Universidad Carlos III de Madrid

OpenCourseWare (2023)

CHEMISTRY II

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SOLUTIONS OF CORROSION EXERCISES

Exercise 1. A copper bar is immersed in a solution of hydrochloric acid. If the amount of oxygen available in the cathode is negligible, write the balanced oxidation and reduction half-reactions and the global reaction.
Data: E^0 (Cu^{2+}/Cu) = + 0.34 V.

SOLUTION

In oxygen free liquids like HCl, H_2 is evolved in the cathode (hydrogen electrode):

Cathode: $2\ H^+ + 2\ e^- \rightarrow H_2$ $E^0 = 0$ V

Anode: $Cu \rightarrow Cu^{2+} + 2\ e^-$ $E^0 = -0.34$ V

Overall reaction: $Cu + 2\ H^+ \rightarrow Cu^{2+} + H_2$ $E^0 = -0.34$ V

Exercise 2. Explain electrochemically the formation of the solid $Fe(OH)_3$ commonly known as rust in an electrolytic corrosion cell.
Data: E^0 (Fe^{2+}/Fe) = – 0.44 V.

SOLUTION

Oxygen will be available in the cathode and iron will be the anode (oxygen electrode):

Cathode: $\frac{1}{2}\ O_2 + H_2O + 2\ e^- \rightarrow 2OH^-$ $E^0 = 0.4$ V

Anode: $Fe \rightarrow Fe^{2+} + 2\ e^-$ $E^0 = 0.44$ V

Overall reaction: $Fe + \frac{1}{2}\ O_2 + H_2O + \rightarrow Fe^{2+} + 2\ OH^-$ $E^0 = 0.84$ V

Formation of $Fe(OH)_2$: $Fe + \frac{1}{2}\ O_2 + H_2O \rightarrow Fe(OH)_2$

The reaction continues to give rust: $Fe(OH)_2 + \frac{1}{2}\ O_2 + H_2O \rightarrow 2\ Fe(OH)_3$ (s).

Exercise 3. A piece of corroded metal alloy plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 800 cm^2 and that approximately 7.6 kg had corroded away during the submersion. Assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years. The density of the alloy is 4.5 g/cm^3.

SOLUTION

Corrosion Penetration Rate: CRP = KW / rAt

Time of submersion: $t = 87.6 \times 7.6 \times 10^6$ mg / 4 mm $yr^{-1} \times 4.5$ g $cm^{-3} \times 800$ cm^2

t = 46233.3 h = 5.27 yr.

Exercise 4. A sample of magnesium corrodes uniformly with a current density of 1.8×10^{-5} A/cm^2 in an aqueous solution. What is the corrosion rate of magnesium in mol/m^2 s?

SOLUTION

Oxidation (Anode): $Mg \rightarrow Mg^{2+} + 2\ e^{-}$

Corrosion rate: $r = I / nF$

$r = 1.8 \times 10^{-1}$ A m^{-2} / 2 × 96500 C mol^{-1}

$r = 9.3 \times 10^{-7}$ mol / m^{-2} s.

Exercise 5. Why does chromium in stainless steels make them more corrosion resistant in many environments than plain carbon steels?

SOLUTION

Chromium forms a very thin oxide film on the metal surface. This film acts as a protective barrier to further corrosion. This phenomenon is known as passivity.

In the plain carbon steel, the oxide film does not protect iron from the oxygen attack.

Exercise 6. Several types of metallic coatings are used to protect steel, including zinc, lead, tin, aluminium, and nickel. In which of these cases will the coating provide protection even when the coating is locally disrupted? Justify your answer.
Data: $E^0\,(Fe^{2+}/Fe) = -\,0.44$ V; $E^0\,(Zn^{2+}/Zn) = -\,0.76$ V; $E^0\,(Pb^{2+}/Pb) = -\,0.13$ V; $E^0\,(Sn^{2+}/Sn) = -\,0.14$ V; $E^0\,(Al^{3+}/Al) = -1.66$ V; $E^0\,(Ni^{2+}/Ni) = -0.25$ V.

SOLUTION

Zn and Al can provide protection to steel because they oxidize easier than Fe. They are anodic to steel.

Exercise 7. A steel nut is securely tightened onto a bolt in an industrial environment. After several months, the nut is found to contain numerous cracks. Explain why cracking might have occurred. Could this be avoided by using inhibitors? And coatings?

SOLUTION

It is an example of stress corrosion. When a tensile stress is applied to the material under a corrosive environment, several cracks propagate in a direction perpendicular to the stress.

Inhibitors (eliminate active species in solution) and coatings (prevent diffusion of O_2 and H_2O vapor) can modify the corrosive environment but not the tensile stress.