

CATHODIC PROTECTION FOR SMALL CRAFT



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The first practical use of cathodic protection is generally credited to Sir Humphrey Davy in the 1820s. Davy's advice was sought by the Royal Navy in investigating the corrosion of copper sheeting used

for cladding the hulls of naval vessels. Davy found that he could preserve copper in sea water by the attachment of small quantities of iron or zinc; the copper became, as Davy put it, "cathodically protected".

To understand cathodic protection, it is necessary first to understand how corrosion is caused. For corrosion to occur, three things must be present:

1. Two dissimilar metals
2. An electrolyte (water with any type of salt or salts dissolved in it)
3. A metal (conducting) path between the dissimilar metals

The two dissimilar metals may be totally different alloys – such as steel and aluminium – but are more likely to be microscopic or macroscopic metallurgical differences on the surface of a single piece of steel. In this case, we will consider freely corroding steel, which is non-uniform.

If the above conditions exist, the following reaction takes place at the more active sites: (two iron ions plus four free electrons).



The free electrons travel through the metal path to the less active sites, where the following reaction takes place: (oxygen gas is converted to oxygen ion - by combining with the four free electrons - which combines with water to form hydroxyl ions).

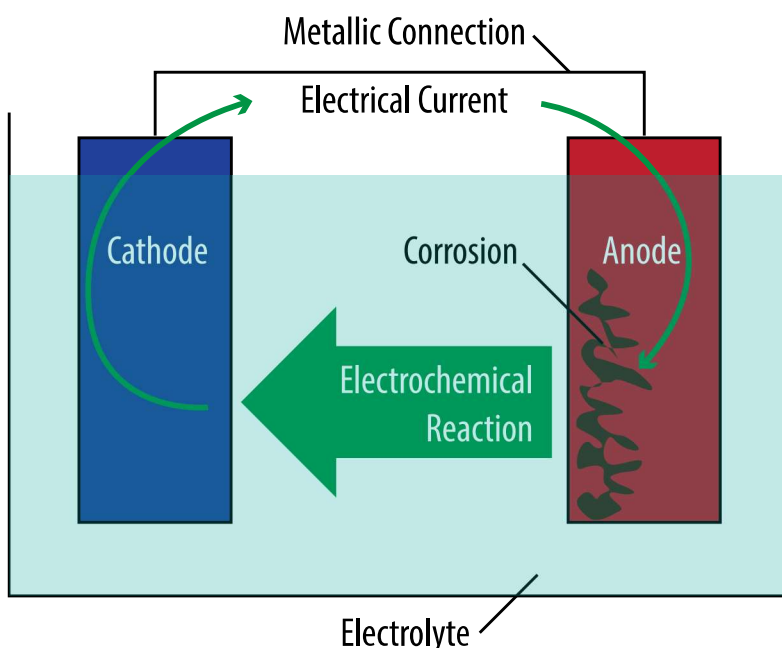


Recombination of these ions at the active surface produce the following reaction, which yields the iron corrosion product: (iron combining with oxygen and water to form ferrous hydroxide).



This reaction is more commonly described as 'current flow through the water from the anode (more active site) to the cathode (less active site).'

Basic Cell Corrosion



How does cathodic protection stop corrosion?

Cathodic protection prevents corrosion by converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites by supplying electrical current (or free electrons) from an alternate source.

Usually this takes the form of anodes, which are more active than steel. This practice is also referred to as a sacrificial system, since the anodes sacrifice themselves to protect the structural steel from corrosion.

In the case of aluminium anodes, the reaction at the aluminium surface is: (four aluminium ions plus twelve free electrons)



and at the steel surface: (oxygen gas converted to oxygen ions which combine with water to form hydroxyl ions).



As long as the current (free electrons) arrives at the cathode (steel) faster than oxygen is arriving, no corrosion will occur.

The electrical current that an anode discharges is controlled by Ohm's law, which is:

$$I = E/R$$

I = Current flow in amps

E = Difference in potential between the anode and cathode in volts

R = Total circuit resistance in ohms

Initially, current will be high because the difference in potential between the anode and cathode are high but as the potential difference decreases due to the effect of the current flow onto the cathode, the current gradually decreases due to polarization of the cathode.

The circuit resistance includes both the water path and the metal path, which includes any cable in the circuit. The dominant value here is the resistance of the anode to the seawater.

For most applications, the metal resistance is so small compared to the water resistance that it can be ignored (although that is not true for sleds or long pipelines protected from both ends). In general, long, thin anodes have lower resistance than short, fat anodes.

They will discharge more current but will not last as long.

Therefore, a cathodic-protection system designer must recommend anodes so that they have the right shape and surface area to discharge enough current to protect the structure and enough weight to last the desired lifetime when discharging this current.

As a general rule of thumb:

The weight of the anode determines how much current the anode can produce, and consequently, how many square metres of steel can be protected.

Galvanic corrosion - often misnamed electrolysis - is one common form of corrosion in marine environments. It occurs when two (or more) dissimilar metals are brought into electrical contact under water. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone.

Either (or both) metal in the couple may or may not corrode by itself (themselves) in seawater. When contact with a dissimilar metal is made, however, the self corrosion rates will change: corrosion of the anode will accelerate; corrosion of the cathode will decelerate or even stop. The choice of material depends upon the position of the metals concerned in what is

known as the galvanic series. For information, the galvanic series is given in the table below. It is a list of metals and alloys ranked in order of their tendency to corrode in marine environments.

Metals at the top of the scale are called noble and those at the bottom base. The galvanic series can be used to predict which metal will become the anode and how rapidly it will corrode. If any two metals from the list are coupled together, the one closer to the anodic (or active) end of the series, the upper end in this case, will be the anode and thus will corrode faster, while the one toward the cathodic (or noble) end will corrode slower. For example, suppose an aluminium alloy with a voltage range of -0.7 to -0.9 V (an average of -0.8 V) as shown on the series, is coupled to a 300 series stainless steel with an average voltage of -0.07 V.

The galvanic series predicts that aluminium will be the anode, and the voltage difference between the two alloys will be about 0.73 V (obtained by subtracting the two average voltages). It is this voltage difference that drives the current flow to accelerate corrosion of the anodic metal.

The two major factors affecting the severity of galvanic corrosion are:

- the voltage difference between the two metals on the galvanic series
- the size of the exposed area of cathodic metal relative to that of the anodic metal.

The weight of the anode determines how much current the anode can produce, and consequently, how many square metres of steel can be protected.

The Galvanic Series

MATERIAL	ELECTRICAL POTENTIAL RANGE (IN VOLTS)
TITANIUM AND ALLOYS	+0.06 to -0.05
300 SERIES STAINLESS STEELS	0.00 to -0.15
MONEL METAL	-0.04 to -0.14
COPPER	-0.14
COPPER NICKEL	-0.13 to -0.22
LEAD	-0.19 to -0.25
SILICON BRONZE	-0.24 to -0.27
MANGANESE BRONZE	-0.25 to -0.33
CAST BRASSES AND BRONZES	-0.24 to -0.40
NAVAL BRASS	-0.30 to -0.40
ALUMINIUM BRONZE	-0.30 to -0.40
HIGH STRENGTH STEELS	-0.60 to -0.63
LOW STRENGTH ALLOY STEELS	-0.57 to -0.63
PLAIN CARBON STEELS	-0.60 to -0.70
CAST IRONS	-0.60 to -0.72
ALUMINIUM ALLOYS	-0.70 to -0.90
ZINC	-0.98 to -1.03
ALUMINIUM	-1.25 to -1.50
MAGNESIUM	-1.60 to -1.63

Corrosion of the anodic metal is both more rapid and more damaging as the voltage difference increases and as the cathode area increases relative to the anode area. The approximate voltage difference for any two metals can be taken directly from the table. It is worth noting that marine slime films composed primarily of microscopic bacteria and diatoms can change the potentials of many of the alloys near the noble end of the galvanic series as indicated.

The potentials of these alloys become more positive in the presence of slime films thus increasing the voltage difference when these metals are placed in contact with more anodic alloys. This has been found to increase the corrosion rate of copper, steel and aluminium anodes by a factor of 2 to 5 but to have no effect on the

corrosion rate of zinc anodes. It may also change which metal in the couple becomes the anode.

When the two metals in a galvanic couple are close together on the series, such as manganese bronze and silicon bronze, their voltage ranges overlap and either one can be the anode, depending on the exact exposure conditions. In this case, more detailed information would be needed to predict the behaviour of the couple. The effect of the second factor above, the cathode to anode area ratio ($R_{C/A}$) is illustrated by the example of a rivet in a plate. In the first situation the rivet is of aluminium and is comparatively small and the plate of stainless steel and the $R_{C/A}$ ratio is large. In the second the situation is reversed: the stainless steel rivet is small and the $R_{C/A}$ ratio is also small.

In both aluminium is the anode and stainless steel is the cathode. Corrosion of the aluminium rivet in the first arrangement would be severe. However, corrosion of the large aluminium plate in the second arrangement would be much less even though the potential difference is the same in each case.

The cathodic member of the couple is one of those alloys identified as being influenced by slime films and, if there is a reason not to paint, periodic cleaning of the bare metal surface can minimize the effect of the slime and reduce the corrosion rate of the anode. Periodic cleaning is not recommended for reducing galvanic corrosion of other alloys because removal of corrosion product films from those metals usually increases corrosion rates.

Whenever the vessel is slipped, the existing anodes should be wire brushed back to bright metal and then coated with soft soap before painting the hull. Any paint accidentally applied to the anodes will then wash off with the soft soap when the vessel is placed in the water. If it is necessary at some time for the vessel to change from a salt to a fresh water environment or vice versa then it should be borne in mind that this will have a deleterious effect on the anodes fitted.

Magnesium or aluminium anodes (which are suitable for fresh water) have a much higher driving potential than anodes manufactured from zinc. If a vessel fitted with magnesium or aluminium anodes passes into salt water for anything longer than about seven days, the anodes will waste away very quickly.

Vessels which are fitted with magnesium or aluminium anodes moving into a salt water environment for longer than a week, should therefore be fitted with a replacement zinc anodic system. Conversely vessels fitted with zinc anodes (suitable for use in salt water) will find over a period

exceeding about seven days that the metal will be coated with an impervious off-white crust of zinc salt which will very effectively prevent it working even when returned to salt water.

After any trip into a fresh water environment a vessel fitted with zinc anodes should have these thoroughly scaled clean back to bright metal. If proceeding into fresh water for longer than about seven days a vessel should be fitted with replacement magnesium or aluminium anodes. In no case should magnesium anodes be fitted to the hull of wooden boats.

The selection of sacrificial anodes for a vessel is dependent on the surface areas and type of metals to be protected taking into account their electronegative potentials. The marine surveyor should note that the ABYC inter alia states that a sacrificial anode should induce and maintain a minimum negative shift of 200 mV relative to the least noble (or most negative) metal.

The issue of under protection is, of course, well understood. Put simply, too little protection results in corrosion. The various Formulae and methods given above were designed with that requirement in mind and are backed up by the author's experience.

Over Protection

The marine surveyor should also be aware that it is possible to put too many anodes on a boat, a danger which is called over-protection. That occurs when the sacrificial anodes generate a current higher than necessary to protect the more noble metallic fittings. Common issues on metal, frp, ferro-cement and wooden hulls given over protection include: -

1. **Paint stripping** – This is the hydrogen blistering of paint and occurs because of the destruction of the adhesion between the coating and underlying metal to which it has been applied. The

defect can be often seen near where sacrificial anodes are attached to steel or fibreglass hulls. The process often results in local blistering of the paint coat near the anodes and is often referred to as cathodic disbondment. It is sometimes mistaken as osmotic blistering.

2. **The repulsion of anti-fouling and propeller coatings** – In the same manner as hull paint stripping, over protection can lead to the non-retention of these coatings due to the incompatibility of the application with sacrificial anodes. It can render the application ineffective and often leads to increased barnacle and other marine growth attachment.

3. **Marine Growth** – Excessive cathodic protection accelerates the formation of calcareous deposits on a vessel's hull, rudders and propellers including a calcium carbonate coral like structure.

4. **Alkali Attack** – This can also arise as a result of excessive cathodic protection systems and can lead to the formation of alkaline conditions on metallic hulls when there is insufficient flow of water to return the water to its natural pH, resulting in accelerated corrosion. This can be accentuated as the paint blisters to create an even more alkaline condition and further lead to rapid deterioration of the submerged metal. Also seen on wood – see below.

5. **Embrittlement and Metal Blistering** - Studies have also shown that the metal-hydrogen interaction which is effected by the entry of hydrogen into the interstices within the metal's crystal structure by the over protection potentials may significantly influence the strength behaviour of mild steel by the influence of the hydrogen on the rate of increase of lattice dislocation multiplication i.e. the metal tends to become brittle. Ductility may be retained if the potential does not exceed

-900 mV. In wrought iron, the hydrogen tends to collect inside the metal causing metal blistering near the anodes.

Defects due to over protection can also be found on wooden hulls. Cellulose is the natural polymer which gives wood its remarkable strength and is a major component of the material where lignin holds the cellulose together. Over protection resulting from the galvanic current flowing between the anode and cathode destroys the lignin and that results in the effects of localised wood decomposition and the defect called angel's hair.

The images below show the result of installing too many anodes



The Images below show the results of Over Protection within the confines of a small water ballast tank.



Anode Calculations for Iron and Steel Hulls.

The surface area of the hull and anode determines the amount of protection given. The voltages of all metals will vary depending on the salinity of the electrolyte and the total weight of anodic material determines the useful life of the protection system. On a metal hull, it is common to use the standard formula for sea water immersion:

For the hull's wetted surface: in square metres it is usually accurate enough to use Kirk's formula. The current density: mA per square metre is approximately 35 for steel, the immersion hours factor is (8760 hours/year times the number of years intended service (usually 2) times the fraction of the year the vessel is in the water

and the energy content in amp-hours is 368 for zinc anodes at 99% efficiency. The factor for other metals is usually obtainable from the Galvanic Table.

For FRP hulls it is necessary to determine the amount of exposed underwater metals of different type, but easier to install standard anodes and then attach fish anodes until the desired potential is reached.

$$\text{Anode Weight} = (\text{Hull's Wetted Surface}) \times (\text{Current Density}) \times (\text{Immersion}) / (\text{Energy Content}) \times (1000\text{mA/Amp})$$



Estimated remaining life of existing anodes is calculated from

$$L = \frac{12 + 19.2k(1 - \%_A)}{\%_A} \text{ months}$$

L = Life months
 %_A = percent loss of anodic material per anode
 k = 1.00 for zinc, 0.90 for magnesium

Weight of one anode is calculated from

$$W_A = \frac{aqld}{10^3} \text{ kg}$$

l, b, d = the dimensions of the anode cm
 q = 7.13 zinc
 1.74 magnesium
 a = 0.38 for ovoid anodes
 0.55 for long anodes
 0.89 for flat anodes
 0.59 for circular anodes

The Wetted Surface Area of the Hull is calculated from a modification of the well known Kirk's analysis:

$$S_A = k.L(B + 2d) \text{ m}^2$$

L = Length m
 B = Breadth m
 d = Mean draught m
 k = Constant -

Required current amperage is calculated from

$$A = S_A \times C_D / 1000 \text{ Amps}$$

S_A = Wetted Surface area m²
 C_D = Current Density mA/m²
 10 – 30 generally about 20

Total weight of anodic material required to give this amperage is calculated from

$$W^A = \frac{A \times Y \times 8760}{C} \text{ kg}$$

W^A = Weight of required anodic material kg
 Y = Required life in years Y
 8760 = Number of hours in one standard year h
 C = Capacity of Anodic Material ah/kg
 = 780 for zinc
 = 2700 for aluminium
 = 2000 for magnesium

Recommended life of anodes for small craft is two years (3 years maximum).



It is generally recognised that it is good practice to place the anode(s) at a point where it or they can 'see' the item it is or they are protecting. For example, one can often inspect transom sterned motor boats where the anodes have been placed on the transom. While there is nothing intrinsically wrong with that, the anodes cannot 'see' the items they are protecting and, therefore, work less efficiently than those that would be placed under the flat of the bottom. The anodes are generally reckoned to have a working range of about 5 metres (15 feet) and should be so spaced to include that idea.

Again, for example, one often inspects narrow boats of, say, fifty feet length with an anode fitted each side on the forward swim and another on the after swim. Careful inspection of the hull will show that the middle section out of the 5 metre range will be badly pitted. Such boats should have an anode fitted at mid length each side taking care not to thereby put the boat 'out of gauge'.



It has become common practice on such canal boats to place anodes inside small boxes inset into the hull. Experience will show that the steel forming the interior of the box will be in pristine condition while that plating surfaces even quite nearby will be badly pitted. The anode cannot see the steel it is supposedly protecting.