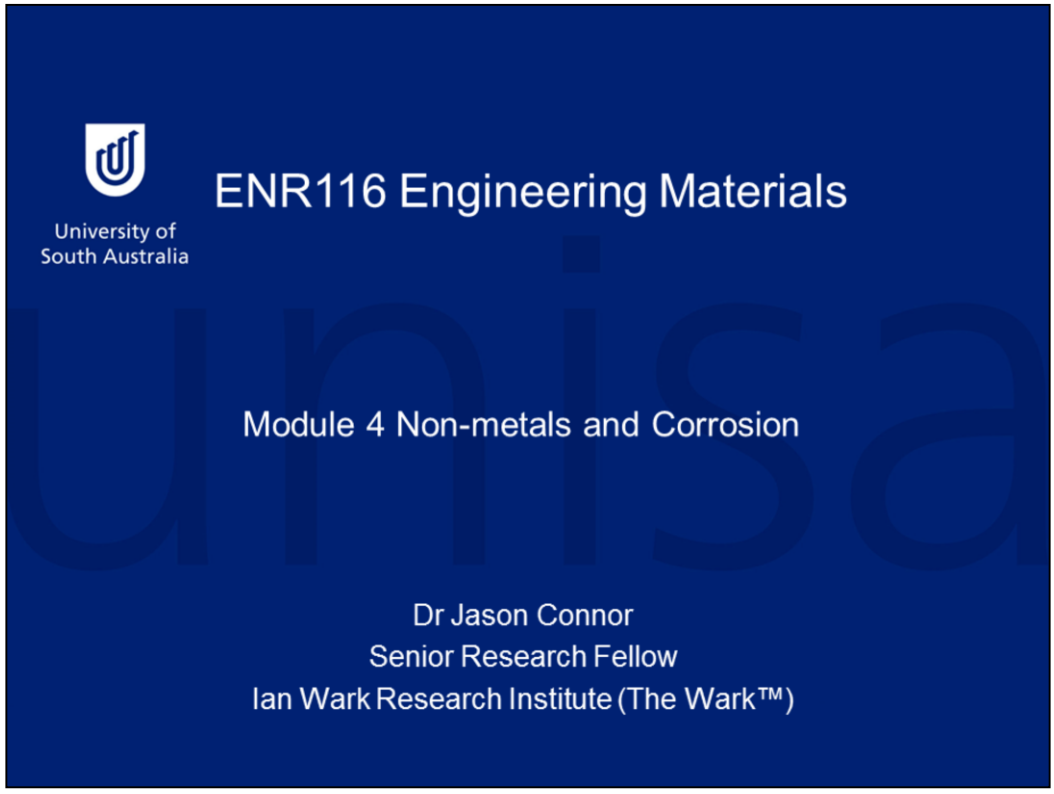
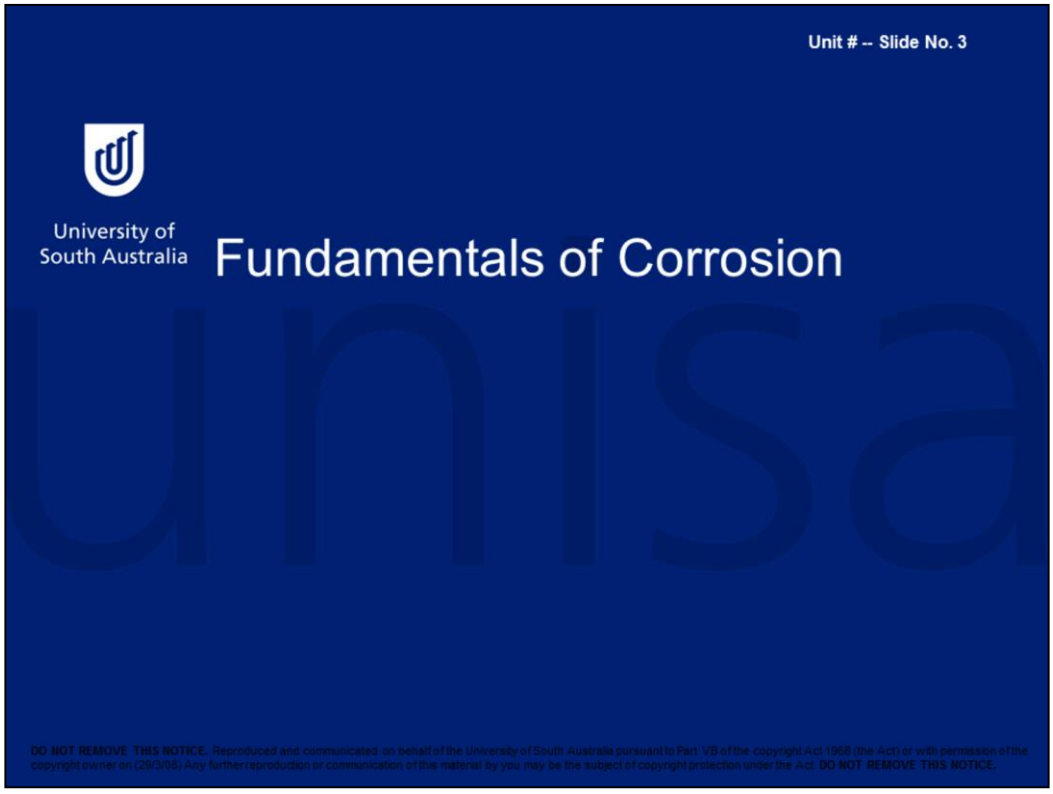


Hello and Welcome to Module 4 and Non-metals and Corrosion which is part of ENR116 Engineering Materials



In this lecture we will be looking at some fundamental aspects of corrosion and in particular some of the basic electrochemical concepts that underpin our understanding of why corrosion occurs.

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Intended Learning Outcomes

At the end of this section, students will be able to:-

- Understand why corrosion occurs.
- Appreciate the concepts of oxidation and reduction.
- Identify the four requirements for corrosion to occur.
- Use the standard EMF series to determine whether a metals will corrode under a particular set of conditions.

What I hope you will be able to take away from this presentation is a basic understanding of the corrosion process and of the concepts of oxidation and reduction and how they relate to corrosion. You should also be able to identify the four requirements for corrosion to occur and begin to appreciate how these could be exploited to prevent corrosion. Finally, you should be able to use the standard EMF series to predict whether a metal will corrode in a particular environment.

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Why is corrosion important?

Corrosion can affect anything from household items to high tech industries.

Oil drip tray under bag of fertiliser.

Surgical spinal rod.

It is well known that corrosion is an expensive problem often costing between 1 and 3 % of a countries GDP to address either directly or indirectly. The problems it can cause range from the trivial to the disastrous. In this slid we see two examples of objects corroding. In the first case the drip tray underneath a bag of fertiliser is heavily corroded. In the second case we have corrosion of a surgical spinal rod. I'm sure all of you will be familiar with other examples of corrosion like rusting cars, tools or iron roofs.

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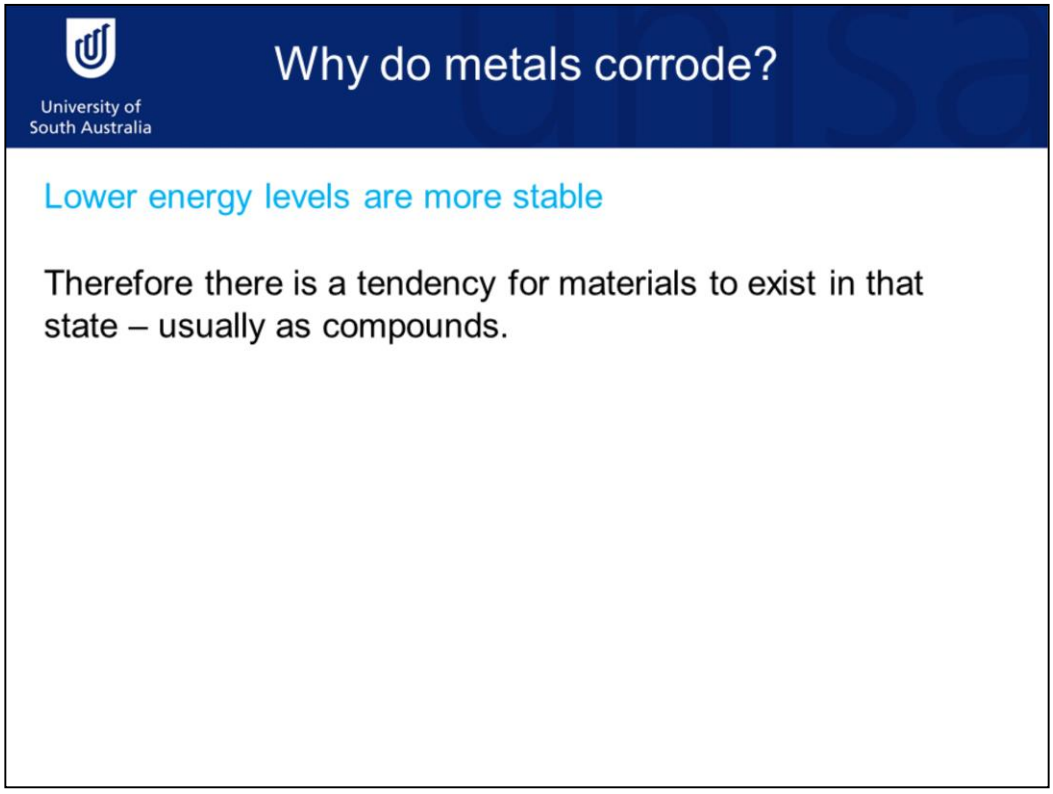
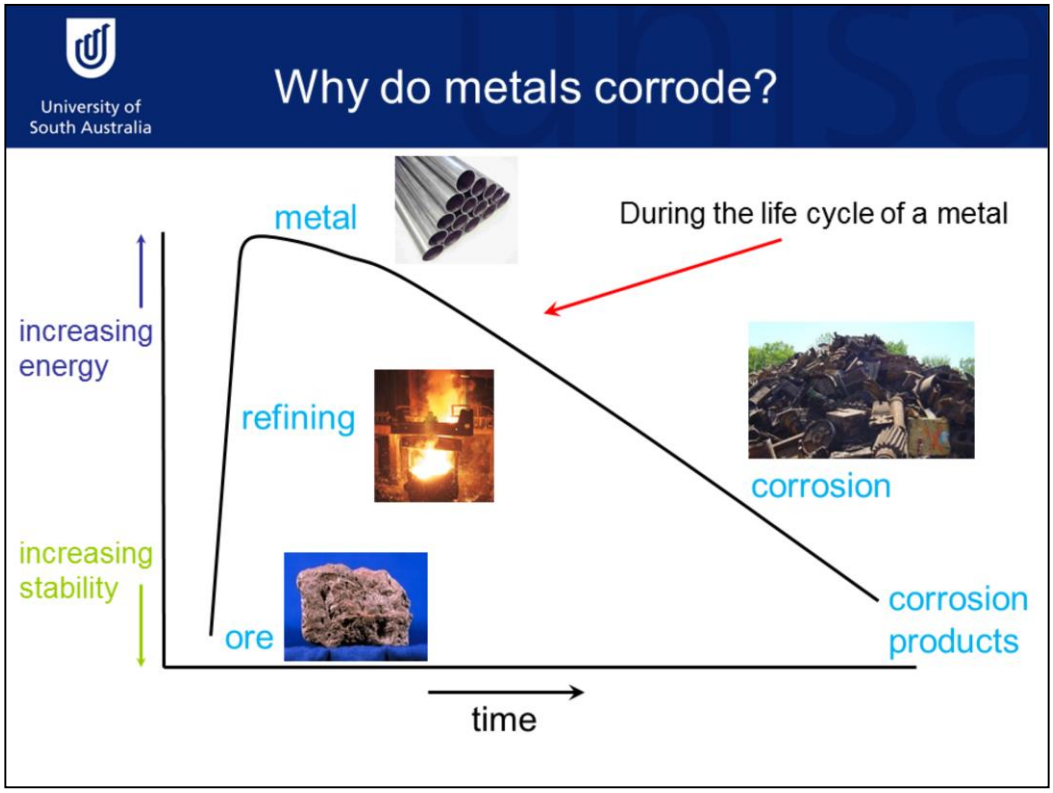
Corrosion can strike anywhere

What caused the mid-air breakup of the F-15? The main structure behind the cockpit failed due to corrosion.

My predecessor for this course presented a great sequence of images, shown here, of an expensive aircraft falling apart in midair as a result of corrosion. Organisations in Australia such as the DSTO have invested many research hours in developing sensors suitable for monitoring corrosion hotspots in the defence forces air fleet in an effort to prevent similar catastrophes. Fortunately in this example the pilot survived. As future engineers working in process plants, production lines, construction and mine sites I will not be surprise if at some stage in your career you will be required to deal with corrosion issues. I am hoping that this series of presentations will provide enough information that you will be able to expand your knowledge to be able to deal with the problems you are likely to face.



OK, so now we ask the question – why do metals corrode in the first place? In nature things tend toward minimising their energy. This is because lower energy levels are more stable. Metals like most materials are no different – they also prefer to exist in their most stable form which are usually compounds. In the next slide we will work through the lifecycle of a metal part to illustrate this point.



So if we now consider the lifecycle of a metal over time we see that when it is in the ore the metal has the highest stability. In this example we are looking at iron.

Iron is typically extracted from hematite which is an iron oxide. We should also note that this stability is associated with a low energy.

During the refining process we put energy into extracting just the iron (so that it is no longer an oxide).

With some additional energy we can then turn the iron into a useful product. However, you will also notice that this corresponds to the least stable form of the metal.

Finally, over time, the metal will eventually degrade via corrosion, with the final corrosion products again being the most stable state. In this example the iron rusts to form iron oxide again.

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Why do metals corrode?

Lower energy levels are more stable:

Therefore there is a tendency for materials to exist in that state – usually as compounds.

Energy level is related to the potential:

$$\Delta G = -n E F$$

ΔG = change in Gibbs free energy.
n = valency (number of electrons involved).
F = Faradays constant.
E = electrochemical potential.

ΔG must be negative for a reaction to be spontaneous.

Therefore potential of the **reaction** must be positive.

I think when most people think of corrosion they think of an chemical reaction. In fact corrosion is a result of an electrochemical reaction with charge, in the form of electrons, moving from one material to another. However, there must be an impetus for the charge to move and this is provided by an electrochemical potential. As the charge moves the free energy of the system has to change. So clearly there is a relationship between energy and electrical potential and this is show in this equation.

In most cases it is only necessary to worry about the change in energy rather than the absolute value hence delta G is the change in Gibbs free energy. This change in energy is related to the number of electrons involved in the process, a constant – known as Faradays constant - and the electrochemical potential which provides the driving force for the reaction. If delta G is negative the reaction will be spontaneous. It should be clear that for this to happen the electrochemical potential has to be positive, since n and F are always positive values. We now have a way of evaluating whether corrosion will spontaneously occur or not and we will explore this more a little later on.

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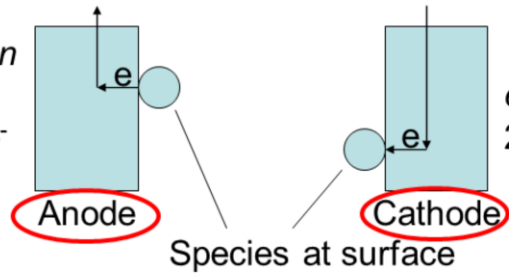
Basic electrochemical concepts

metal oxidation
i.e. corrosion
$M \rightarrow M^{n+} + ne^-$



e.g. reduction
$2H^+ + 2e^- \rightarrow H_2$

From Hibbert, D.B. Introduction to Electrochemistry, The Macmillan Press Ltd, 1993

Oxidation occurs at the ANODE
Reduction occurs at the CATHODE

Oxidation Is Loss of electrons (OIL)
Reduction Is Gain of electrons (RIG)

Before we go any further though I want to give you a little background electrochemistry to describe generally what happens in an electrochemical reaction as well as define some terms. At a very basic level what we are dealing with is the movement of charge from one place to another. If this occurs within an “electrode” nothing much happens however if the charge is near an interface there is an opportunity for the electron to move to a different phase and we may see something interesting.

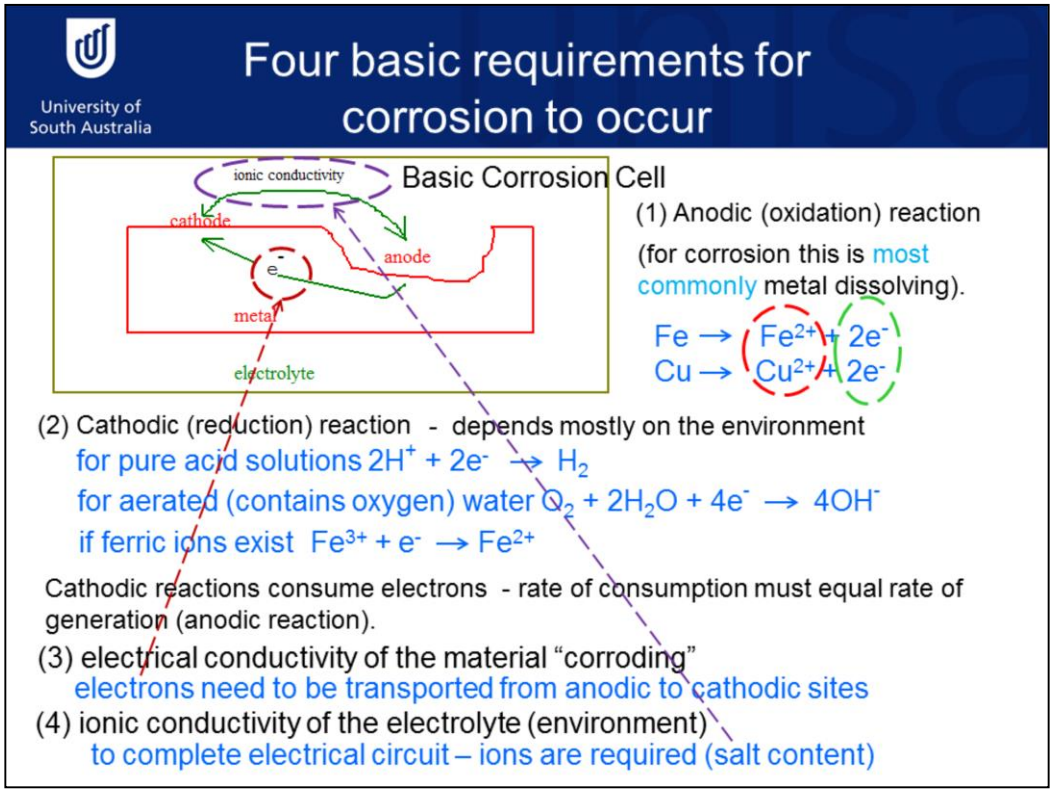
So if we do this by example, in the picture shown we have two metal electrodes. One is known as the anode and this is where electrons are lost and oxidation occurs. The other electrode is the cathode and it will gain electrons and reduction takes place.

If you need to remember the definitions of oxidation and reduction you can use the pneumonic OIL RIG where OIL stands for oxidation is loss of electrons and RIG stands for reduction is gain or electrons. In the picture given the metal at the anode is corroding. The electrons are lost from the metal close to the surface and travel through the anode to the cathode via a conductor.

What's left at the anode surface is a metal ion that is positively charged (since it lost some of the negatively charged electrons) and this ion will end up in the solution.*

At the cathode on the other hand we have gained these electrons which can be transferred to some positively charged species in solution. In this example the hydrogen ion is positively charged but ideally wants to be neutral so it accepts the electrons and becomes hydrogen gas.

The reactions are shown next to each electrode. M is used generically to indicate a metal, n is the number of electrons that the metal looses and e is the electron. At the cathode we have a more specific, but common, example of the reduction process in an aqueous environment where hydrogen ions gain an electron and become hydrogen gas.



In order for corrosion to occur 4 requirements have to be satisfied. Here we have a basic corrosion cell consisting of a piece of metal immersed in a solution. You will notice that metal acts as both the anode and cathode but these are at different positions on the metal. Let us first consider what happens at the anode. Without an anode corrosion can not occur. This is where the metal will be oxidised and most likely removed by dissolving in solution. If the metal were iron or copper the anoditic reaction would result in the products shown. For iron we would have Fe 2+ and 2 electrons and for copper Cu 2+ and 2 electrons.

The next requirement is a cathode. There has to be a place for the reduction reaction to take place. Electrons travelling to the cathode will be available to react with positively charged ions in solution. The nature of this reaction depends on the environment so for pure acid solutions where there will be an abundance of H+ ions the electrons will combine with the hydrodren ions to produce hydrogen gas. If the solution contains oxygen hydroxide ions will be produced. And in the final example where we have a ferric ion the addition of the electron will reduce its charge and it will become a ferrous ion.

Now the electrons require a conductive path to travel from the anodic to the cathodic sites and this is the third requirement shown. In this case the metal itself is also the conductor. In the previous slide where

we had physically separated the anode and cathode a wire would have to be connected between the two to enable the transport of the electrons.

Finally, we need to complete the electrical circuit since the rate of electrons generated by the anode has to equal that consumed by the cathode. This other conductive path is provided by the ionic conductivity of the electrolyte. Adding salt will increase the ionic conductivity.

If any of the requirements are missing the metal will not corrode. Methods of controlling corrosion involve removing one or more of these.

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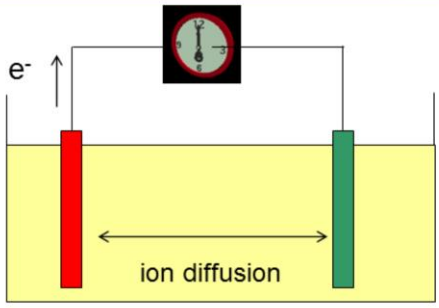
Driving force for corrosion



ΔG must be negative, reaction potential positive.
Potential difference between anode and cathode so that electrons will flow from anode to cathode sites.

Some sources of potential in a corrosion cell

usually mV or less but can be ~ volt

Dissimilar metals (galvanic corrosion)

the more active material is the anode
e.g. Mg in Mg-Cu

Oxygen variations at the surface

low oxygen areas are the anode

We said previously that the change in Gibbs free energy must be negative for corrosion to occur and the reaction potential has to be positive.

Electrons cannot flow between the anode and cathode without this potential difference.

What magnitude of potential difference is required for corrosion to proceed and where does it come from? Typically the potential difference can be quite small, of the order of mV but can be up to a volt.

One common source of a potential difference is the presence of dissimilar metals in solution. This will lead to galvanic corrosion where the more active material is the anode and will corrode. For example if we have magnesium and copper rods that have been connected together externally by a wire and immersed in an electrolyte solution the magnesium will corrode because it is the more active of the two. Some of you may recognise this as a very basic battery where the potential difference produced during the corrosion process can be used to do useful work.

Another source of the potential difference can be due to variations of oxygen levels at the surface of the metal. Regions that are low in oxygen become the anode.

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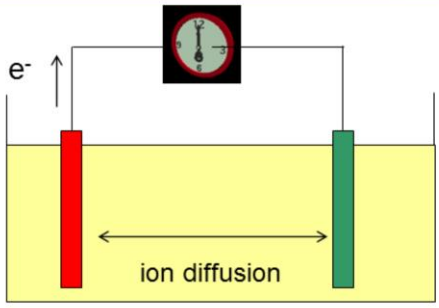
Driving force for corrosion



ΔG must be negative, reaction potential positive.
Potential difference between anode and cathode so that electrons will flow from anode to cathode sites.

Temperature variations at the surface

hotter areas are the anode

Localised plastic strain at the surface

greater amounts of plastic strained and stressed areas are the anode

Microstructural variations in the material corroding

some microstructural phases are more active than others

Other factors that may contribute to creating a potential difference between the anode and cathode are:

Temperature variations at the surface where the hotter areas behave as the anode.

Localised plastic strain where the stressed regions become the anode and microstructural variations within the metal itself where some phases can be more active than others.

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Standard EMF series

EMF series - a series of reactions arranged according to the tendency for the reduction reaction relative to the standard hydrogen reference electrode.

reaction	E° [volts vs SHE]
$Au^{3+} + 3e^{-} \rightarrow Au$	+1.498
$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$	+1.229
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$	+0.401
$Cu^{2+} + 2e^{-} \rightarrow Cu$	+0.337
$2H^{+} + 2e^{-} \rightarrow H_2$	0.000
$Ni^{2+} + 2e^{-} \rightarrow Ni$	-0.250
$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.440
$Cr^{3+} + 3e^{-} \rightarrow Cr$	-0.744
$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.763
$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$	-0.828
$Al^{3+} + 3e^{-} \rightarrow Al$	-1.662
$Mg^{2+} + 2e^{-} \rightarrow Mg$	-2.363

Will copper corrode in pure air free acid?

$Cu \rightarrow Cu^{2+} + 2e^{-}$ -0.337 V

$2H^{+} + 2e^{-} \rightarrow H_2$ 0.000 V

$Cu + 2H^{+} \rightarrow Cu^{2+} + H_2$ -0.337V

$\Delta G = -nEF$ will be positive – reaction as written will **not** be spontaneous.

Will copper corrode in aerated acid?

To predict whether corrosion is likely to occur we can use what is known as the standard EMF series. This series describes the reaction potential for reduction reactions relative to the standard hydrogen reference electrode under standard conditions of temperature and ion concentration. We will work though some examples to show how it can be used.

The first case we will consider is a copper electrode in pure, air free, acid. The reduction reaction we are interested in EMF series is the reaction where copper 2+ plus 2 electrons is reduced to copper metal. The potential associated with this process is positive 337 mV with respect to a standard hydrogen electrode. However, because we want to know whether the copper will corrode we need to rewrite it as an oxidation reaction so that copper metal oxidises to copper 2+ plus 2 electrons. Since we have reversed the reaction the sign of the associated potential has to be swapped which means our potential is negative 0.337 V.

The cathodic reaction will be the reduction of 2 hydrogen ions plus 2 electrons to hydrogen gas. This has a potential of 0 mV.

We can combine these two reactions by simply adding the left hand side of the anodic and cathodic reactions together and adding the right hand side anodic and cathodic reactions. You will notice that because the 2 electrons are present on both the left and right hand side these will cancel out. In a similar fashion we can add the anodic and cathodic potentials together and you will see we arrive at a value of negative 0.337 V.

Because delta G is positive the reaction as written will not be spontaneous.

In the second example we consider the case of a copper electrode in aerated acid. Details of the calculation are provided on the next slide.

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Calculation of EMF: Single metal

Reaction	E^0 [volts vs SHE]
$Au^{3+} + 3e^- \rightarrow Au$	+1.498
$O_2 + 4H^+ + 4e^- \rightarrow 2H_20$	+1.229
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.250
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.828
$Al^{3+} + 3e^- \rightarrow Al$	-1.662
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.363

Oxidation Reaction:

$Cu \rightarrow Cu^{2+} + 2e^-$ **- 0.337 V**

Reduction Reaction:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_20$ **+1.229 V**

Add reactions:

$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$

Add potentials:

Eo = - 0.337 + (+1.229)

Eo = **+0.892V**, ΔG is negative

The first of the two reduction reactions we are interested in are copper 2+ plus 2 electrons goes to copper metal. Again, because we are interested in whether the copper metal corrode we rewrite this as an oxidation reaction so the potential is negative 0.337 V.

The cathodic reaction will be O2 plus 4 H+ plus 4 electrons goes to 2 water molecules. This has a potential of positive 1.229 V. The combined anodic and cathodic reaction is shown. You will notice that when we add negative 0.337 V and 1.229 V together the value is positive 0.892 V. Because it is positive, delta G will be negative and the reaction will proceed spontaneous and the copper metal will corrode.

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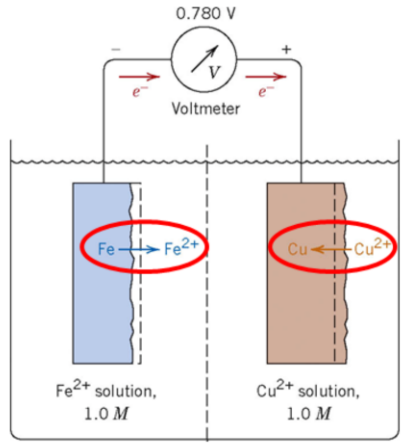
Calculation of EMF: Two metals

reaction	E^0 [volts vs SHE]
$Au^{3+} + 3e^- \rightarrow Au$	+1.498
$O_2 + 4H^+ + 4e^- \rightarrow 2H_20$	+1.229
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.250
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.828
$Al^{3+} + 3e^- \rightarrow Al$	-1.662
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.363

Fig. 17.02, *Callister & Rethwisch 8e.*



Anodic (oxidation)
$Fe \rightarrow Fe^{2+} + 2e$ (+0.440 V)

Cathodic (reduction)
$Cu^{2+} + 2e \rightarrow Cu$ (+0.337V)

The previous example was for a single piece of metal where the other half of the corrosion cell was provided by ions in solution interacting with the metal surface at a different sites. Now we look at what happens when we have two metals coupled together (i.e. two half cells). You will notice that the iron is in a solution containing Fe 2+ and the copper is in a solution containing Cu 2+ ions. A membrane is placed between the two solutions to prevent the two ions mixing. The two pieces of metal are also connected together to enable electron transport from the anode to the cathode. It should be clear we have satisfied the four requirements for corrosion to take place.

Now lets look at the individual reactions at each electrode. The reaction at the anode has to have a lower potential than that at the cathode to ensure the change in Gibbs free energy is negative and the reaction is spontaneous. In this case the iron reduction reaction is more negative than the copper reduction reaction so it will behave as the anode. Remember this must be re-written as an oxidation reaction so the sign of the potential will change from negative to positive. So the potential for the iron oxidation is positive 0.440 V. The reduction reaction occurs at the copper cathode and has a potential of positive 0.337 V.

When we add the two potentials together we have a potential of

positive 0.780 V hence the change in Gibbs free energy is negative. In this cell, which by the way is essentially a battery, the metal iron will corrode and Fe 2+ will dissolve in solution while Cu 2+ will combine with 2 electrons to form metallic copper. This copper will plate the copper cathode.

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Calculation of EMF: Two metals

reaction	E^0 [volts vs SHE]
$Au^{3+} + 3e^- \rightarrow Au$	+1.498
$O_2 + 4H^+ + 4e^- \rightarrow 2H_20$	+1.229
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.250
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440
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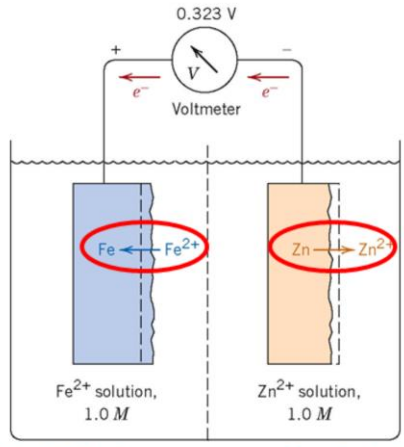
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.828
$Al^{3+} + 3e^- \rightarrow Al$	-1.662
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.363

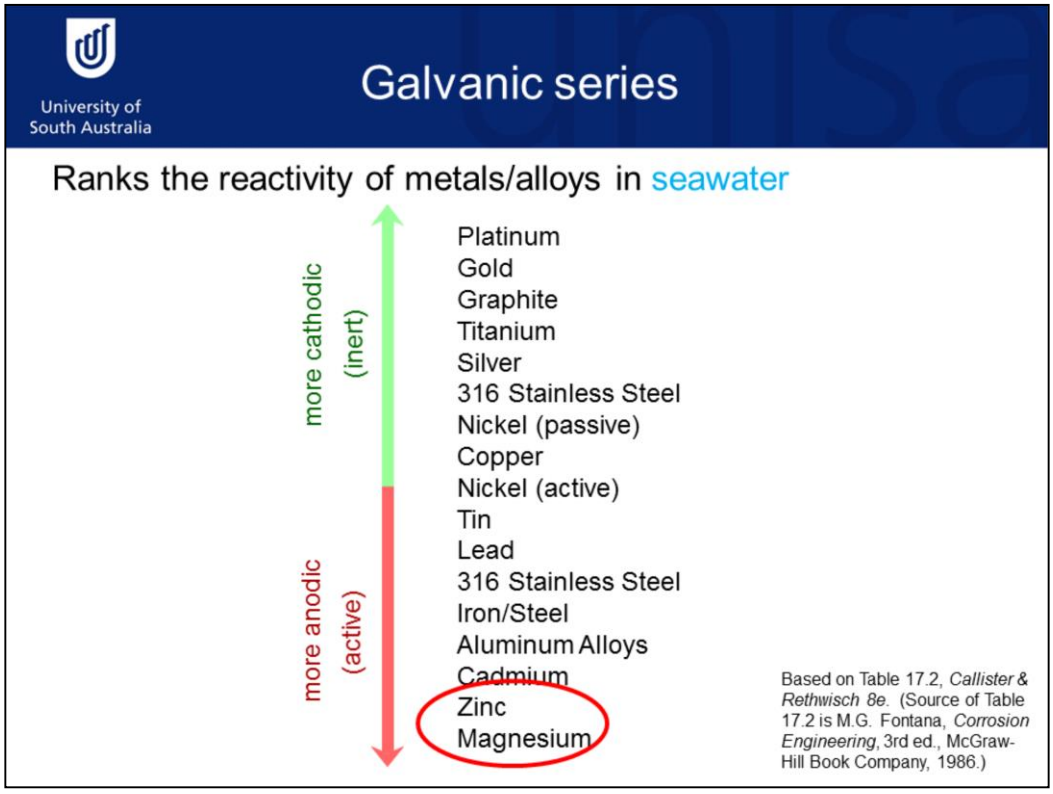
Fig. 17.03, *Callister & Rethwisch 8e.*



Cathodic (reduction)
$Fe^{2+} + 2e \rightarrow Fe$ (-0.440 V)

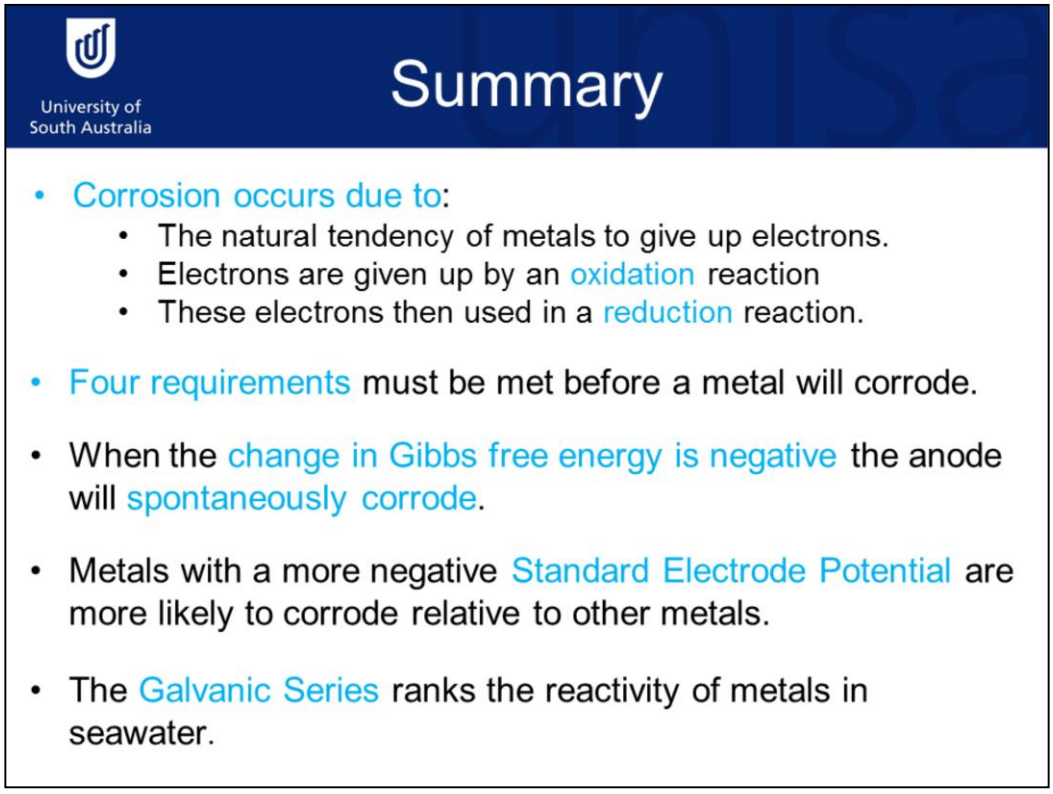
Anodic (oxidation)
$Zn \rightarrow Zn^{2+} + 2e$ (+0.763)

In this case the Fe reduction reaction is now more positive than the Zn reduction reaction – hence Zn now corrodes and Fe deposits on the Fe electrode.



The previous standard EMF series generally deals with pure metals. In practise it is more useful to have a similar set of information for common engineering materials. The galvanic series shown here ranks the reactivity of both metals as well as alloys in seawater. You will notice that zinc and magnesium are very low in this series. This means that these materials will corrode when coupled with any other metal or alloy higher up the series in the same way reactions lower down the EMF series are anodic when coupled with reactions higher up the series.

In the next presentation we will revisit the galvanic series and look at how it can be used to help in corrosion control strategies.



In this presentation we have looked at some basic information regarding the nature of corrosion.

The key points to take away from this are:

Corrosion occurs because metals tend to give up electrons easily. When they do an oxidation reaction occurs at the anode. For corrosion to take place there also needs to be a cathodic site where a reduction reaction also occurs. The number of electrons given up by the anode has to equal the number gained by the cathode. This is simply the conservation of matter. Having and anode and cathode is not sufficient to initiate corrosion, there must also be a conductive path between the solids and one through the liquid. For an anodic reaction to be spontaneous the change in Gibbs free energy has to be negative. This change in energy can be determined by considering the standard EMF series which ranks the potentials of a set of reduction reactions. Reactions that have more negative potentials are more likely to corrode than those with more positive potentials. In a similar vain to the standard EMF series, the Galvanic series ranks the reactivities of metals and alloys.

Thank you