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.*)

Results from the cell shown in figure 6.9 are depicted in figure 6.11. Different area ratios shown in the figure were simulated by moving the experimental cathodic curve to higher or lower values with respect to the anodic curve. The intersections of the cathodic and the anodic curves show the couple potentials for the different surface area ratios.



FIGURE 6.11 Experimental cathodic (\bigcirc) and anodic (O) polarization curves in aerated 20% NaCl at room temperature for brass and steel, respectively, having surface area ratio of 12:1. Other surface area ratios simulated by moving cathodic curve with respect to the anodic curve. (*From D. A. Jones, Corrosion, Vol. 40, p. 181, 1984, Reprinted by permission, National Association of Corrosion Engineers.*)

The couple potentials graphically determined from figure 6.11 are shown as a function of the surface area ratio in the solid line in figure 6.12. The points in this figure are from actual experiments with the corresponding surface area ratio. One can see a rather good fit between experiment and theory.



FIGURE 6.12 Graphically simulated couple potential (———) compared with experimental measurements (\bigcirc) versus cathode/anode area ratio. (*From D. A. Jones*, Corrosion, *Vol. 40, p. 181, 1984. Reprinted by permission, National Association of Corrosion Engineers.*)

In principle one should be able to measure the coupled current by simply putting an ampere meter between the two electrodes. But due to the resistance of the ampere meter one gets a wrong current, as shown in figure 6.13. This problem can be avoided by using zero resistance ampere meters, which can be realized using a special electronic setup.



FIGURE 6.13 Separation of anode and cathode potentials when measuring galvanic current *I* with ammeter of resistance R_m .

The zero resistance ampere meter can be realized with the usual electrode setup combined with a potentiostat. In this case one can measure I_{couple} continuously and automatically. The measurement principle is shown in figure 6.14.



FIGURE 6.14 Potentiostatic zero resistance ammeter for continuous and automatic measurement of couple current at short circuit. (*From D. A. Jones*, Corrosion, *Vol. 40, p. 181, 1984. Reprinted by permission, National Association of Corrosion Engineers.*)

The potentiostat senses a difference between REF and WE and controls the difference at a preset value by automatically varying the current between WE and AUX. When WE and REF are shorted as shown in the figure the potentiostat will control the potential between cathode and anode at any specified value. If this value is zero the circuit will continuously and automatically read the I_{couple} at short circuit on the ampere meter. The result of such a measurement of short circuit current with time is shown in figure 6.15. In addition the effect of a dichromate inhibitor is shown in this figure.



FIGURE 6.15 Galvanic couple currents between brass and steel recorded automatically from a potentiostatic zero resistance ammeter. Effect of added $K_2Cr_2O_7$ in aerated 20% NaCl. (From D. A. Jones, Corrosion, Vol. 40, p. 181 1984. Reprinted by permission, National Association of Corrosion Engineers.)

Determining Rates of Galvanic Corrosion:

The rate of galvanic attack in a two metal couple is measured by the galvanic current density at the anode. The anodic current density on any point on the anode depends on the polarization of both, anode and cathode, on the conductivity of the solution and the physical geometry of the couple.

Anodic and cathodic polarization curves are used to visualize the polarization within a galvanic couple. The two curves can be obtained in two separate experiments using a potentiostat. A composite polarization diagram for different metals and alloys in aerated 3% NaCl is shown in figure 6.17. The intersection of an anodic curve with a cathodic curve of a more noble metal gives the couple current and potential. The dashed vertical lines in figure 6.17 represent the spread of values for the limiting current for reduction of dissolved oxygen, which is essentially the same for all alloys listed. A prediction of the surface area ratio (figure 6.17 corresponds to 1 cm² surfaces for both electrodes) can again be made by graphically increasing the cathodic current. This is shown in more detail in figure 6.19. The new galvanic current has risen by a factor of 10. But the anodic surface area is still 1 cm², the anodic current density is now 700 μ Acm⁻². However, the surface of the cathode has increased leading to a

cathodic current density of only 70µAcm⁻².



FIGURE 6.17 Potentiostatic polarization curves for various metals and alloys for prediction of galvanic corrosion in aerated 3% NaCl. (*From Bennett and Greene⁷*.)



FIGURE 6.19 Predicting galvanic corrosion rates of aluminum-copper couples: Effect of Cu:Al surface area ratio. Polarization curves for Cu and Al taken from Figure 6.17.

Potentiostatic polarization curves again have to be used with caution, for predicting corrosion behavior, as real environments tend to differ from controlled experiments. The influence of the solution can be seen when figure 6.17 for NaCl is compared to figure 6.18 for a deaerated 1N surfuric acid solution.



FIGURE 6.18 Potentiostatic polarization curves for various metals and alloys for prediction of galvanic corrosion in deaerated $1N H_2SO_4$. (From Bennett and Greene⁷)

Galvanic Passivation of Titanium:

When Ti is coupled to Pt, Pd, Rh or Ir the couple current is dominated by the hydrogen reaction at a potential within the passive range of Ti. This is used to give Ti corrosion resistance to hot acidic solutions can therefore be obtained by alloying these elements to Ti. A

similar effect can be reached using Ni. The polarization curves for Ti and Pt (Ni) are shown in figure 6.20.



FIGURE 6.20 Polarization curves taken from Figure 6.17 illustrating galvanic passivation of Ti when coupled to Pt or Ni.

Current and Potential Distributions:

Until now uniform current distribution on the surface was assumed. In practice this assumption does not hold. The current and potential distributions between two coupled metals depend on the conductivity of the electrolyte, the physical geometry and on the polarization of anode and cathode. Solution conductivity leads to an ohmic drop R_{Ω} , between any pair of points on anode an cathode. This leads to a reduced current I<I_{couple}. The potential distribution within the solution under a steel and Ni couple is shown by lines of constant potential in figure 6.21.



FIGURE 6.21 Potential distribution around a coplanar galvanic couple between iron and nickel. (*From H. R. Copson,* Trans. Electrochem. Soc., *Vol. 84, p. 71, 1943. Reprinted by permission, The Electrochemical Society.*)

The Ni cathode is obviously highly polarized in contrast to the steel anode. This leads to increased corrosion near the contact point on the steel and decreased corrosion near the contact point in the Ni.

Concentration Cells:

Corrosion is often affected by concentration calls. Differential aeration with different concentrations of dissolved oxygen on a single metal surface or on electrically connected surfaces are common. Such cells are especially important for Fe and carbon steels. Acid chloride concentration cells are important for the initiation and growth of pitting and crevice corrosion in stainless steel.

A laboratory setup of a differential aeration cell is shown in figure 6.23. Two iron electrodes are immersed in 0.1 N NaCl on both sides of a porous diaphragm, allowing charge transfer, but not sufficient mass transfer to affect the dissolved oxygen content.



FIGURE 6.23 Differential aeration cell. (*From H. Grubitsch, cited by U. R. Evans,* The Corrosion and Oxidation of Metals, *Arnold, London, p. 129, 1960.*)

For uncoupled electrodes the anodic and cathodic reactions on the nitrogen side are

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2.$$

As there is hardly any dissolved oxygen, reduction of dissolved oxygen as the cathodic reaction is impossible. On the aerated side the anodic reaction is still the oxidation of Fe, but the cathodic reaction is the reduction of the dissolved oxygen by

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$