## **Galvanic and Concentration Cell Corrosion**

A galvanic cell is formed, when two different metals are connected electrically, while both are immersed in an electrolyte. In this case one of the two is corroded preferentially by galvanic corrosion. When different solution concentrations are present on the same metal surface, a concentration cell is formed, which leads to preferential corrosion, too. When attack on the junction of two dissimilar alloys is limited to one of the two, one usually has galvanic corrosion. The preferentially corroded alloy is the anode in the galvanic couple and the unattacked alloy is the cathode. The cathode may be damaged by hydrogen or by cathodic polarization out of the passive into the active zone.

Any metal or alloy has a unique corrosion potential  $E_{corr}$  immersed in a corrosive electrolyte. When two metals are coupled, the one with the more negative  $E_{corr}$  will lose electrons, which leads to an increased corrosion rate. The anodic dissolution, or corrosion reaction is

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

for the active metal. The rate for the more noble metal N is decreased due to the excess electrons from M.

$$N \rightarrow N^{m^+} + me^-$$

N is the cathode of the galvanic cell and M is the anode. The corrosion rate decrease in the cathode is the basis of cathodic protection by a sacrificial anode.

The corrosion potentials of different metals and alloys in a specified electrolyte give a galvanic series. Such a series gives a qualitative prediction, which alloy or metal will corrode first in a galvanic couple. But the quantitative corrosion rate can not be predicted from this series, as the influences of solution velocity and temperature are neglected. And the series is not necessarily the same for a different electrolyte, although people sometimes try to draw conclusions from the seawater series for different electrolytes.

## Area Effects:

A large ratio of the cathode to anode surface area should be avoided. For small anodes the galvanic attack is concentrated and penetration of the attack through the metal is faster. A larger anode surface will give a more uniform attack and will slow down the rate of penetration. A classic example are storage tanks with new stainless steel bottoms and coated sides made of normal steels. The galvanic corrosion penetrated the sides quickly, due to small

defects in the protective coating which are unavoidable. The new tanks started to leak already after a few months. The problem is shown in figure 6.2.



**FIGURE 6.2** Painted steel storage tank which developed penetration through a coating due to galvanic coupling to a new stainless steel bottom. (*From M. G. Fontana*, Corrosion Engineering, 3rd ed., McGraw-Hill, New York, pp. 46–49, 1986. Reprinted by permission, McGraw-Hill Book Company.)

Prevention:

The best way to prevent galvanic corrosion is to eliminate the galvanic couple by design, whenever possible. Using materials with similar  $E_{corr}$  reduces the driving force for galvanic corrosion drastically. Insulated flanges can be used to avoid a galvanic couple (figure 6.3).



**FIGURE 6.3** Insulated flange to eliminate a galvanic couple. (From M. G. Fontana, Corrosion Engineering, 3rd ed., McGraw-Hill, New York, pp. 46–49, 1986. Reprinted by permission, McGraw-Hill Book Company.)

But soluble corrosion products can be deposited on active metals downstream and form in situ galvanic couples. If the galvanic couple cannot be avoided a large anode area and a large anode thickness should be used. The anode can also be designed foe easy replacement. Coating is usually not advisable (example with the tanks). If coating is applied it should be put on the cathode to prevent the cathodic reaction. In this case small defects in the coating do not have such severe effects as on the anode.

Fundamental Aspects:

Corroding Metal – Inert Metal Couple:

When zinc is coupled to platinum in dilute acid solutions experiments show that,

1. the corrosion potential of Zn is shifted to a more noble value

2. the corrosion rate of Zn is increased and

3. the hydrogen evolution on Zn is reduced.

These effects are due to cathode and anode polarization within the couple, as shown in figure 6.4.



**FIGURE 6.4** Schematic polarization in a galvanic couple between zinc and platinum in dilute acid solution.

The electrons from the anodic reaction (Zn Zn2+ + 2e-) flow to Pt until both electrodes are at the same potential  $E_{couple}$ , which is a similar effect as an impressed current  $i_{app}$ , shown in figure 3.14. The exchange current density of the hydrogen evolution reaction also affects the galvanic cell as shown in figure 6.5.



**FIGURE 6.5** Effects of platinum and gold galvanically coupled to zinc in dilute acid solution.

Increasing the surface area of the cathode leads to an increase in the corrosion rate of the anode. As the current from the reduction reaction increases, the anodic oxidation reaction needs to increase too, to maintain a constant charge. The effect is schematically shown in figure 6.6.



**FIGURE 6.6** Effect of increased cathode surface area on the galvanic interaction between zinc and platinum in dilute acid solution.

Corroding Metal – Corroding Metal Couple:

Two metals M and N are corroding metals. M is the cathode metal and N is the anode metal. Again the coupled potential is found where the total reduction is equal to the total oxidation, as shown in figure 6.7.



log CURRENT

FIGURE 6.7 Schematic polarization in a galvanic couple between corroding metals M (anode) and N (cathode).

The potential of the couple always falls between the corrosion potentials of the two active metals. The rate of the metal with the more active  $E_{corr}$  is increased and the rate of the metal with the more noble  $E_{corr}$  is decreased. At breaks in a Zn coated steel, the Zn is galvanically corroded to protect the exposed steel cathodically.

## Experimental Measurements:

A schematic of an experimental result is shown in figure 6.8. The dashed lines represent the half cell reactions defining the uncoupled corrosion potentials for anode and cathode. The solid lines represent data from a galvanic couple, where the couple potential is established when cathode and anode are polarized to equal potentials by the same current  $I_{couple}$ .



FIGURE 6.8 Schematic experimental polarization of anode and cathode in a galvanic couple.

For experimental measurements one uses a high surface area ratio cathode to anode (e.g. 12:1 in figure 6.9) and due to the large cathode area one does not need the auxiliary electrode, from polarization measurements.



**FIGURE 6.9** Cell for electrochemical study of steel anode, A, and brass cathode, C. (*From D. A. Jones*, Corrosion, *Vol. 40, p. 181, 1984. Reprinted by permission, National Association of Corrosion Engineers.*)