday's law this gives for the current density:

$$i = -nFD \cdot (C^0 - C) / \delta$$

The rate of transport of a certain species through this layer is maximum if the concentration at the electrode surface is zero. In that case the maximum possible current density is reached; usually called the limiting current i_L , which is equal to:

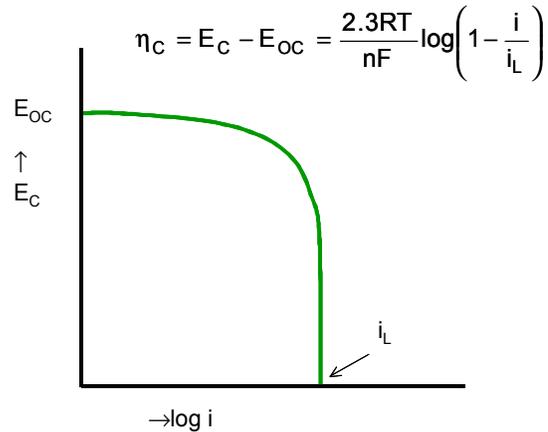
$$i_L = -nFD \cdot C^0 / \delta \quad \text{for } C = 0.$$

Especially at high current densities diffusion is rate determining for the electrode reaction. The relationship between diffusion or concentration overvoltage η_c , the limiting current density i_L and the current density i is:

$$\eta_c = 2.3 \cdot RT/nF \cdot \log(1 - i/i_L)$$

The diffusion polarization of a cathodic reaction is illustrated in figure 2.3.6.3. It is obvious that the limiting diffusion current density increases with increasing electrolyte velocity.

Figure 2.3.6.3
Diffusion or concentration polarization of cathodic reaction.

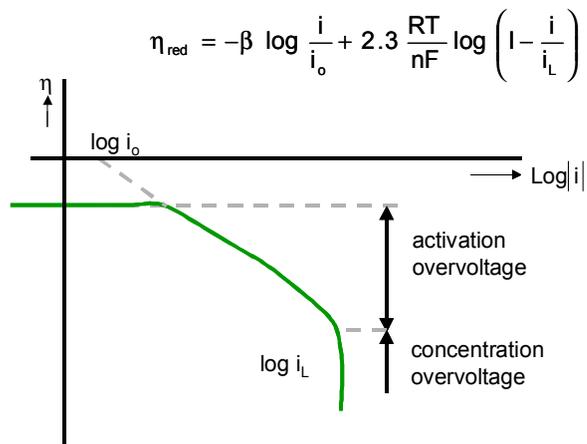


Combined polarization

Usually, at an electrode charge transfer polarization (at low reaction rates) as well as diffusion polarization (at higher reaction rates) may occur.

Especially at reduction processes like oxygen reduction concentration polarization is combined with activation polarization. This combined concentration and activation polarization ($\eta_c = \eta_a + \eta_c$) is illustrated in figure 2.3.6.4.

Figure 2.3.6.4
Combined activation and diffusion polarization of a cathodic reaction



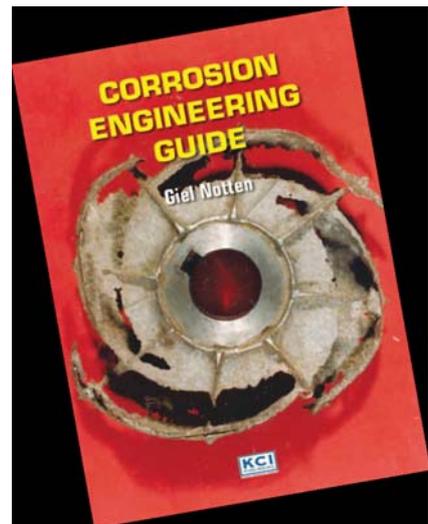
Using only three basic parameters, namely, β , i_o and i_L , the kinetics of virtually every corrosion reaction can be precisely described. Previous mentioned equations represent a simplification of the complex phenomena observed during corrosion reactions. The use and application of some equations will be discussed more in detail in chapter 5 "Corrosion Examination, Inspection and Monitoring".

Giel has written the Corrosion Engineering Guide, a valuable asset for any engineer working in a urea plant.

This guide is available via:

<http://www.stainless-steel-world.com/>

Please find the Table of Content of this Corrosion Engineering Guide herebelow.



About Giel Notten

Giel is a true materials and corrosion expert who, before his retirement in 2004, spent thirtyeight years working with DSM in The Netherlands. After gaining his Engineering degree at the Higher Technical School of Heerlen, The Netherlands, he joined DSM's central laboratory.

He was to remain with the company for the rest of his career and held several positions as a materials and corrosion expert there. For the last twenty years before he retired, Giel worked in the Corrosion Department as Managing Senior Corrosion Engineer. He has further participated in numerous conferences spreading the word about his broad experiences as a corrosion and materials specialist in chemical process plants.

For Stamicarbon, a subsidiary company of DSM, and licensing DSM's know-how, he set up programmes for lifetime extension studies in urea and ammonia plants and supervised them.

He was also involved in the development of Safurex[®], the super-duplex stainless steel grade (developed by Sandvik in cooperation with Stamicarbon) for application in Stamicarbon urea plants.

Giel has always enjoyed teaching so, after only five years working in the field at DSM, he already began to develop a Corrosion Engineering course. Since then he has taught many young engineers from both inside and outside DSM about the ins and outs of corrosion control in chemical plants. He was also a board member of NACE Benelux and a member of the Contact Group Corrosion of the Dutch Chemical Process Industry and the Studiekern Corrosion of the Dutch Corrosion Society (NCC).

Since his retirement from DSM, Giel Notten has remained active as a corrosion engineering consultant. He has devoted much of his time to passing on his extensive knowledge and experience on the complicated topic of corrosion engineering to a new generation of engineers.

He has done this in the form of numerous corrosion courses and workshops.

Alongside his professional career, Giel has been very active in local societies and has been a Rabobank board member for about thirty-five years, twenty-five years of which as Chairman of the Board. Furthermore, he is an active cyclist. Together with his wife, Lianne, he has made trips up to 2500 km by bicycle to Santiago de Compostela, Spain and Rome, Italy.



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