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Practical Electrochemistry for Conservators and Conservation Scientists: Part I – The Basics of Potential Measurement

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Electrochemical techniques are used in conservation to identify metals or corrosion products, or to monitor or treat metal objects. Although there are many published reports on these techniques, it is difficult to find practical information on how to get started to use them. This paper provides some of this information for one important application of these techniques, namely measurement of corrosion potential (the potential of an object immersed in a liquid electrolyte with respect to a reference electrode). Topics covered include electrochemical cells, multimeters, electrical connection to objects, electrolytes and, especially, reference electrodes – common types of reference electrodes, how to use, protect and maintain them, and how to troubleshoot problems. Examples are given of measuring corrosion potential and using Pourbaix diagrams.

Les techniques électrochimiques servent en conservation pour identifier des métaux ou des produits de corrosion ou encore pour surveiller ou traiter des objets métalliques. Bien qu'il existe un grand nombre de rapports publiés sur ces techniques, il est difficile de trouver de l'information pratique lorsqu'on veut commencer à les utiliser. Cet article fournit quelques renseignements à ce sujet à propos d'une importante application de ces techniques, soit la mesure du potentiel de corrosion (le potentiel d'un objet submergé dans un électrolyte liquide par rapport à une électrode de référence). L'article traite notamment des cellules électrochimiques, des multimètres, de la connexion électrique aux objets, des électrolytes et, plus particulièrement, des électrodes de référence (types courants d'électrodes de référence, comment les utiliser, les protéger, les entretenir et régler les problèmes). L'article présente des exemples de mesure du potentiel de corrosion et de l'utilisation des diagrammes de Pourbaix.

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INTRODUCTION

Electrochemical techniques have been adapted to conservation use for identifying metals or corrosion products, and for monitoring the stability of metal objects or for treating them.[1-4] For a conservator or conservation scientist who would like to use these techniques, the problem is getting started – finding detailed, practical information on how to set up and use electrochemical equipment appropriate for conservation.

This is the first of two papers discussing information that is essential in applying electrochemistry to conservation. This paper, Part I, discusses how to measure corrosion potential, and gives practical advice in choosing and caring for reference electrodes, choosing a voltmeter, making electrical contact with a metal object, choosing an electrolyte and understanding potential measurements. Part II discusses aspects of using electrochemical techniques that combine current and potential measurements to characterize the corrosion on a metal object, or to reduce corrosion products either to a different compound or back to the metallic state.[5]

The following section of this paper reviews some of the terminology of electrochemistry. The next section covers the equipment and materials needed to make a potential measurement. A large part of this section is devoted to the reference electrode because it is a key component in these measurements. The next section provides a procedure for making potential measurements, followed by another section containing two examples. The final section before the conclusion gives background information about equilibrium potentials, corrosion potentials and Pourbaix diagrams.

TERMINOLOGY

Two metals placed in a liquid electrolyte (a liquid containing ions from dissolved salts) form an electrochemical cell.[6] The voltage between the two metals, which are called electrodes, can be measured with a high-impedance voltmeter. This voltage, called the cell potential, is caused by oxidation and reduction reactions that occur at the electrode surfaces. In these reactions, some substance loses electrons (oxidation) and another gains electrons (reduction). The size and variation of the cell potential contain information on these reactions.

An electrochemical cell can be used to study the reactions at one of the electrodes, provided the other contributes a fixed value to the cell potential. The electrode under study is called the working electrode and abbreviated WE in the terminology of electrochemistry, and the electrode with the fixed contribution is called the reference electrode or RE.[6] A schematic diagram of an electrochemical cell is illustrated in **Figure 1**. In this case, the cell potential can be referred to as the potential of the working electrode relative to the reference electrode, or simply as the potential.

The term "cell potential" or "potential" applies whether or not current is flowing through the electrodes.[6] In the case illustrated in **Figure 1**, where the current is negligible when a high-impedance voltmeter is used, the potential is called the open-circuit potential. When the open-circuit potential is determined by a single reaction at equilibrium occurring at the metal surface, the potential is called an equilibrium potential or equilibrium electrode potential.[6,7] If the metal is inert, the reaction involves species in solution and not the metal itself, and the open-circuit potential is called an oxidation-reduction

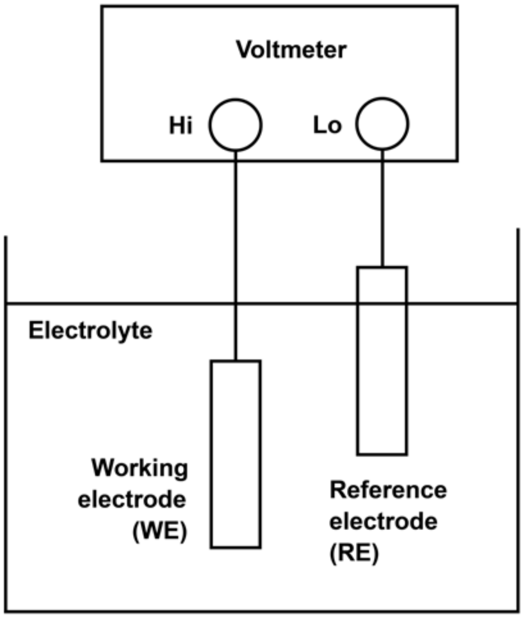

Figure 1. Schematic diagram of an electrochemical cell connected to a voltmeter.

potential or redox potential.[8] When the species involved in the reaction have a standard concentration and a specific reference electrode is used, as explained later, the potential is called the standard potential or standard electrode potential.[7,9]

When the open-circuit potential is determined by more than one reaction occurring at the metal surface, the potential is called a mixed potential, rest potential or corrosion potential (E_{corr}).[7] For example, oxygen (O_2, dissolved in the electrolyte) may be reduced to form hydroxide (OH^-) ions on one part of the working electrode, while the metal is oxidized to form soluble metal ions or solid corrosion products on another part. The corrosion potential depends on many factors, the main one being the concentration of all the species involved in the reactions – oxygen, hydroxide ions, metal ions and so on. But even when these concentrations are not known, corrosion potential measurements can be put to use – to monitor the progress of a treatment of a metal object in solution, for example, or to evaluate the stability of a metal object in solution.

EQUIPMENT AND MATERIALS

Reference Electrodes

The potential of a metal is always measured with respect to (or relative to, or versus) a reference electrode. In **Figure 1**, the metal (the working electrode) is connected to one terminal of a voltmeter (often labelled Hi or V) and the reference electrode is connected to the other (often labelled Lo or Com). More information about meters is given below in the section on multimeters. Each type of reference electrode shifts the measurement by a different value. For a reference electrode that is working properly, this value is constant with time and is unaffected by the small currents that flow through the electrode during a measurement.[10]

Standard Hydrogen Electrode (SHE)

A hydrogen reference electrode is constructed by bubbling hydrogen gas (H_2) over platinum (Pt) metal immersed in an acid. The reaction at the platinum surface involves the hydrogen molecules in the gas, hydrogen ions (H^+) in the solution, and electrons (e^-) in the platinum:

$$2H^+ + 2e^- \rightleftharpoons H_2 \text{ (gas)}$$

For the special case where the hydrogen ion activity is unity (the pH in solution is near 0) and the hydrogen gas partial pressure is exactly 1.00 atmosphere (about 1 bar), the hydrogen electrode is called a standard hydrogen electrode (SHE) or a normal hydrogen electrode (NHE).[6] The hydrogen reference electrode is important because the SHE was adopted as the zero value in the standard scale for potentials.[6] When a potential is determined by a single reaction at equilibrium under standard conditions, the equilibrium potential given on this scale (that is, versus SHE) is called a standard potential (E^0). In tables of standard potentials,[11] the hydrogen reaction has a value of zero at all temperatures.

Three Common Reference Electrodes

Hydrogen electrodes require hydrogen gas, making them difficult to use as well as a fire hazard. Other reference electrodes (called secondary reference electrodes) are generally used instead. Three common reference electrodes are the saturated mercury-mercury(I) sulfate electrode (SSE or MSE), the saturated calomel electrode (SCE) and the silver-silver chloride electrode (Ag/AgCl). Equilibrium potentials versus SHE for these three reference electrodes at 20ºC and 25ºC are given in **Table I**.[10,12]

Table I. Comparison of Three Common Reference Electrodes

Reference Electrode (name and short form)	Abbreviation	Electrochemical Reaction	Equilibrium Potential vs. SHE (mV)
Saturated mercury-mercury(I) sulfate; Hg|Hg_2SO_4 (sat'd), K_2SO_4 (sat'd)	SSE	Hg_2SO_4 (solid) + $2e^- \rightleftharpoons$ 2Hg (liquid) + SO_4^{2-}	655 (20°C) 651 (25°C)
Saturated calomel; Hg|Hg_2Cl_2 (sat'd), KCl (sat'd)	SCE	Hg_2Cl_2 (solid) + $2e^- \rightleftharpoons$ 2Hg (liquid) + $2Cl^-$	248 (20°C) 244 (25°C)
Silver-silver chloride; Ag|AgCl (sat'd), KCl (sat'd)	Ag/AgCl	AgCl (solid) + $e^- \rightleftharpoons$ Ag(solid) + Cl^-	204 (20°C) 199 (25°C)

As an example, the SSE is shown schematically in **Figure 2**.[13] It consists of liquid mercury (Hg) and solid mercury(I) sulfate (Hg_2SO_4) in an inner glass body, enclosed in an outer glass body that contains the filling solution, which is a solution saturated in potassium sulfate (K_2SO_4). The filling solution in the outer glass body is usually separated from the electrolyte in an electrochemical cell by a porous frit. Once added to the reference electrode through the filling hole, the filling solution becomes saturated in Hg_2SO_4, so the electrode is designated in short form as $Hg|Hg_2SO_4$ (sat'd), K_2SO_4 (sat'd).[14]

The equilibrium potential of the SSE is determined by the reduction of Hg(I) in Hg_2SO_4 to Hg metal, as shown in **Table I**. The equilibrium potential remains constant as long as solid Hg_2SO_4 and liquid mercury are present and remain in contact, and the filling solution remains saturated. The SSE is usually only used with a saturated solution of K_2SO_4, not with more dilute solutions.[13]

The other two common reference electrodes follow a similar pattern to the SSE. The SCE is based on reduction of Hg(I) in calomel (Hg_2Cl_2) to Hg metal and the filling solution is saturated potassium chloride (KCl). The calomel electrode is sometimes prepared with a filling solution that is not saturated in chloride ions (Cl^-). The equilibrium potential depends on the concentration of chloride ions; for example, at 25ºC the equilibrium potential vs. SHE is 0.250 V for 3.5 M KCl, 0.283 V for 1.0 M KCl, and 0.336 V for 0.1 M KCl.[12]

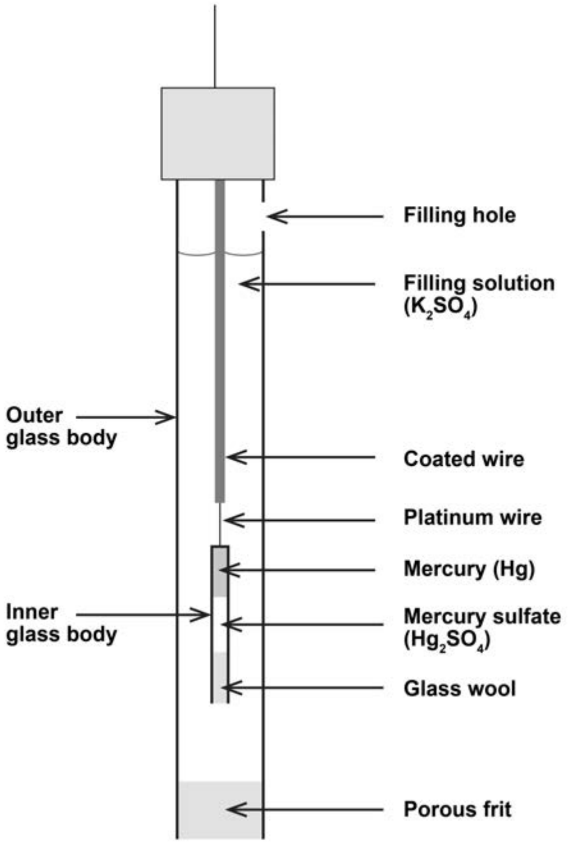

Figure 2. Schematic diagram of a saturated mercury-mercury(I) sulfate reference electrode (SSE).

The Ag/AgCl electrode is based on reduction of Ag(I) in AgCl to Ag metal and the filling solution is saturated KCl and saturated AgCl. The electrode is sometimes used with other concentrations of KCl; for example, the equilibrium potential relative to SHE at 25ºC is 205 mV for 3.5 M KCl,[12] 235 mV for 1 M KCl, 250 mV for 0.6 M Cl^- (seawater), and 288 mV for 0.1 M Cl^-.[15] Ag/AgCl electrodes can have a simpler design than the SSE in **Figure 2**, and it is straightforward to make one.[16-18]

One important difference between Ag/AgCl and the other two electrodes has to do with the filling solutions. The filling solutions for the two mercury-based electrodes do not have to contain mercury salts. The small amount of Hg_2SO_4 or Hg_2Cl_2 required to saturate the filling solution can be supplied by the mercury salt in the interior section of the electrode. For the Ag/AgCl electrode, however, the filling solution should be prepared saturated in both potassium chloride and silver chloride,[19] because otherwise all of the solid silver chloride could be dissolved after a few replacements of the filling solution. Although the solubility of silver chloride in pure water is low (about 10^{-5} M at 25ºC), it increases in saturated potassium chloride to 6×10^{-3} M due to the formation of soluble complexes such as $AgCl_2^-$.[19] The storage solution for a Ag/AgCl reference electrode should also be saturated in AgCl and KCl.

All three of these reference electrodes give good results. The electrodes containing mercury have to be disposed of as hazardous waste and are becoming more difficult to purchase because of restrictions on mercury. Those containing chloride ions might be unsuitable if it is critical to avoid chloride ion contamination of test or treatment solutions, although the salt bridges discussed below will largely eliminate contamination.

Converting Between Reference Electrodes

In practice, a secondary reference electrode is used instead of the SHE for measurement, whereas the potential versus SHE is often given in published diagrams, such as the Pourbaix diagrams to be discussed below. Thus it is necessary to convert potentials between values measured versus different secondary reference electrodes as well as to convert potentials to the SHE scale. The conversion is based on the following relationship between the potential, E, of a metal versus some reference electrode RE, the potential of the metal versus SHE, and the potential of the reference electrode versus SHE:

$$E \text{ (metal vs. RE)} = E \text{ (metal vs. SHE)} - E \text{ (RE vs. SHE)}$$

Values for E (RE vs. SHE) for 20°C and 25°C are listed in **Table I**. **Table II** gives the conversion factors for the three common reference electrodes at 20°C and 25°C. For example, if the potential of a metal object at 25°C is measured to be −151 mV when the reference electrode is an SSE, this value is converted to the SHE scale by adding 651 mV, giving $E = (-151 + 651) = +500$ mV vs. SHE.

Whenever potentials are reported in a publication, the values should be given with respect to some reference electrode, as in "500 mV vs. SHE." Without this information, the reader must hunt through the publication to find which reference electrode was used, and then must decide whether the potentials are being given with respect to that reference electrode, or whether they

Table II. Conversion Factors between Three Common Reference Electrodes and the SHE

	From a value versus a reference electrode to the SHE scale		From the SHE scale to a value versus a reference electrode	
	20°C	25°C	20°C	25°C
SSE	add 655 mV	add 651 mV	subtract 655 mV	subtract 651 mV
SCE	add 248 mV	add 244 mV	subtract 248 mV	subtract 244 mV
Ag/AgCl	add 204 mV	add 199 mV	subtract 204 mV	subtract 199 mV

have been converted to the SHE scale. The best way to avoid confusion is to specify the reference electrode each time a potential is quoted. Various conventions can be used, such as 500 mV vs. SHE (as used here), 500 mV (SHE), 500 mV/SHE, 500 mV (vs. SHE) or 500 mV_{SHE}. Also, the reference electrode information should be stated clearly at some point, usually in the experimental section. For example, a sentence such as the following could be used:

> All potentials were measured and quoted against a mercury-mercury(I) sulfate (Hg/Hg_2SO_4) saturated potassium sulfate (K_2SO_4) reference electrode, which has a potential of 0.651 V versus a standard hydrogen electrode (SHE) at 25ºC.

If graphs are presented showing the potential versus some reference electrode other than an SHE, a second axis should be added, if possible, showing the potential versus SHE.[15]

Protecting Reference Electrodes and the Electrolyte Solution with a Salt Bridge

The electrolyte in the filling solution of a reference electrode generally is different from the electrolyte around the metal object being studied or treated. To keep the two electrolytes from mixing, the end of the reference electrode is sealed with a frit (a porous glass or ceramic plug). These frits leak, by necessity; with no leakage, there can be no ionic current, and the cell potential cannot be measured. Typical glass frits used in reference electrodes leak at a rate of about 1 μL/h.[20] At this rate, for example, if a reference electrode that contains a saturated solution of KCl (about 4 M) is placed in an electrochemical cell containing 100 mL of electrolyte, then the concentration of K^+ and Cl^- in the cell will increase by 40 μM (1.4 ppm Cl^-) every hour as electrolyte from the reference electrode leaks through the glass frit. In most circumstances, this is not significant over a few hours, but it could become significant if the reference electrode is used continuously for several days. In a larger cell, such as a treatment tank, the concentration of K^+ and Cl^- will increase more slowly. Similarly, the electrolyte in the cell will leak back into the filling solution of the reference electrode.

One way to reduce this problem of cross-contamination is to use a salt bridge, or bridge tube, between the reference electrode and the electrolyte of the electrochemical cell. A salt bridge has an open end for the reference electrode, and a frit at the end that is inserted into the electrolyte. The solution in the salt bridge can be chosen to avoid contaminating the cell or the reference electrode, whichever is more important. For example, if the only reference electrode available is Ag/AgCl, but the treatment solution should not be contaminated with chloride ions, then an electrolyte without chloride ions should be chosen for the salt bridge. As with the glass frit in the reference electrode, the leakage through the glass frit in the salt bridge is small enough that the salt bridge should provide protection against chloride ion contamination for several hours.[2] Once a salt bridge has been wetted, it should not be allowed to dry out; when it is not in use, it should be stored in a container of the same solution.[2]

A salt bridge is shown in **Figure 3**, partly filled with electrolyte, and with the end of a reference electrode immersed in the electrolyte. Both the reference electrode and the salt bridge end in porous ceramic frits. This particular salt bridge has a fill hole on the side, visible under the lower clamp.

Porous frits introduce a small error into the measurement of potential. These errors are normally not a concern in applications in conservation, but if they are, they can be minimized by the choice of electrolyte in the salt bridge. Potassium chloride, sodium sulfate (Na_2SO_4) or potassium nitrate (KNO_3) at high concentrations are common choices.[10]

Reference Electrode Reliability

It is recommended that two reference electrodes of the same kind always be available, one to be used for regular electrochemical measurements and the other to be kept aside as a control.[10,20] The control reference electrode is used only to check that the regular-use reference electrode is in good working order. The potential of the regular-use electrode versus the control should be measured often (ideally on a daily basis during use) using the following procedure, illustrated in **Figure 4**. The potential should be almost zero, because the two electrodes are the same type.

For this measurement, it is best to use an electrolyte that is similar to the filling solution for the reference electrodes.[20] In this example, the electrolyte is potassium sulfate and the reference electrodes are both SSEs. Both the regular-use reference electrode and the control reference electrode are placed in a beaker containing an electrolyte and connected to a voltmeter. The regular-use electrode is connected to the "high" terminal and the control electrode is connected to the "low" terminal. Ideally, the difference between two electrodes of the same type is zero, but in practice, there is some variation between electrodes. If the meter reads less than about 3 mV, then the regular-use electrode is in good working order. If the

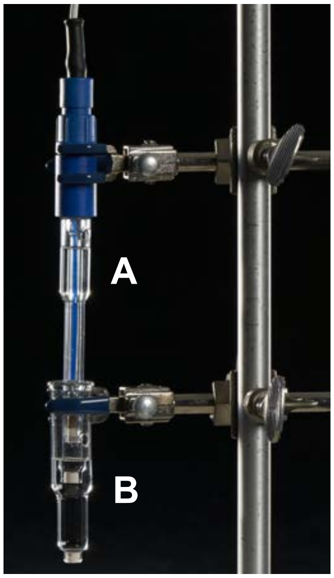

Figure 3. Reference electrode (A) and salt bridge (B), held in place with tri-grip clamps attached to the vertical pole of a laboratory stand.

Figure 4. Two reference electrodes (one for regular use, one reserved as a control) immersed in an electrolyte (here, saturated potassium sulfate), with the potential measured on a digital voltmeter. The meter reads 0.001574 volts (~1.6 mV).

meter reads greater than 5 mV difference, the filling solution in the regular-use electrode should be replaced. If that does not fix the problem, the electrode should be replaced if possible. If it is used, then the reading of the electrode will have to be corrected for the error and the electrode will have to be checked frequently. Before it is thrown out, however, another electrode should be tested, just in case the control electrode is the problem.

Electrode Storage and Troubleshooting

For most reference electrodes with liquid filling solutions, it is critical that the reference electrodes be kept wet and not be allowed to dry out. When the measurements are finished, the reference electrode should be removed and rinsed with distilled water, wicked dry and returned to its storage container, a bottle that contains the filling solution. A dark bottle or a bottle wrapped in aluminum foil is recommended, because some electrodes, such as Ag/AgCl, will degrade slowly in light. To prevent evaporation, the filling hole should also be sealed when the electrode is stored. The filling solution in some electrodes can be flushed out with distilled water and the electrodes can be stored dry; the manufacturer's instructions should be consulted in such cases. The electrolyte in a salt bridge should be replaced after a few hours of use.

A common problem with reference electrodes and with salt bridges is an air bubble trapped at the tip when it is inserted into a solution. A gentle tap on the electrode to dislodge the air bubble usually solves the problem. Gas bubbles may also accumulate under the reference electrode or salt bridge if gas is generated during a treatment. In electrodes and salt bridges where the frit is held in place with heat-shrink tubing, the tubing will trap bubbles if it extends past the open end of the tip.

The symptom of an air bubble is the appearance of sudden jumps or noise in the cell potential. Noise can also be caused by a poor electrical connection. The connection to some commercial electrodes has two parts that must be pushed straight together, and then a sleeve is rotated to hold them in place. If the parts are not pushed together properly, the electrical connection may be poor, even though the sleeve appears to be holding the parts properly.

If the fill hole on a reference electrode is sealed with a plug, the plug should be loosened or removed before the electrode is placed in an electrochemical cell. Otherwise, the electrolyte may not flow properly through the porous frit because of changes in atmospheric pressure. The electrolyte in a salt bridge should not be too close to the fill hole in the bridge, in case the electrolyte overflows through the fill hole when the reference electrode is inserted. If this occurs, the electrolyte in the cell may have to be replaced.

In reference electrodes with saturated filling solutions, salt may precipitate out onto the glass frit and block the pores in the frit. If this occurs, the precipitate can be dissolved by gently heating the electrode. One approach is to place the end of the electrode in a container of filling solution and place that container in a larger container of hot tap water. The electrode should be periodically lifted out and the electrolyte in it swirled around, to mix the warm and cool parts of the electrolyte and to see if the precipitate has been dislodged. The hot tap water should be replaced every few minutes.

When frits are held in place with heat-shrink tubing, the frit can be replaced if it becomes contaminated or begins leaking excessively. Instructions are available from the manufacturer (for example, Gamry[21]). The key step is heating the heat-shrink tubing with a hot air gun: the electrode or bridge must be rotated so that all sides of the heat-shrink tubing are heated evenly, avoiding excess heat that could damage the new frit. After the frit has cooled, any excess heat-shrink tubing at the end of the frit should be trimmed off, so that it cannot trap a gas bubble in solution. The tip should be examined once the filling solution is added to the electrode. If any electrolyte can be seen leaking around the tip, the tip must be replaced again.

Glass frits are not recommended for highly alkaline solutions. Ceramic frits can be used in strong bases.[13]

Multimeters (Voltmeters)

A digital voltmeter or multimeter can be used to measure the potential of a metal relative to a reference electrode. It is usually recommended that the input impedance of the meter be large, for example greater than 10^{10} ohms (10 GΩ).[22] Typical modern multimeters often have an impedance this large, at least on the low-voltage scales that would be used in a measurement in conservation. The voltage input terminals on these meters are often labelled "high" or "Hi" and "low" or "Lo." Less expensive or hand-held multimeters may have lower internal impedances, typically 10^7 ohms (10 MΩ). Voltage input terminals on these are often labelled "V" and "Com." With an input impedance below 10 GΩ, the current that flows through the reference electrode and the meter may interfere with processes of interest on the metal objects, such as corrosion.[22] Also, the current that flows through the meter may produce changes in the reference electrode. It could, for example, convert the silver chloride in a Ag/AgCl reference electrode to silver, if the working electrode is at a negative potential versus the reference electrode. If the Ag/AgCl reference electrode was made with a procedure[19] that produces only a small amount of silver chloride, the current through an impedance of 10^7 ohms could consume all the silver chloride in a few weeks of continuous use.

More sophisticated instruments called potentiostats can also be used for measuring potential. These instruments are used for treatments or scientific studies involving current in electrochemical cells with a third electrode (called a counter electrode). A potentiostat need not be purchased just for measuring potential, but it is convenient to use if available because it generally comes with data collection software included.

Making Contact with Immersed Metal Objects

Although expensive, platinum metal is one of the best inert materials for making contact with an immersed metal object. It does not corrode in most electrolytes and it is a good conductor. It can be used either as an electrode on its own (to measure the redox potential of a solution, for example, as discussed later) or as an inert metal to make electrical contact with an immersed object. A platinum electrode can be made with platinum wire and epoxy putty,[23] or can be purchased commercially. The wire must be thick enough to be stiff (1 mm diameter works well), and only a short length (about 1 cm) should be exposed to the solution. Platinum electrodes can be cleaned with nitric acid using a 1:1 mixture by volume of concentrated acid and deionized water.[24]

When the tip of a platinum electrode is immersed in the electrolyte so as to contact a metal, the measured potential will have a contribution from the platinum. But this contribution is small as long as the surface area of the metal is much larger than that of the platinum. Alternatively, if only part of the metal is immersed, contact can be made to the dry part of the metal, with an alligator clip, for example. The teeth on the alligator clip can be filed off to protect the metal from being scratched. Aluminum foil can be placed between the clip and the metal for further protection. If an organic coating is present on the object, it will interfere with electrical contact; it must be removed before carrying out a potential measurement.

In some cases it is possible to solder a wire to a test sample, but the solder connection and the wire must be covered with an insulating layer (such as epoxy or wax) to isolate them from the solution.[25] For objects that would be damaged by applying solder, silver paint covered with epoxy has been used.[26] For large corroded objects (an iron cannon, for example), stainless steel rods have been used for contact.[27] The rods can be sharpened to a point and inserted in a hole drilled through a corrosion or concretion layer.

Electrolytes

Potential measurements require some conducting ions in solution to carry the small current needed by the voltmeter. Often the potential measurements are done as part of a measurement or treatment in which larger currents flow through the solution; in those cases the concentration of the solution is high, typically about 0.1 M. Potential measurements by themselves can be done in solutions of lower concentration. For example, one study reported the measurement of the potential of metal threads as the object (a textile) was being rinsed in distilled water after treatment.[28] Presumably residual salts from the object made the solution conducting enough for the measurements to be made. Erratic measurements can be expected if the conductivity is too low. In measurements of pH (which are actually measurements of potential with a dedicated electrode and meter), low conductivity solutions near neutral pH have to be made more conducting with addition of a salt called an ionic strength adjuster.[29]

The choice of electrolyte depends on many factors, including the stability of the metal and its corrosion products. The metal's stability in an electrolyte can be evaluated using a Pourbaix diagram,[30] a plot of potential versus pH, discussed later in the paper. The electrolyte should have a pH in a range where the metal is passivated.[1,31] For example, at high pH (e.g., pH 13), iron is passivated, but aluminum is not. When possible, the pH of the electrolyte solution should be measured,[29] so that the pH and measured potential can be plotted on the appropriate Pourbaix diagram.

In some cases solutions near neutral pH must be used to protect other materials in an artifact, such as in the electrochemical treatment of tarnish on metal threads in textiles. For one such treatment,[32] different electrolytes were considered and the final choice was 0.1 M sodium nitrate ($NaNO_3$) buffered with acetic acid (CH_3COOH) and sodium acetate (CH_3COONa).

Electrolytes with chloride ions should be avoided if the purpose of a treatment is to remove chloride ions from iron objects. On the other hand, chloride ions are necessarily present in measurements of the potential of objects in seawater.[4]

EXAMPLE PROCEDURE FOR MEASURING THE CORROSION POTENTIAL

As discussed in connection with **Figure 1**, the corrosion potential, E_{corr}, of a metal is measured by making the metal one electrode of an electrochemical cell and using a high-impedance voltmeter so that a negligible amount of current flows through the cell. Measurement of corrosion potential is discussed here; the interpretation of it is discussed later in the paper. The procedure given here is appropriate for small objects. It needs to be adapted for large objects; for example, the platinum contact discussed here could be replaced with a contact such as stainless steel, as mentioned earlier.

Figure 5 shows a schematic diagram of one way to measure the corrosion potential of an immersed metal using a reference electrode and a platinum electrode. In this case, the metal is completely immersed in the chosen electrolyte and a platinum electrode is used to touch the metal and make electrical contact with it. In general, corrosion products or concretions are not conducting, so it may be necessary to remove the concretion or corrosion to allow electrical contact. The reference electrode is also immersed in the solution, or alternatively a salt bridge is inserted in the solution (as shown) and the reference electrode is inserted in the salt bridge. Before the reference electrode is immersed in the cell, it should be rinsed with distilled water to remove the storage solution (and avoid contamination), and excess water wicked dry with clean tissue (e.g., Kimwipes). The wires from the reference electrode and the platinum electrode are attached to the voltmeter. By convention, the reference electrode is attached to the low (negative) side of the voltmeter and the platinum electrode is attached to the high (positive) side.[15]

The container for the electrolyte is chosen to fit around the metal and the reference electrode. A small piece of metal could possibly fit in a beaker or a crystallizing dish; a large object might require a large plastic tub. Laboratory stands and clamps are convenient for supporting the electrodes. **Figure 6** is a photograph of a cell, with a platinum electrode contacting a small piece of copper metal on the left, and a reference electrode in a salt bridge on the right. The copper is supported on a small Plexiglas stand.

If it is important that data be obtained the instant the metal touches the electrolyte, then the electrical contacts should be in place before the electrolyte is added, and the electrodes should be placed so that the electrolyte reaches the reference electrode first. The reading on the voltmeter will fluctuate rapidly until contact is made. Once both electrodes are in the electrolyte, the reading will stabilize, but it will continue to change slowly as the corrosion potential varies with time. If the rapid fluctuations do not stop, there must be a problem, such as a poor contact or a bubble under the reference electrode.

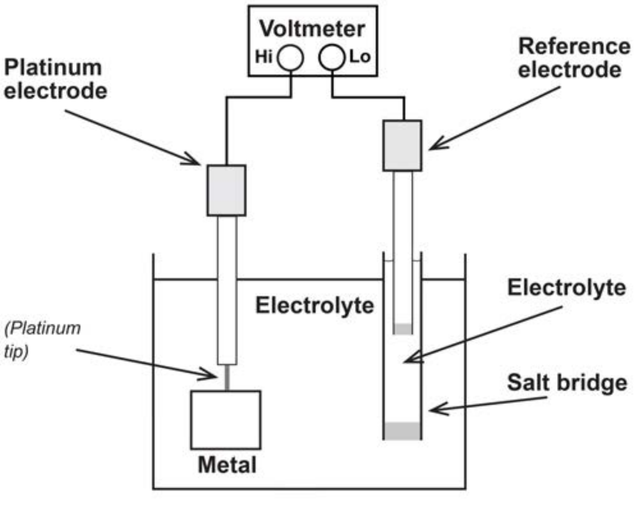

Figure 5. Schematic diagram for the measurement of corrosion potential. The platinum tip of the platinum electrode is pushed against the metal to make contact.

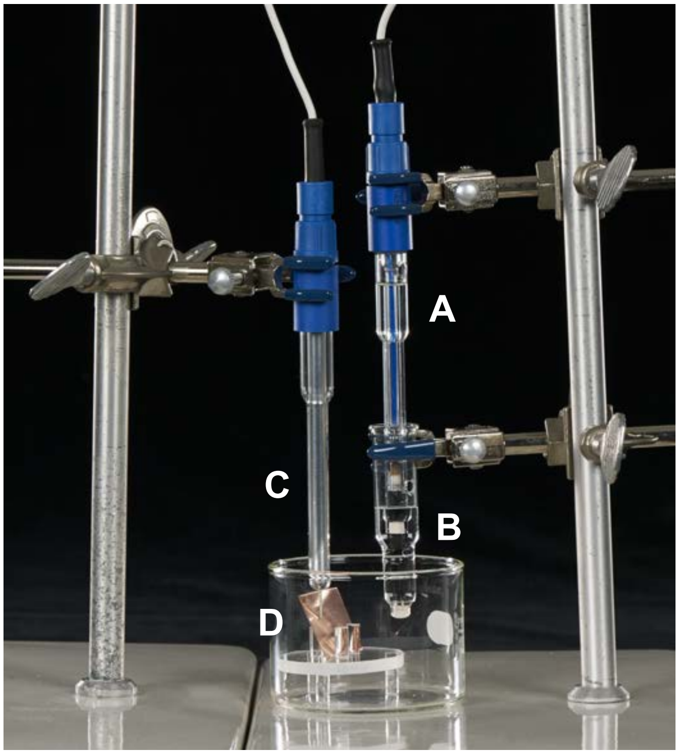

Figure 6. Configuration of an electrochemical cell to measure the corrosion potential of copper: (A) reference electrode, (B) salt bridge, (C) platinum electrode and (D) copper sample. For clarity, the electrolyte has not been added to the cell. The container is a 7 cm diameter crystallizing dish.

If available, data collection software on a personal computer can be used to record the corrosion potential as a function of time. Otherwise, readings can be noted by hand. How often and how long to record the data depends on the sample or object. For example, the corrosion potential can be monitored for a fixed time;[2] until there is a reasonably constant value (as in the two examples shown below); or for the duration of a treatment.[25,33] The readings of corrosion potential can be converted to the SHE scale (see **Table II**).

TWO EXAMPLES OF MEASURING THE CORROSION POTENTIAL

Two examples are given of monitoring corrosion potential with a cell like that in **Figure 6** using a Radiometer Analytical Ref621 SSE reference electrode and either a Solartron 1284 potentiostat or an Agilent 34401A digital multimeter. The purpose of these examples is to present typical results of the way in which corrosion potential changes with time. Some general comments on the interpretation of changes in corrosion potential are given later in the paper.

Example 1: Iron in Sodium Hydroxide (NaOH)

Figure 7 shows corrosion potential as a function of time for iron (cold-rolled steel freshly cleaned with sandpaper) placed in a solution of either 0.1 M sodium hydroxide (theoretical pH 13) or 0.01 M sodium hydroxide (theoretical pH 12) in deionized water. The measurements were made using a potentiostat and an SSE reference electrode. Only part of the iron was immersed in the solution; an alligator clip was used to make a connection to the dry part of the iron. The SSE was protected with a salt bridge containing saturated potassium sulfate. The magnitude of the corrosion potential and the variation with time are similar to measurements on uncorroded steel plates in 0.1% (w/v) potassium hydroxide (KOH).[33]

Example 2: Copper in Potassium Nitrate

In this example, the corrosion potential was measured locally on a small area of copper, following an approach used to identify copper-based alloys.[2] **Figure 8** shows the arrangement used for this example. The tip of a salt bridge was placed about 1 mm above a piece of copper cleaned with sandpaper. A drop of electrolyte (about 40 µL of 0.1 M potassium nitrate in deionized water) was placed in the gap between the salt bridge and the copper sample. The same electrolyte was used in the salt bridge.

Figure 9 shows the corrosion potential as a function of time. The measurements were made using a digital voltmeter and an SSE reference electrode.

EQUILIBRIUM POTENTIALS, CORROSION POTENTIALS AND POURBAIX DIAGRAMS

Although potential measurements are an important part of more sophisticated techniques used in conservation that involve a third electrode and the flow of current (to be discussed in Part II[5]), there are times when a potential measurement on its own may be important. The case where the cell potential is determined by a single reaction will be considered first. In general, however, the cell potential is determined by two or more reactions and is often called the corrosion potential. Corrosion potentials are usually discussed together with Pourbaix diagrams. Measurements of corrosion potential have been done in conservation to monitor the stability[4] and treatment[28] of objects.

Equilibrium Potential from a Single Reaction

When the cell potential is determined by the equilibrium of a single reaction in solution, where it is called the equilibrium potential or equilibrium electrode potential,[7,34] there is a relationship between the equilibrium potential and the concentration of species involved in the reaction. For the reversible reaction:

$$a\mathrm{A} + b\mathrm{B} + ne^{-} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

where the capital letters represent dissolved species and the lower case italic letters indicate the number of moles of each species, the equilibrium potential E (in volts) can be calculated from the Nernst equation:[35]

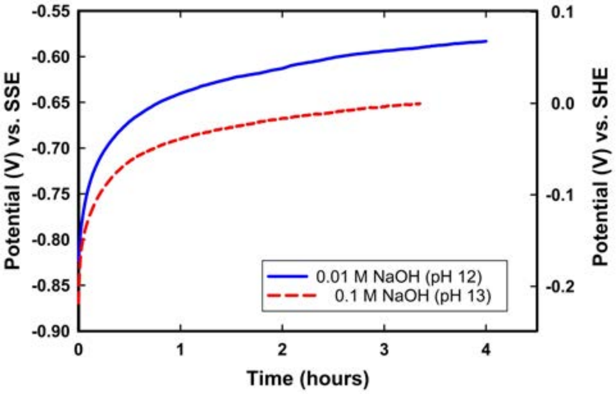

Figure 7. Corrosion potential as a function of time for freshly cleaned cold-rolled steel in 0.1 M sodium hydroxide (solid line) or 0.01 M sodium hydroxide (dashed line).

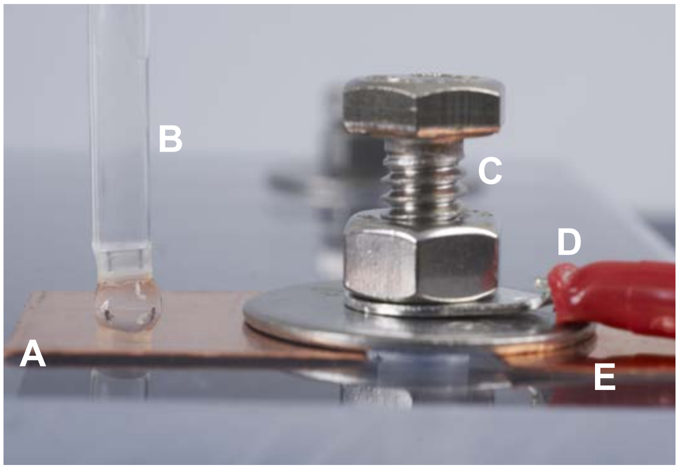

Figure 8. Measuring the corrosion potential of a copper sample (A) using a local measurement. Components include: (B) salt bridge, (C) nut and bolt, (D) ring terminal and (E) copper spacer.

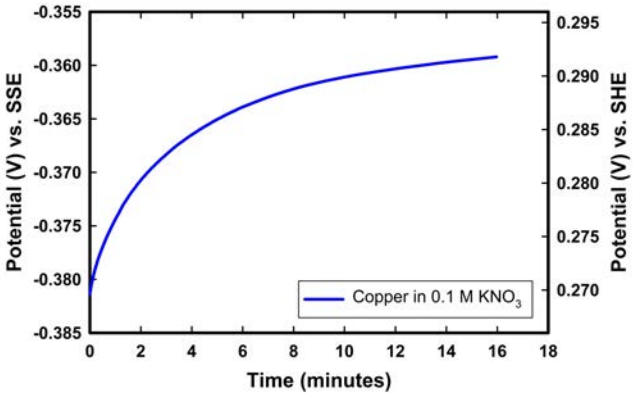

Figure 9. Corrosion potential as a function of time for freshly cleaned copper using a local measurement. The electrolyte was 0.1 M potassium nitrate.

$$E = E^o - \frac{2.303\,R\cdot T}{n\cdot F}\log_{10}\frac{[\mathrm{C}]^c\cdot[\mathrm{D}]^d}{[\mathrm{A}]^a\cdot[\mathrm{B}]^b}$$

Here E^0 is the standard potential or standard electrode potential,[7,9] R is 8.314 J K^{-1} mol^{-1}, T is the absolute temperature (K), n is the number of moles of electrons and F is 96,485 C (coulombs) per mole. The symbols [A] through [D] denote the activity of species A through D in moles per litre. Activity is a thermodynamic quantity closely related to the concentration and equal to concentration at small values.

An example is the equilibrium involving iodide ions (I^-) and triiodide ions (I_3^-):

$$I_3^- + 2e^- \rightleftharpoons 3I^-$$

Triiodide ions can be produced by reacting iodine with an excess of iodide ions (from potassium iodide, KI, for example).[36] The Nernst equation for this reaction at 25°C is:

$$E = E^o - \frac{0.0592}{2}\log_{10}\frac{[I^-]^3}{[I_3^-]}$$

Here E^0 is 0.536 V vs. SHE, and $[I^-]$ and $[I_3^-]$ are the activities in moles per litre of the two types of ions.

The equilibrium potential of such a reaction can be measured with an electrode made from an inert metal such as platinum, together with a reference electrode. This potential is also called the oxidation-reduction potential of the solution or the redox potential of the solution.[8] The equilibrium potential of the iodine reaction can be used in calibrating reference electrodes.[24,37]

Corrosion Potential

In general, more than one reaction occurs at the surface of a corroding metal, and these reactions never come to equilibrium. In this case, the potential of the metal measured relative to a reference electrode is called the corrosion potential, E_{corr}. The corrosion potential often stabilizes at a nearly constant value when a steady state is reached. For example, a metal such as iron (Fe) may be corroding, producing iron(II) ions (Fe^{2+}), while oxygen is being consumed, producing hydroxide ions (OH^-). In the simplest case, where no solid corrosion products are being formed, the reactions are:

$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$

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

These two reactions are called anodic and cathodic, respectively. The reactions can carry on indefinitely as long as there is a supply of oxygen and iron metal, because electrons are released by one reaction as fast as they are consumed by the other. If the Fe^{2+} ions and OH^- ions produced by the reactions diffuse away from the surface into the solution at a constant rate, their concentrations at the surface can reach a steady value, and then the corrosion potential will be constant. But this does not mean the corrosion has stopped; in fact, iron is being continually removed from the metal.

The corrosion potential provides a way to monitor conditions at the surface of a metal. The corrosion potential reflects a balance between various quantities, such as the concentration of the ions in the solution, or the area of the metal that is exposed to the solution and not covered up by corrosion products. When this balance is disturbed, the corrosion potential changes, perhaps because one of the concentrations in the solution near the metal surface is changing, or because the surface of the metal is being modified. In the example of iron, Fe^{2+} ions could be reacting with oxygen to form insoluble Fe(III) compounds, which can precipitate onto the surface and reduce the area where the reactions can occur.

Pourbaix Diagrams

Pourbaix diagrams, also known as stability diagrams or potential-pH diagrams, are calculated to provide a visual summary of the stability of metals against corrosion. They are plots of potential against pH, divided into regions according to which chemical form of a metallic element is the most stable. Pourbaix diagrams became well known through the work of Marcel Pourbaix, who calculated them for various metals in contact with water.[30] **Figure 10** shows a Pourbaix diagram for iron. In the region labelled "Immune," the most stable form is the metal itself, and the metal will not corrode. In the "Active" region, the most stable form is an ion of the metal (in **Figure 10**, these ions are Fe^{2+}, Fe^{3+} or dihypoferrite, $HFeO_2^-$), and the metal will corrode; it is said to be actively corroding. Finally, in the "Passive" region, the most stable form is a solid compound of the metallic element (in **Figure 10**, these compounds are iron(III) oxyhydroxide, FeOOH, or magnetite, Fe_3O_4). In this region, the metal can corrode, but may do so slowly or perhaps not at all if the compound coats the metal and protects it. A metal protected in this way is said to be passivated. It should be noted that the diagram indicates when solid

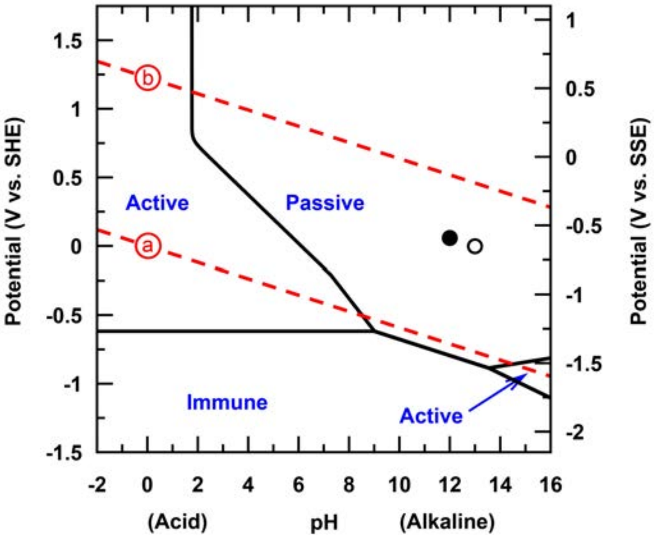

Figure 10. Pourbaix diagram for iron, calculated for 10^{-6} M concentrations of iron ions. Dashed lines (a) and (b) indicate the stability of water. Solid lines separate Active, Passive and Immune regions. Data points are from corrosion potential measurements made on iron after three hours at pH 12 (solid circle) and pH 13 (open circle) from **Figure 7**.

corrosion products form, but does not say how well the corrosion products protect the metal from further corrosion. The terms "Active," "Immune" and "Passive" are defined in **Table III**. For convenience, the potential scale versus SSE has been added to the right hand side of **Figure 10**, but this is not normally shown in Pourbaix diagrams. The water is assumed to be pure except for the ions added to adjust the pH, such as Na^+ ions from NaOH. These ions are assumed to be inert; that is, they do not react with iron or form insoluble iron salts. Pourbaix diagrams can also be calculated with ions that are not inert, such as chloride ions or carbonate ions.[38]

Table III. Definition of States used in Pourbaix Diagrams

State	Definition
Active	Condition in which a metal is thermodynamically unstable and the most stable corrosion product is soluble, so the metal will react with its environment and freely corrode.
Immune	Condition in which a metal is thermodynamically stable, and so does not react with its environment.
Passive	Condition in which a metal is thermodynamically unstable, and the most stable corrosion product is an insoluble solid; if the corrosion product forms a protective film, it can protect the metal from corrosion.

Most Pourbaix diagrams, such as **Figure 10**, include lines to indicate the stability region of water. The Pourbaix diagram for water is shown in **Figure 11**, again assuming the water is pure except for the inert ions needed to adjust the pH. In the region between the two dashed lines (a) and (b), water is stable. Below the lower line (a), water is unstable and can be reduced to gaseous hydrogen. Along the line (a), water is in equilibrium with hydrogen at one atmosphere pressure, according to the reaction:

$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$$

Above the upper line (b), water is also unstable and can be oxidized to gaseous oxygen. Along the line (b), water is in equilibrium with oxygen at one atmosphere pressure according to the reaction

$$2H_2O \rightleftharpoons O_2(g) + 4H^+ + 4e^-$$

The lines "a" and "b" are calculated from the equilibrium potential for the two reactions using the Nernst equation to account for changing pH.

In the Pourbaix diagram for iron, **Figure 10**, the immune region for iron lies outside the stable region of pure water, indicating that in the area where water is stable, iron is either actively corroding or passivated. **Figure 10** was calculated for concentrations of iron(II) or iron(III) ions in solution of 10^{-6} M, a value that is normally taken as a threshold[39] below which iron is not corroding enough to generate a significant concentration of iron ions in solution and above which significant corrosion is taking place. Passivation is assumed to be due to FeOOH and Fe_3O_4. The small active region above pH 14 is associated with the $HFeO_2^-$ ion, which is also included in the calculation. Collections of Pourbaix diagrams are available[30,40] and can also be generated using software packages, such as MEDUSA.[41]

The lines in a Pourbaix diagram often slope down to the right (that is, the potential decreases as pH increases). This occurs because the reactions associated with the lines involve H^+ or OH^- ions. Examples are the lines (a) and (b) in **Figure 11**. Another example is the line segment between pH 9 and 14 in **Figure 10**, which is associated with the reaction between Fe and Fe_3O_4:

$$Fe_3O_4 + 8H^+ + 8e^- \rightleftharpoons 3Fe + 4H_2O$$

The potential (in volts) of this line segment in **Figure 10** depends on pH as follows:[42]

$$E = -0.085 - 0.0592\ \text{pH}$$

If the pH of the electrolyte solution used for an E_{corr} measurement is known, the value of E_{corr} can be plotted on a Pourbaix diagram. For example, the two data points in **Figure 10** are taken from the corrosion potential measurements in **Figure 7**, after a time of 3 hours, at which point the corrosion potential has almost reached a steady state. The points are inside the passive region of the Pourbaix diagram, indicating that the iron is passivated. The corrosion potential is lower for the higher pH, as expected if the reactions involve OH^- or H^+. Pourbaix diagrams have been used in conservation to assess the suitability of electrolytes for treatment of artifacts,[1,31] as well as to evaluate whether an artifact is passivated or actively corroding.[43,44]

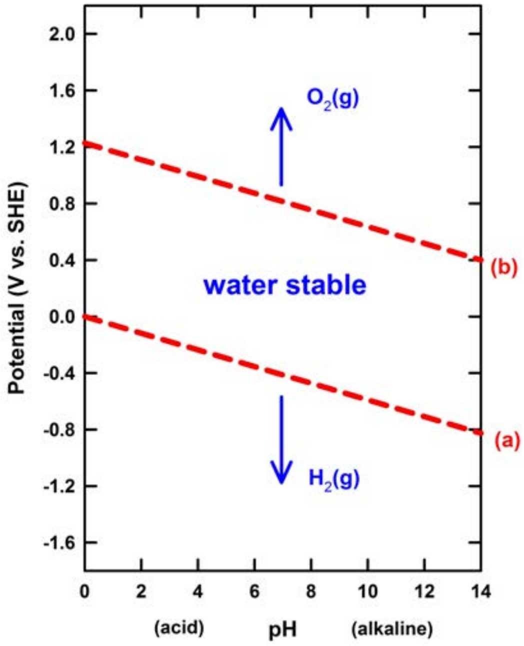

Figure 11. Pourbaix diagram showing the stability region of water. For line (a), the potential is given by $E = 0.000 - 0.059\ \text{pH} - 0.030 \log_{10} p_{H2}$, and for line (b), $E = 1.228 - 0.059\ \text{pH} + 0.015 \log_{10} p_{O2}$, where the partial pressures p_{O2} and p_{H2} of oxygen and hydrogen are both set equal to 1 atm.

Interpreting Changes in Corrosion Potential

This paper is mainly concerned with describing procedures to measure corrosion potential, rather than interpreting what the corrosion potential means. But it is important to be aware that the corrosion potential can change for different reasons, and so changes can have different interpretations.

The corrosion potential depends on a balance between anodic (oxidation) and cathodic (reduction) reactions, such as the iron and oxygen reactions given above. Shifts in the balance cause the corrosion potential to change. If the anodic reaction (iron corrosion in the above example) is inhibited, the corrosion potential increases; on the other hand, if the cathodic reaction (oxygen in the example) is inhibited, the corrosion potential decreases.[45] Thus a rise in the corrosion potential could either indicate that the anodic reaction is being inhibited and the corrosion rate is decreasing, or that the cathodic reaction is being enhanced and the corrosion rate is increasing.

For example, when a bare metal was placed in a solution without reactive ions such as chloride ions in **Figure 7** and **Figure 9**, the metal surface passivated, inhibiting the anodic reaction. The observed increase in corrosion potential was associated with a decreased corrosion rate.[31] On the other hand, when an iron anchor was moved from deep to shallow water, the corrosion potential was also observed to increase, but in that case the increase was associated with an increase in corrosion rate.[46] The higher concentration of oxygen in the shallow water enhanced the cathodic reaction.

These examples illustrate that the interpretation of corrosion potential requires additional information on changes occurring in the object being measured. With that proviso, the corrosion potential has proven useful in monitoring objects during treatment[31] or marine artifacts before they are recovered.[46] It has also been used to identify the major elements in copper alloys.[2]

The results shown in **Figure 7** and **Figure 9** were for bare metal samples placed in a solution. Corroded objects may have a more complicated behaviour. For example, the corrosion potential may first decrease and then increase as the electrolyte penetrates the corrosion layer.[25] Measurements on artificially corroded samples can be useful in understanding such behaviour.[33]

Finally, although a changing corrosion potential indicates that changes are occurring at a metal surface, a constant corrosion potential does not prove that all the changes have stopped. Measurements of corrosion potential only monitor some aspects of the metal surface, and so even when the corrosion potential has stabilized, the surface can still be changing. As one example, it was found that the corrosion potential was not a good monitor for removal of chloride ions from a corroded copper surface.[47] In that case, spectroscopic and structural measurements showed that chloride ions were still being removed from the object after the corrosion potential had stabilized.

CONCLUSIONS

This paper has provided basic information on equipment and methods for measuring the corrosion potential of a metal in a solution and some guidance on interpreting it. In conservation, the corrosion potential of a metal in an electrolyte is sometimes used to characterize the state of the metal. More often, however, the measurement of potential is only one aspect of an electrochemical measurement or treatment that involves a flow of electric current through the metal of an object and an associated ionic current through the electrolyte. Various techniques combine measurements or control of both current and potential. A subsequent publication discusses the essential elements of applying these techniques to problems in conservation.[5]

ACKNOWLEDGEMENTS

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MATERIALS

Electrochemical equipment and its suppliers are constantly changing. Those listed below are given as a starting point for setting up electrochemical measurements.

Chemicals and laboratory equipment: Chemical supply houses, such as Fisher Scientific <www.fishersci.com/>, are a source for chemicals (e.g., salts for electrolytes) and laboratory equipment (e.g., support stands, tri-grip clamps and suitable glassware, such as beakers and crystallizing dishes).

Digital multimeters with high impedance: Keysight Technologies (formerly part of Agilent Technologies) <www.keysight.com/>; Keithley (now part of Tektronix) <www.tek.com/>; Fluke <www.fluke.com/>

Platinum electrode: Radiometer Analytical <www.radiometer-analytical.com/>

Platinum wire: Sigma-Aldrich <www.sigmaaldrich.com/>

Reference electrodes and salt bridges: Gamry Instruments <www.gamry.com/>; Radiometer Analytical <www.radiometer-analytical.com/>

REFERENCES

[1] Degrigny, Christian, "Application of electrochemical techniques to the conservation of metal artefacts: a review," in: *Ligas Metálicas: Investigação e Conservação*, edited by A.C.F. da Silva and P.M. Homem (Porto, Portugal: Universidade do Porto, 2008), pp. 29–45.

[2] Degrigny, Christian, Geoffroy Guibert, Stephan Ramseyer, Guillaume Rapp and Antonin Tarchini, "Use of E_{corr} vs time plots for the qualitative analysis of metallic elements from scientific and technical objects: the SPAMT test project," *Journal of Solid State Electrochemistry*, vol. 14, no. 3, 2010, pp. 425–435.

[3] Letardi, P., "Electrochemical measurements in the conservation of metallic heritage artefacts: an overview," in: *Corrosion and Conservation of Cultural Heritage Metallic Artefacts*, edited by P. Dillmann, D. Watkinson, E. Angelini and A. Adriaens (Oxford: Woodhead, 2013), pp. 126–148.

[4] MacLeod, I.D., "Monitoring, modelling and prediction of corrosion rates of historical iron shipwrecks," in: *Corrosion and Conservation of Cultural Heritage Metallic Artefacts*, edited by P. Dillmann, D. Watkinson, E. Angelini and A. Adriaens (Oxford: Woodhead, 2013), pp. 466–477.

[5] Selwyn, Lyndsie and W. Ross McKinnon, "Practical Electrochemistry for Conservators and Conservation Scientists: Part II – Characterizing and Treating Corroded Metals," *Journal of the Canadian Association for Conservation*, vol. 42, 2017, pp. 16–32.

[6] Bard, Allen J. and Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edition (New York: John Wiley & Sons, 2001), pp. 2–5.

[7] Bard, Allen J., György Inzelt and Fritz Scholz (eds.), *Electrochemical Dictionary*, 2nd edition (Berlin: Springer, 2012), pp. 736–749.

[8] Bard et al., *Electrochemical Dictionary*, 2012, p. 663.

[9] Bard and Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2001, p. 50.

[10] Kahlert, Heike, "Reference electrodes," in: *Electroanalytical Methods: Guide to Experiments and Applications*, edited by F. Scholz (Berlin: Springer-Verlag, 2002), pp. 261–278.

[11] Bard, Allen J., Roger Parsons and Joseph Jordan (eds.), *Standard Potentials in Aqueous Solution* (New York: Marcel Dekker, 1985), pp. 787–802.

[12] Sawyer, Donald T., Andrzej Sobkowiak and Julian L. Roberts, Jr., *Electrochemistry for Chemists*, 2nd edition (New York: John Wiley & Sons, 1995), p. 192.

[13] Smith, Timothy J. and Keith J. Stevenson, "Reference Electrodes," in: *Handbook of Electrochemistry*, edited by C.G. Zoski (Amsterdam: Elsevier, 2007), pp. 71–110.

[14] Skoog, Douglas A., Donald M. West, F. James Holler and Stanley R. Crouch, *Fundamentals of Analytical Chemistry*, 9th edition (Belmont, CA: Brooks/Cole, 2014), p. 537.

[15] ASTM-G3, "G3-14. Standard practice for conventions applicable to electrochemical measurements in corrosion testing," in: *Annual Book of ASTM Standards 2015, vol. 03.02. Corrosion of Metals; Wear and Erosion* (West Conshohocken, PA: American Society for Testing and Materials, 2015), pp. 35–43.

[16] Thomas, James M., "Student construction of a gel-filled Ag/AgCl reference electrode for use in a potentiometric titration," *Journal of Chemical Education*, vol. 76, no. 1, 1999, pp. 97–98.

[17] East, Gaston A. and M.A. del Valle, "Easy-to-make Ag/AgCl reference electrode," *Journal of Chemical Education*, vol. 77, no. 1, 2000, p. 97.

[18] Inamdar, Shaukatali N., Mohsin A. Bhat and Santosh K. Haram, "Construction of Ag/AgCl reference electrode from used felt-tipped pen barrel for undergraduate laboratory," *Journal of Chemical Education*, vol. 86, no. 3, 2009, pp. 355–356.

[19] Sawyer et al., *Electrochemistry for Chemists*, 1995, p. 189.

[20] Kelly, Robert G., John R. Scully, David W. Shoesmith and Rudolph G. Buchheit, *Electrochemical Techniques in Corrosion Science and Engineering* (New York: Marcel Dekker, 2003), pp. 15–16.

[21] "Care of Vycor Porous Glass Frits," in: Gamry Instruments website, <www.gamry.com/application-notes/electrodes-cells/care-of-vycor-porous-glass-frits/>. Accessed June 2018.

[22] Stansbury, E.E. and R.A. Buchanan, *Fundamentals of Electrochemical Corrosion* (Materials Park, OH: ASM International, 2000), pp. 240–241.

[23] Selwyn, Lyndsie, *Analysis of the chloride ion concentration in aqueous solutions by potentiometric titration*, CCI Research Report No. 2 (Ottawa: Canadian Conservation Institute, 2001).

[24] ASTM-D1498, "D1498-14. Standard test method for oxidation-reduction potential of water," in: *Annual Book of ASTM Standards 2015, vol. 11.01. Water(I)* (West Conshohocken, PA: American Society for Testing and Materials, 2015), pp. 250–255.

[25] Hjelm-Hansen, N., J. van Lanschot, C.D. Szalkay and S. Turgoose, "Electrochemical assessment and monitoring of stabilisation of heavily corroded archaeological iron artefacts," *Corrosion Science*, vol. 35, nos. 1–4, 1993, pp. 767–774.

[26] Argyropoulos, Vasilike, Christian Degrigny and Elodie Guilminot, "Monitoring treatments of waterlogged iron-wood composite artifacts using Hostacor IT-PEG 400 solutions," *Studies in Conservation*, vol. 45, no. 4, 2000, pp. 253–264.

[27] Guilminot, Elodie, Gilles Baron, Jean-Bernard Memet, Nathalie Huet, Eric le Noc and Jean Philippe Roze, "Electrolytic treatment of archaeological marine chloride impregnated iron objects by remote control," in: *Metal 2007: Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group*, Amsterdam, The Netherlands, 17–21 September 2007, edited by Christian Degrigny, Robert van Langh, Ineke Joosten and Bart Ankersmit (Amsterdam: Rijksmuseum, 2007), vol. 3, pp. 38–43.

[28] MacLeod, Ian D. and Rinske Car, "Conservation of a mid-18th-century Italian embroidered ecclesiastical cope and treatment of corroded metal threads using neutral dithionite solutions," in: *Preprints, 17th Triennial Conference, ICOM Committee for Conservation*, Melbourne, Australia, 15–19 September 2014, edited by J. Bridgland (Paris: International Council of Museums, 2014), article 1306, 7 pp.

[29] Tse, Season, *Guidelines for pH measurement in conservation*, Technical Bulletin No. 28 (Ottawa: Canadian Conservation Institute, 2007), <http://publications.gc.ca/collections/collection_2016/pch/CH57-3-1-28-2007-eng.pdf>. Accessed June 2018 on the Government of Canada publications website.

[30] Pourbaix, Marcel, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd edition (Houston: National Association of Corrosion Engineers, 1974).

[31] Degrigny, Christian, "Use of electrochemical techniques for the conservation of metal artefacts: a review," *Journal of Solid State Electrochemistry*, vol. 14, no. 3, 2010, pp. 353–361.

[32] Stemann-Petersen, Karen and Bodil Taarnskov, "Electrolytic cleaning of silver and gilt silver threads in silk textiles – possibilities and limitations," *Zeitschrift für Kunsttechnologie und Konservierung (ZKK)*, vol. 20, no. 2, 2006, pp. 278–290.

[33] Degrigny, Christian and L. Spiteri, "Electrochemical monitoring of marine iron artefacts during their storage / stabilisation in alkaline solutions," in: *Metal 2004: Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group*, Canberra, Australia, 4–8 October 2004, edited by John Ashton and David Hallam (Canberra: National Museum of Australia, 2004), pp. 315–331.

[34] Bard and Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2001, p. xi.

[35] Skoog et al., *Fundamentals of Analytical Chemistry*, 2014, p. 460.

[36] Vogel, A.I., J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis, including Elementary Instrumental Analysis*, 4th edition (London: Longman Scientific & Technical, 1978), pp. 370–372.

[37] West, Steven J., *Calibration Method Using a Stable and Safe Redox Standard Solution*, United States Patent US6350367, February 2002, <www.google.ca/patents/US6350367>. Accessed June 2018 on the Google Patents website.

[38] Pourbaix, Marcel, "Some applications of potential-pH diagrams to the study of localised corrosion," *Journal of the Electrochemical Society*, vol. 123, no. 2, 1976, pp. 25C–36C.

[39] Scott, David A. and Gerhard Eggert, *Iron and Steel in Art: Corrosion, Colorants, Conservation* (London: Archetype, 2009), p. 51.

[40] Schweitzer, George K. and Lester L. Pesterfield, *The Aqueous Chemistry of the Elements* (Oxford: Oxford University Press, 2010).

[41] Puigdomenech, Ignasi, *MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms)*, <www.kth.se/che/medusa>. Accessed June 2018 on the KTH Royal Institute of Technology website.

[42] Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 1974, p. 309.

[43] MacLeod, I., P. Morrison, V. Richards and N. West, "Corrosion monitoring and the environmental impact of decommissioned naval vessels as artificial reefs," in: *Metal 2004: Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group*, Canberra, Australia, 4–8 October 2004, edited by John Ashton and David Hallam (Canberra: National Museum of Australia, 2004), pp. 53–74.

[44] MacLeod, Ian Donald, "In situ conservation of cannon and anchors on shipwreck sites," *Studies in Conservation*, vol. 41, supp. 1 (Preprints of the Contributions to the Copenhagen Congress, Archaeological Conservation and its Consequences, 26–30 August 1996), 1996, pp. 111–115.

[45] Frankel, G.S., "Fundamentals of corrosion kinetics," in: *Active Protective Coatings: New-Generation Coatings for Metals*, edited by A.E. Hughes, J.M.C. Mol, M.L. Zheludkevich and R.G. Buchheit (Dordrecht, the Netherlands: Springer, 2016), pp. 17–32.

[46] MacLeod, Ian Donald, "Conservation of corroded iron artefacts – new methods for on-site preservation and cryogenic deconcreting," *The International Journal of Nautical Archaeology and Underwater Exploration*, vol. 16, no. 1, 1987, pp. 49–56.

[47] Adriaens, Annemie, Mark Dowsett, Gareth Jones, Karen Leyssens and Sergey Nikitenko, "An *in-situ* X-ray absorption spectroelectrochemistry study of the response of artificial chloride corrosion layers on copper to remedial treatment," *Journal of Analytical Atomic Spectrometry*, vol. 24, 2009, pp. 62–68.