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Practical Electrochemistry for Conservators and Conservation Scientists: Part II – Characterizing and Treating Corroded Metals

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Electrochemical techniques can be used to characterize corrosion on a metal object and to reduce the corrosion either to a different compound or back to the metallic state. These techniques involve the flow of electrical current, and so are more involved than the measurement of the potential between an object and a reference electrode in a two-electrode cell. Information is given here for techniques where current flows, including the choice of a third electrode (the counter electrode) and the additional equipment needed (a power supply or potentiostat). Examples are given of methods varying the potential (potentiodynamic), holding the potential constant (potentiostatic), or holding the current constant (galvanostatic). The following aspects are discussed: identifying the features associated with oxygen reduction, associating the peaks in potentiodynamic scans with specific compounds in the corrosion, choosing the potential for treating an object, and estimating the amount of corrosion on an object or a test sample.

Les techniques électrochimiques peuvent servir à caractériser la corrosion d'un objet métallique et à réduire celle-ci en un composé différent ou à l'état métallique. Ces techniques reposent sur la circulation d'un courant électrique et sont plus complexes que la mesure d'un potentiel entre un objet et une électrode de référence dans une cellule à deux électrodes. L'article fournit de l'information sur les techniques impliquant la circulation d'un courant, y compris le choix d'une troisième électrode (électrode auxiliaire) et l'équipement supplémentaire nécessaire (bloc d'alimentation ou potentiostat). Il présente également des exemples de méthodes faisant varier le potentiel (potentiodynamique), maintenant le potentiel constant (potentiostatique) ou maintenant le courant constant (galvanostatique). Il traite des aspects suivants : la détermination des caractéristiques associées à la réduction d'oxygène, la mise en correspondance des pics dans les balayages potentiodynamiques avec des composés particuliers dans la corrosion, le choix du potentiel pour le traitement d'un objet, et l'estimation de la quantité de corrosion sur un objet ou un échantillon d'essai.

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INTRODUCTION

Electrochemical techniques have been adapted to the treatment and characterization of metal artifacts in conservation.[1,2] With these techniques, conservators can reduce the corrosion on lead, silver and copper back to the metal. Even with iron, where the corrosion layers can only be partially reduced under most conditions, electrochemical techniques can be used to remove chloride ions (Cl^-) more quickly than rinsing in alkaline solutions.[3,4] Electrochemical techniques can also be used to stabilize objects or samples while they are being treated,[5] to estimate the composition of corrosion layers,[2] or to identify metals.[6]

This is the second of two papers intended to introduce electrochemical techniques as a way to monitor or treat artifacts, or to study treatments. The first paper, Part I,[7] discusses potential measurements and reference electrodes. This paper extends the discussion to include electric current. The use of electric current to force chemical reactions is called electrolysis. In the older conservation literature, the term electrolysis usually referred to reducing the corrosion on a metal, most often iron, by connecting it to a power supply,[8] but the actual definition is more general. This paper gives some of the background information necessary to understand techniques involving electrolysis and illustrates these techniques with examples of characterizing and treating corrosion on metals, including a description of the changes needed to the electrochemical cell in Part I and the additional equipment required.

The history of electrolysis in conservation has been reviewed recently.[1] In older treatments using electrolysis, the metal object or sample being treated was placed in an electrolyte bath together with a second metal. A power supply was used to apply a potential or a current between the two electrodes. More sophisticated techniques have been introduced into conservation since then, using a third electrode, the reference electrode, and more sophisticated equipment, the potentiostat. Reference electrodes are used to monitor the potential of the object, and potentiostats can be used to control the potential, especially for small and fragile objects.[1] With these modifications, conservators and conservation scientists have more control over a treatment. But the techniques are only slowly being adopted in conservation. One problem is that the methods described in most publications are not detailed enough for a conservator or conservation scientist with little experience in electrochemistry. This paper fills in some of the details, assuming a reader with a basic understanding of chemistry, but not necessarily of electrochemical methods.

This paper discusses electrochemical techniques for characterizing corrosion compounds on metals and for reducing corrosion products either to a different compound or back to the metallic state. It also discusses the use of electrochemistry to measure the amount of corrosion on an object, a technique used in conservation science to evaluate methods for producing corrosion layers for further testing,[9,10] or to measure test coupons in studies of indoor air quality.[11,12]

It does not discuss electrochemical methods used to estimate corrosion rates (polarization methods), to measure thickness and effectiveness of coatings (impedance methods), or to measure reaction and diffusion rates (rotating electrode techniques).[13] It considers one of the most basic techniques for characterizing corrosion compounds, known as linear-sweep voltammetry, but not more sophisticated and more sensitive techniques such as digital-pulse voltammetry or square-wave voltammetry,[14] even though these are starting to be used in conservation.[15]

EQUIPMENT AND MATERIALS

This paper provides information about techniques and equipment needed to use electrolysis in measurements and treatments. Almost all of the information in Part I is essential for understanding this paper, including familiarity with electrochemical cells, reference electrodes, voltmeters, electrolytes, and the concepts of cell potential and corrosion potential.

Three-electrode Cell

When only cell potential is being measured, the electrochemical cell has two electrodes, the working electrode (WE, the object or sample being tested or treated) and the reference electrode (RE), both immersed in an electrolyte. Reference electrodes are not intended to handle large electric currents, so a third electrode, called the counter electrode (CE), is needed when currents are passed through the cell, hence the term "three-electrode cell." This is illustrated in **Figure 1**.

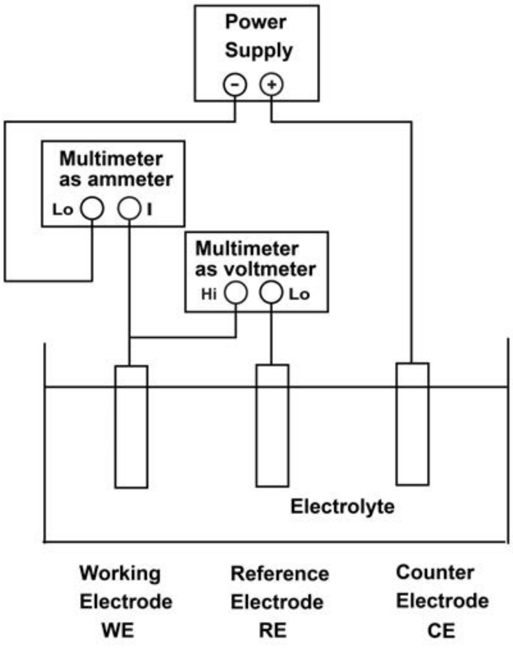

Figure 1. Schematic diagram of a three-electrode cell attached to a power supply and two multimeters. The three electrodes are immersed in an electrolyte. The positive terminal on the ammeter, labelled I (for current) in the figure, may be labelled A (for amperes) or mA (for milliamperes) on some meters.

In **Figure 1** the working electrode and counter electrode are connected to a power supply, a component that provides a potential and a current between the two electrodes. A typical power supply can operate in constant voltage (CV) mode, maintaining a constant potential between the two electrodes and providing the current necessary to do this, or in constant current (CC) mode, maintaining a constant current and providing the necessary potential.

The current that flows between the working electrode and the counter electrode can be measured with an ammeter placed in series with the power supply. In practice, the ammeter is usually a digital multimeter set to measure current, but the term "ammeter" will be used in this paper.

The potential is measured between the working electrode and the reference electrode; this is not the same potential as that set or supplied by the power supply. It can be measured with a voltmeter (or another digital multimeter, which is set to measure voltage). Since the counter electrode is excluded from the potential measurement, any changes in the counter electrode do not affect the measured potential.

Counter Electrode

The counter electrode is usually an inert metal that does not react during electrolysis. The reaction at the counter electrode is usually decomposition of water. One of the best materials for the counter electrode is platinum (Pt). Platinum mesh electrodes, also called platinum gauze electrodes, are available, but platinum is so expensive that it is only practical for use with small objects or test coupons. When possible, the counter electrode should be large enough that it can be placed around the object, to ensure that the current flows evenly to all metallic parts of the object. **Figure 2** shows a platinum mesh electrode suitable for small samples. The mesh can be bent to fit into various sizes of containers.

For larger objects, the choice of a substitute for platinum depends on the electrolyte. Stainless steel has been used for counter electrodes with working electrodes of iron (Fe) or copper (Cu) in alkaline solutions.[1] High quality stainless steel such as 316 is preferable and this is available in the form of wire mesh or expanded metal, which are easier to handle than solid sheets. Hardware such as nuts and bolts for making connections to counter electrodes or objects in the electrolyte is also available in 316 stainless steel. Lead (Pb) has been used as a counter electrode with lead artifacts in neutral lead sulfate ($PbSO_4$) solutions.[1,16] These counter electrodes must be monitored regularly to ensure they are not corroding, because such corrosion can contaminate the working electrode. For example, a lead counter electrode can produce lead ions (Pb^{2+}). If the lead ions in solution migrate to the working electrode, lead can plate out on it.

Test Cell for Measuring Small Samples

Figure 3 shows a picture of a three-electrode cell used for electrolysis of small metal samples. The test sample is only partly immersed in the electrolyte. If a corroded sample is treated while immersed like this, there will be a corrosion line on the sample at the surface of the water. This may be acceptable for a test sample, but for an actual object, it is better to immerse the object completely, to avoid producing the corrosion line. In this case, a piece of platinum wire can be used to make contact with the sample. A stainless steel wire can also be used when the working electrode is being reduced (potential being decreased), because then the wire is protected by the applied potential.

When current is involved in electrochemistry, the reference electrode is usually placed as close to the object as is practical. It is also crucial to make good electrical contact with the object. Electrical contact can be checked with an ohmmeter. The electrolyte must have good conductivity, which means high concentration. Concentrations of 0.1 M and higher are generally used. Other considerations in choosing an electrolyte are discussed in Part I.[7] The pH of the electrolyte is chosen so the metals are passivated, or so that other materials such as textiles are exposed to neutral solutions. The electrolytes in the examples below were chosen because they are close to neutral pH: 0.1 M sodium sulfate (Na_2SO_4) has a pH of 6.7; 0.5 M Na_2SO_4 has a pH of 7.1; and 0.1 M potassium chloride (KCl) has a pH of 5.9.

Multimeter and Power Supply

For measuring current, a multimeter should have a range appropriate for the size of the working electrode. Currents in small objects can range from less than 1 μA (10^{-6} A) to 1 A. Most benchtop multimeters can measure currents throughout this range. For larger objects the current can exceed several amperes, in which case a more specialized meter is needed.

For power supplies, it is best to have one with both a constant voltage mode and a constant current mode. The maximum voltages and currents should not be higher than necessary. Voltage settings above 5 V are rarely needed, so it is not recommended to use a power supply that can provide 100 V, for example, because of the difficulty in adjusting the setting to low voltage values. The maximum current for the power supply depends on the size of the object. For small objects or samples, a small benchtop power supply is adequate, but for larger objects, a power supply with a higher current capability is needed. For example, treatment of cannon can require currents of 5 A or greater.[17,18]

Many power supplies have a built-in display for the voltage and current. The voltage on the display is the potential between the working electrode and the counter electrode and is usually not of interest. What is important is the potential between the working electrode and the reference electrode, which must be measured with a separate voltmeter, as shown schematically in **Figure 1**. The built-in display for current does give the current flowing through the cell, but it usually has a limited range, so it is best to have a separate ammeter as well (also shown in **Figure 1**).

If a power supply is to be used for large objects, it must be powerful enough to provide the current needed. On the other hand, a large power supply may have too large a residual current (the actual current when the setting is zero) for small objects. One way to confirm the suitability of a power supply for small objects is to check that the potential of the working electrode does not change when the power supply is turned on and set to

Figure 2. Platinum mesh electrode used as the counter electrode, shown connected to an alligator clip. The mesh is 5 cm high.

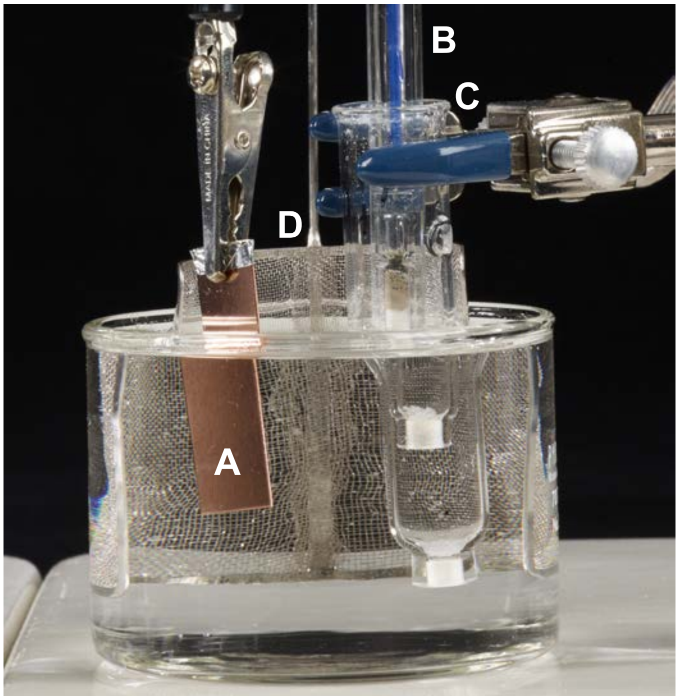

Figure 3. Configuration of electrodes in a three-electrode cell. The copper working electrode (A) is 3.8 cm high. The reference electrode (B) is immersed in a salt bridge (C). The platinum mesh counter electrode (D) is at the back.

zero voltage or zero current. A three-electrode cell is used to test this, as shown schematically in **Figure 1**, with the same inert metal, such as platinum or stainless steel, used for both the working electrode and the counter electrode. The voltmeter is turned on, and the potential of the working electrode versus the reference electrode is noted. The power supply is set to zero current and zero voltage, and then turned on. The potential of the working electrode should not change. The potential should also not change if the voltage setting on the power supply is increased and then turned back to zero while the current setting is kept at zero, or if the current setting is increased and turned back to zero while the voltage setting is kept at zero. If the potential does change, this indicates that the power supply is supplying current or potential when it is not supposed to. The ammeter can be used to confirm that any currents are small while the adjustments are made.

It is often useful to record the potential and current as a function of time on a computer. This requires programmable meters that can communicate with the computer, as well as data acquisition software and the necessary expertise to get the software running.

Potentiostat

The power supply in **Figure 1** determines the current or potential between the working and counter electrodes. If the experiment calls for a specific current, such as the constant current technique discussed below, this can be set on the power supply. But other experiments or treatments call for specific potentials to be set between working and reference electrodes (not between working and counter electrodes). In these cases, the power supply must be adjusted regularly, because any change at the counter electrode will change the potential between the working electrode and the reference electrode. The adjustment can be made manually or by an electronic control circuit. In the latter case, the meters and power supply are housed together with the control circuit, in what is called a potentiostat.

Figure 4 shows a schematic diagram of a potentiostat connected to the three electrodes. Modern potentiostats are controlled by a computer, with software designed to carry out a variety of electrochemical measurements, where the current I or potential E is either held constant or varied in a prescribed way with time t. The computer can record E, I and t, and produce plots of various combinations of these variables, such as current as a function of time, $I(t)$, potential as a function of time, $E(t)$, and current as a function of potential, $I(E)$. The computer also can calculate the charge Q as a function of time from $I(t)$.

Some potentiostats have two inputs for reference electrodes, labelled RE1 and RE2, or RE and SE (for sense electrode). The second reference electrode is used for specialized experiments. For the experiments discussed here, where the second reference electrode is not needed, the input RE2 or SE is connected to the working electrode, WE.

EXPERIMENTS AND TREATMENTS

Measurements of the corrosion potential, E_{corr}, of a metal are done with no current flowing (open circuit). With a third electrode and a current flowing, many more types of measurement become possible, depending on what is controlled (potential or current) and how is it controlled (held constant or varied with time). The following sections discuss some of these measurements and their differing methods: those done while controlling potential with time (potentiodynamic in electrochemical terminology[19]) particularly when varying the potential linearly with time (linear sweep voltammetry); those done while holding the potential fixed (potentiostatic); those done while holding the current fixed (galvanostatic); and application of any of these methods for the calculation of the amount of material reduced (coulometry). The reference electrodes used in the following sections were either a Radiometer Analytical Ref621 saturated mercury-mercury(I) sulfate electrode (SSE) or a Princeton Applied Research G0115 saturated calomel electrode (SCE). Measurements involving a potentiostat, as in **Figure 4**, used a Solartron 1284. Measurements with separate power supply and meters (**Figure 1**) used an Agilent E3610A DC power supply, an Agilent 34401A digital multimeter (to measure current) and a Fluke 8840A digital multimeter (to measure voltage).

Varying the Potential (Potentiodynamic Technique)

This section discusses some of the reactions that can happen on a metal object in an electrochemical cell, and how those reactions can be identified with electrochemical measurements. The first example is a cell with a clean silver (Ag) working electrode, a platinum counter electrode and an SSE reference electrode. For the measurements, the electrodes were connected to a potentiostat, as in **Figure 4**. This example is used to introduce the features of a potentiodynamic scan. Later examples include tarnished silver, tarnished copper and tarnished sterling silver (92.5% Ag, 7.5% Cu).

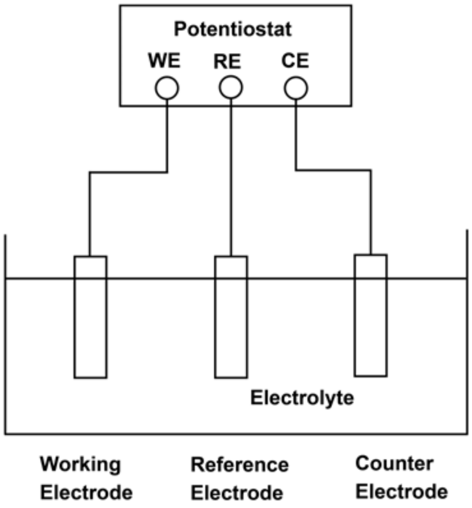

Figure 4. Schematic diagram of a three-electrode cell attached to a potentiostat.

Potentiodynamic Scans of Clean Silver

Before any current flows through the cell, the working electrode has some corrosion potential, E_{corr}, relative to the reference electrode. The counter electrode also has some corrosion potential, but that potential is not measured in the circuit shown in **Figure 4**. **Figure 5** shows current as a function of potential when the potentiostat was programmed first to measure E_{corr} and then to decrease the potential of the working electrode linearly in time at a rate called the scan rate, starting from the measured E_{corr}. The solid curve was taken with the cell open to the air, so there was dissolved oxygen in the electrolyte. As the potential for the solid curve is decreased from E_{corr}, the current becomes increasingly negative until −0.58 V vs. SSE (or +0.07 V vs. SHE) and then becomes less negative. This appears as a dip in the graph because the current is negative, but it is called a peak or negative peak and the current at the most negative part is called the maximum current of the peak or the peak maximum. At potentials below the peak, the current levels out to a plateau and then begins to become increasingly negative near −1.7 V vs. SSE (−1.0 V vs. SHE). The peak at −0.58 V vs. SSE and the subsequent plateau in the solid curve are associated with the reduction of oxygen, as is clear by a comparison with the dashed curve in **Figure 5**, where the cell was sealed and nitrogen (N_2) bubbled through the electrolyte to remove the oxygen before the measurement was done.

When the potential is changed from E_{corr}, current flows between the working electrode and counter electrode. The flow of current produces chemical reactions at the electrodes (electrolysis). When the potential of the working electrode is made negative with respect to E_{corr}, as in **Figure 5**, electrons from the working electrode are captured by some chemical species. At an electrode of clean silver, two possible reactions can occur. Electrons (e^-) can be transferred from the silver to oxygen gas (O_2) dissolved in the electrolyte, producing hydroxide ions (OH^-) by the reaction

$$O_2\,(g) + 2H_2O + 4e^- \rightarrow 4OH^-$$

Electrons can also be transferred to water molecules, producing hydrogen gas (H_2) and hydroxide ions,

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

These are called cathodic reactions; the oxygen or water is reduced and the solution near the electrode becomes more alkaline. These are the only two cathodic reactions on a clean silver electrode, but other reactions are possible when the silver is tarnished, as discussed below. By convention, the current is negative for cathodic reactions[20] and the electrode where these reactions are occurring is called the cathode.

When reducing reactions occur at the working electrode, counterbalancing oxidizing reactions must occur at the counter electrode. For platinum counter electrodes, electrons are pulled into the electrode from water molecules, producing hydrogen ions (H^+) and oxygen gas. The reaction is

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

This is called an anodic reaction and the electrode where the anodic reactions are occurring is called the anode. In this reaction, water is oxidized and the solution near the electrode becomes more acidic. The potential of the counter electrode is not measured in the circuit in **Figure 4**, but the products of the reaction may have effects, as discussed shortly.

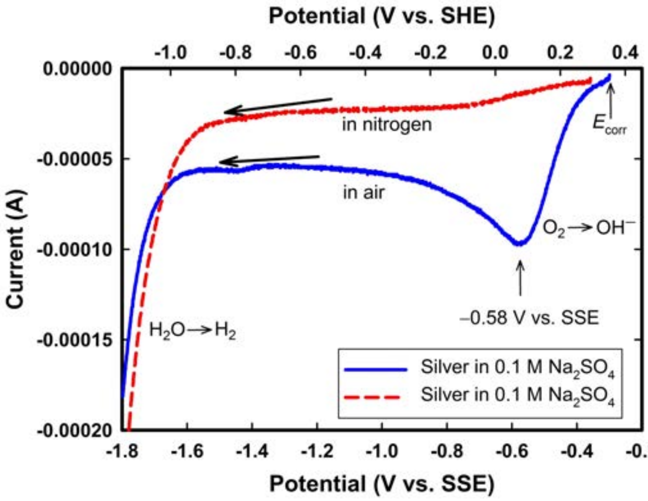

Figure 5. Current versus potential for potentiodynamic scans of clean silver in 0.1 M Na_2SO_4 in air (solid line) or deaerated with nitrogen (dashed line). The counter electrode was platinum mesh. The potential was decreased (indicated by the arrows) at a scan rate of 10 mV/s. The scan started at E_{corr} (−0.30 V vs. SSE in air and −0.36 V vs. SSE under nitrogen) and stopped when the potential reached −1.8 V vs. SSE.

The terms cathode and anode are linked to the type of reaction at the electrode (reduction and oxidation, respectively). As a result, the working electrode is the cathode when reduction occurs there, such as reduction of oxygen or of corrosion products, and the counter electrode is the anode. If the current is reversed, by interchanging the connections on the power supply in **Figure 1**, for example, then the working electrode becomes the anode and the counter electrode the cathode.

Peaks in Potentiodynamic Scans

The peaks observed in potentiodynamic scans are associated with reactions occurring in the electrochemical cell. The shape of a given peak depends on many parameters involving the kinetics of the reaction and the motion of ions, as discussed in electrochemistry texts.[21] The overall position of the peak is set by E^0, the standard potential associated with the reaction. This potential is the value when the reaction is at equilibrium (no current flowing) and the components of the reaction have standard values (1 M concentration for ions and 1 atmosphere pressure for gases). Values of standard potential can be found in various compilations.[22] **Appendix I** gives the standard potentials for various compounds found on corrosion layers of metals of importance in conservation, as well as the potentials for reduction of water and of oxygen.

The first step in identifying peaks in a potentiodynamic scan is to compare the peak position with E^0. For example, for oxygen reduction, the standard potential is −0.250 V vs. SSE; for water reduction, it is −1.459 V vs. SSE. Since the standard potential for oxygen reduction is the more positive of the two, the oxygen reaction should start first (at a higher potential) as the potential is scanned down from E_{corr} if oxygen is present. Thus the negative peak at −0.58 V in **Figure 5** would be identified tentatively with oxygen reduction. In this case, the identification was confirmed by bubbling nitrogen through the electrolyte to remove the oxygen and repeating the scan, shown as the dashed curve in **Figure 5**, but for most reactions such a convenient check is not available.

The value of E^0 is only a rough guide in identifying a peak, for several reasons. First, the equilibrium potential of a reaction is equal to E^0 when concentrations have standard values, whereas in an actual cell the concentrations generally differ from these values. The actual equilibrium potential is related to E^0 and the concentrations by the Nernst equation.[23] Second, at the equilibrium potential the current is zero; when the current is not zero, the potential must be different from the equilibrium value. This difference is called an overpotential. It is a kinetic effect and can be thought of as the extra push needed to get the current to flow. Third, the peak is spread out over a range of potentials, so it is uncertain what potential in this range should be chosen to compare to E^0. Even in simple textbook cases[21] the maximum current does not occur exactly at E^0. For narrow peaks this uncertainty is reasonably small, but the peaks usually broaden and shift for higher scan rates or for thicker corrosion layers. For broad peaks, the onset of a peak rather than its maximum is sometimes used to identify a peak; the onset has been estimated by a graphical method in some studies.[1] For all these reasons, E^0 alone cannot be used to identify peaks that are close together in potential, but it can be used to limit the possibilities.

When the peak is associated with a thin layer of corrosion on an object, as in the examples discussed below, the peak corresponds to the complete reaction of the corrosion layer. In **Figure 5**, however, the peak is followed by a plateau as the potential changes. The peak occurs because the reaction turns on strongly near the standard potential E^0, consuming the dissolved oxygen in the solution near the electrode. Once that nearby oxygen has been consumed, the current levels off to a less negative value, but not back to zero. Since more oxygen is available in the rest of the solution and in the atmosphere around the cell, the current settles to a plateau (a range of potentials where the current is roughly constant). The plateau in the solid curve in **Figure 5** extends between roughly −1.0 V vs. SSE and −1.6 V vs. SSE. The value of current for this plateau is determined by how fast oxygen can diffuse to the electrode from the solution and react there. When the potential reaches −1.6 V vs. SSE, the current suddenly begins to go more negative. This is the onset of reduction of water to form hydrogen gas, a reaction with $E^0 = -1.46$ V vs. SSE.

The Procedure in Practice

For **Figure 5**, the potentiostat was programmed to perform several steps: record the open circuit potential (the potential with no current flowing) for two minutes; hold the potential constant for 10 seconds at the last recorded value of open circuit potential (called potentiostatic mode); and then switch to a voltage sweep (called potentiodynamic mode) from that potential down to a cutoff (in this case −1.8 V vs. SSE) at a scan rate of 10 mV/s. The cutoff is usually chosen to be the point where the current begins to change rapidly due to the evolution of hydrogen. The brief hold at constant potential was found to produce a smaller current spike than switching directly from open circuit to voltage scan. Scan rates are typically 1 mV/s to 10 mV/s, chosen so that a scan can be done in a few minutes.

It is often convenient to position all the electrodes above the electrolyte, start the program for the potentiostat and then raise the electrolyte container up with a lab jack. The positioning must be done with a minimum delay so that the bottom of the salt bridge around the reference electrode does not remain in air too long. If the bottom of the working electrode is higher than the bottom of the other two electrodes, then the working electrode will be the last electrode to touch the electrolyte; this allows the corrosion potential to be measured immediately when the working electrode contacts the electrolyte. The electrodes are immersed in the electrolyte during the first program step (open circuit), and once they are immersed the potential should settle down to a nearly constant value. If it does not, there is a problem with a connection or an air bubble, and the measurement should be stopped until the problem is fixed. Only the data from the potentiodynamic scans are shown in **Figure 5**.

A potentiodynamic scan can be used as a final cleaning step (after polishing and rinsing) for samples used in experiments. The sample is scanned to a potential where hydrogen is being generated and held there for a short time to cathodically clean it.[24] The sample in **Figure 5** was cleaned electrochemically by holding the potential at -1.8 V vs. SSE for 2 minutes before the data were recorded.

The Effect of Deaeration

The results in **Figure 5** were obtained in a cell that could be flushed with an inert gas to remove oxygen from the electrolyte, then sealed to keep oxygen out. The dashed curve shows a potentiodynamic scan taken after oxygen was removed from the cell by flushing with nitrogen gas. Even though the oxygen was removed, this curve shows a plateau in current between about −1.5 V vs. SSE and −0.6 V vs. SSE. This is probably due to the reaction of oxygen that was generated at the counter electrode, diffused across the solution and reacted at the working electrode. The rapid change in current near −1.6 V vs. SSE occurred in the deaerated solution because the reduction of water to hydrogen gas does not depend on the presence of oxygen. When the electrolyte contains dissolved oxygen (the solid curve in **Figure 5**), the plateau current is larger in magnitude, because oxygen is present in the electrolyte in addition to being generated at the counter electrode, and there is a peak due to the reaction of oxygen that was initially near the working electrode.

Deaeration is needed when the oxygen reaction must be eliminated or reduced, such as for accurate measurement of the charge associated with other reactions. Although deaeration has been used in conservation,[25] it is generally not used, so the features associated with reduction of oxygen are to be expected in potentiodynamic scans to negative potentials. Sometimes the peak associated with oxygen is not present for non-deaerated

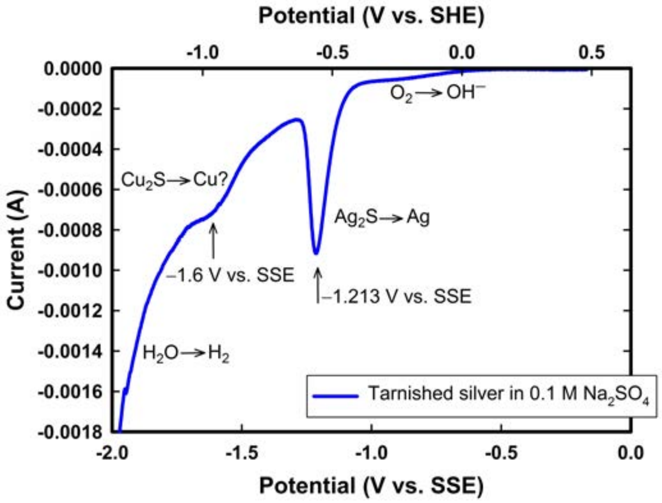

Figure 6. Current versus potential for the potentiodynamic scan of tarnished silver in 0.1 M Na_2SO_4, scan rate of 1 mV/s, from E_{corr} = −0.17 V vs. SSE to −2.0 V vs. SSE. The counter electrode was platinum mesh.

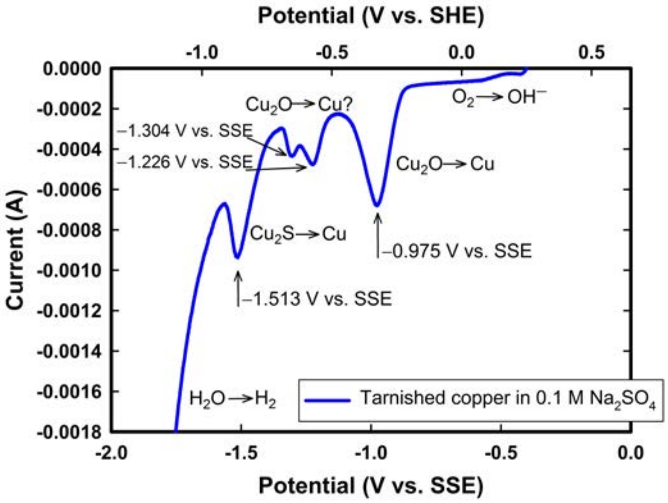

Figure 7. Current versus potential for the potentiodynamic scan of tarnished copper in 0.1 M Na_2SO_4, scan rate of 1 mV/s, from E_{corr} = −0.39 V vs. SSE to −2.0 V vs. SSE. The counter electrode was platinum mesh.

solutions, even though the plateau is seen. The peak may be absent because the metal surface is less reactive to oxygen gas, perhaps due to a tarnish or corrosion layer, so that the reduction of oxygen turns on more slowly as the potential is changed.

Potentiodynamic Scan of Tarnished Silver

When tarnished silver is used instead of clean silver as the working electrode, the potentiodynamic scan shows peaks associated with the tarnish. An example is shown in **Figure 6**. The sample for **Figure 6** was prepared by polishing with a slurry of 1 µm aluminum oxide in water, rinsing (with water, then acetone, then ethanol), and then tarnishing in a sealed container with a freshly hard-boiled egg which generates a small amount of hydrogen sulfide (H_2S). The curve shows a plateau associated with the reduction of oxygen gas and a rapid change in current associated with the production of hydrogen gas. It should be noted that the peak associated with oxygen gas is suppressed, but the plateau is still present.

The set of peaks in a potentiodynamic scan can be viewed as a spectrum of the material on the surface of an object or sample. The prominent negative peak near −1.2 V vs. SSE is associated with silver sulfide (Ag_2S); that is, it has been identified as the reduction of silver sulfide, the main component of silver tarnish, back to silver.[26,27] When silver sulfide is reduced, producing silver, hydroxide ions and hydrosulfide ions (HS^-), the reaction below is driven from left to right:

$$Ag_2S(s) + H_2O + 2e^- \rightarrow 2Ag(s) + HS^- + OH^-$$

The standard potential for this reaction, $E^0 = -1.338$ V vs. SSE (**Appendix I**), is within about 0.1 V of the peak position in **Figure 6**. Given the closeness of E^0 to the peak position, and also given that the tarnish was produced in an atmosphere containing H_2S, it would be a reasonable guess to assign the peak to this reaction even before confirmation from the literature.

The peak is sharper than that associated with reduction of oxygen in **Figure 5**, because there is a limited amount of silver sulfide. The current begins to change rapidly when the silver sulfide first begins to be reduced, with the maximum rate of reduction occurring at the peak maximum. Once the silver sulfide is all converted, the magnitude of the current decreases again, giving a reasonably sharp peak.

The reduction of silver sulfide has the most negative E^0 of all the silver compounds in **Table I** of **Appendix I**, so the slight peak at near −1.6 V vs. SSE may not be associated with the reduction of a silver compound. This peak may be from the reduction of copper sulfide (Cu_2S) produced from low levels of copper alloyed with the silver, based on the position of the peak found from reduction of tarnish on copper and sterling silver in the next two examples. This peak has been observed in other work, and other interpretations have been suggested: reduction of a nonstoichiometric form of silver sulfide,[28] an unspecified reduction of the electrolyte,[12] or the enhanced production of hydrogen catalyzed by the presence of HS^- or sulfide ions (S^{2-}).[29]

Potentiodynamic Scan of Tarnished Copper

As another example, **Figure 7** shows a sample of copper cleaned and tarnished in the same way as the silver sample in **Figure 6**. Since the sample was prepared in a humid atmosphere containing H_2S, it is reasonable to conclude that the peaks are associated with the reduction of copper oxide (Cu_2O or CuO) or copper sulfide. The peak at the lowest potential, near −1.513 V vs. SSE, is identified in **Figure 7** as the reduction of Cu_2S to Cu, since this reaction has the lowest value of E^0 of all the copper compounds listed in **Appendix I** ($E^0 = -1.57$ V vs. SSE). The identification of the other peaks is uncertain. The values of E^0 for copper oxides differ only by 0.2 V: E^0 for Cu_2O is −1.02 V vs. SSE and that for CuO is −0.82 V vs. SSE, suggesting that it can be difficult to distinguish CuO from

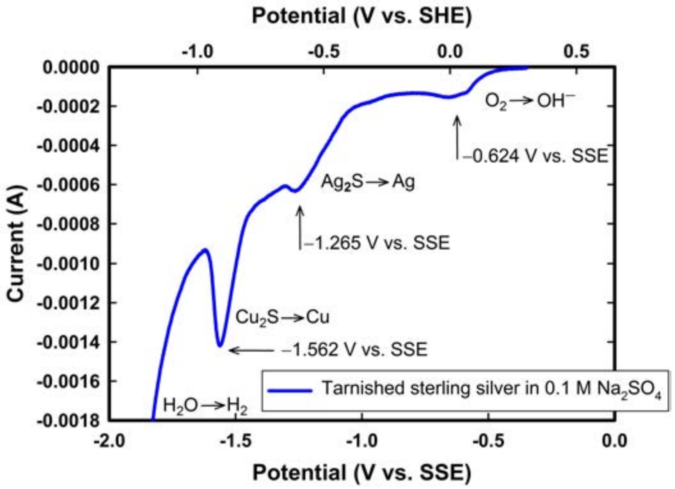

Figure 8. Current versus potential for the potentiodynamic scan of tarnished sterling silver in 0.1 M Na_2SO_4, scan rate of 1 mV/s, from $E_{corr} = -0.35$ V vs. SSE to −2.0 V vs. SSE. The counter electrode was platinum mesh.

Cu_2O. Moreover, it has been reported that reduction of Cu_2O can lead to several peaks.[30] Tentatively, all the peaks in **Figure 7** except that associated with Cu_2S have been identified as reduction of Cu_2O.

Potentiodynamic Scan of Tarnished Sterling Silver

Figure 8 shows the reduction of tarnished sterling silver (prepared in the same way as the two samples discussed above). The largest peak at about −1.6 V vs. SSE is again identified as Cu_2S. The small peak near −1.3 V vs. SSE is labelled Ag_2S, but could also be associated with Cu_2O. The dominant compound is Cu_2S, even though sterling silver is 92.5% silver by weight and only 7.5% copper, because the copper in the sterling silver alloy is more reactive than silver to tarnishing gases such as hydrogen sulfide and carbonyl sulfide (OCS).[31,32] In fact, the slight peak near −1.6 V vs. SSE in the results for silver in **Figure 6** may be associated with low levels of copper alloyed with the silver.

It should be noted that the peak for the reduction of copper sulfide in **Figure 7** and **Figure 8** is superimposed on the background curve associated with the reduction of water to form hydrogen gas. In other words, the two reactions are both occurring at the same time. This is as expected from the standard potentials in **Appendix I**: the values for these two reactions are almost the same (−1.574 V vs. SSE for reduction of Cu_2O and −1.479 V vs. SSE for reduction of water to hydrogen gas). The two reactions are competing for the electrons provided by the potentiostat. This suggests it could be difficult to reduce all the Cu_2S to Cu, and so may explain why the reduction of the sterling silver sample in **Figure 8** did not give as clean a surface as the reduction of the silver sample in **Figure 6**.

The above reactions and several other reactions in **Appendix I** are written for HS^- ions, which are the dominant sulfur species in solution above pH 7. Dissolved hydrogen sulfide gas, H_2S, is also present and becomes the dominant species below pH 7. With reactions like these that can generate H_2S gas, it is best to work in a fume hood if possible, so that the air flow removes hydrogen sulfide gas as it forms. Also, stirring helps move HS^- ions and H_2S gas away from the metal surface; otherwise as soon as the reaction ends, the silver, copper or sterling silver can retarnish by reacting with the HS^- or H_2S that has just formed.

Constant Potential (Potentiostatic Technique)

In conservation, potentiodynamic methods are used to get an idea of what corrosion products are present, to estimate the amount of corrosion, and to select a potential to use for the treatment of an object. The treatment itself (i.e., the reduction of corrosion products) is usually done by holding the potential of the object at the selected value. This is called a potentiostatic technique. If the current is measured, the integrated current (the electric charge) can be used to calculate the amount of material that has been reduced.

Potentiostatic treatments are most often used in conservation to treat silver, lead and iron. This section discusses two examples of potentiostatic technique: first, for reducing the corrosion on a lead object back to lead metal and second, for reducing the corrosion on iron to allow chloride ions to be extracted. Although a potentiostat gives more control over the potential, a power supply can be used in cases where a potentiostat is not available or if the potentiostat cannot supply enough current to treat a large object. If an object is so corroded that there is little or no solid metal core remaining, reduction can destroy the object. Radiography prior to treatment is useful in determining if a solid core is present.

Choosing a Treatment Potential

Usually the key to developing a treatment at constant potential is to find a potential where the corrosion can be reduced without generating hydrogen gas. With marine iron, a slight release of hydrogen bubbles can be used to loosen the concretion on an artifact,[4,17] but excessive hydrogen may cause iron objects to become brittle due to the diffusion of hydrogen into the metal, a phenomenon known as hydrogen embrittlement.[33]

The appropriate potential to use to reduce a specific corrosion product can be found from published treatments, from potentiodynamic techniques, or by trial and error. If the peaks in a potentiodynamic scan are reasonably sharp, a potential can be chosen just to the left of the peak, on the low potential side,[34] or at the position of the peak maximum.[1] For example, the potentiodynamic scan of silvered brass wind instruments[34] gave peaks associated with Ag_2S and Cu_2S at similar positions as in **Figure 8**, and the treatment potential was chosen as −1.36 V vs. SSE, just to the left of the Ag_2S peak, so that the Ag_2S was reduced but the Cu_2S was not. Other studies for reducing tarnished silver chose similar potentials in the range −1.3 to −1.4 V vs. SSE.[28,35,36] If the peaks in the potentiodynamic scan are broad, the reduction can be done in steps, at successively lower potentials.[37] It should be noted that the reduction process may have unwanted consequences, such as changing the colour of the patina on copper alloys.[25] Moreover, repeated cycles of tarnishing and electrolytic cleaning lead to a rougher surface.[38]

If the treatment potential is not known, one approach is to start from E_{corr} and step the potential down (at 50 mV steps, for example), waiting for some time between steps. The potential where the corrosion disappears can then be used for the rest of the treatment. This approach is most feasible for thin corrosion layers, where the time between steps can be fairly short (seconds to a few minutes).

Procedure Using Potentiostat – for Treating Lead

Figure 9 shows the current as a function of time during the potentiostatic reduction of a piece of lead covered with white corrosion. The part of the sample immersed in 0.5 M Na_2SO_4 was 2 cm by 2 cm, giving a total immersed area (counting both sides) of 8 cm^2. The corrosion product, identified by X-ray diffraction, was lead carbonate hydroxide, $Pb_3(CO_3)_2(OH)_2$, also known as lead white, basic lead carbonate or the mineral hydrocerussite. A treatment potential of −1.3 V vs. SSE was chosen, based on the potentiodynamic scan of a corroded lead object in 0.5 M Na_2SO_4.[16] This potential is close to the value of E^0 for the reduction of $Pb_3(CO_3)_2(OH)_2$, $E^0 = -1.240$ V vs. SSE, in **Appendix I**. The potential was held briefly at the open circuit value, swept linearly in time to −1.3 V vs. SSE at a rate of 10 mV/s and held at that potential. This sequence of three steps avoids a large current spike that would be generated if the potential was set directly to −1.3 V vs. SSE. During the potential sweep, the current became increasingly negative until the potential reached −1.3 V vs. SSE, after about 50 s. Then the potential was held fixed at −1.3 V and the current dropped back towards zero as the corrosion was reduced. The experiment was ended when the current reached a stable value, in this case after a few hundred seconds. After the treatment, the sample had turned from white to light gray, indicating that the corrosion had been reduced back to metallic lead. The reduced material adhered well to the sample, but such material can be porous[16] and possibly fragile. Lead corrosion products are non-conducting, so it is important to make good electrical contact with the metal under the corrosion.

Procedure Using Power Supply – for Treating Lead

Figure 10 shows the current versus time for another sample of lead in 0.5 M Na_2SO_4, treated with a power supply and two digital multimeters using the arrangement shown in **Figure 1**. The sample was the same size as that in **Figure 9** but more corroded (mainly lead carbonate hydroxide but also small amounts of other lead carbonates identified by X-ray diffraction). In this case, most of the sample was immersed (a total immersed area of 12.8 cm^2), and contact with the part of the sample left outside the electrolyte was made with a platinum wire.

In this procedure, the three electrodes were connected as shown in **Figure 1**, except that the wire at one terminal of the power supply was left disconnected at first so that no current could flow until everything was ready. The potential and current of the power supply were set to zero. When the electrodes were connected and immersed in the electrolyte, the data-logging program was started to collect the readings of current versus time, and the wire at the power supply was connected. The current setting on the power supply was set to a value higher than the maximum current expected to avoid the power supply switching to constant current mode. Then the voltage setting on the power supply was changed slowly until the voltmeter read the treatment potential of −1.3 V vs. SSE. The voltage did not remain at this value, however, and the power supply had to be adjusted regularly to bring the potential back to the chosen treatment value. These adjustments produced the abrupt steps in current seen in **Figure 10**.

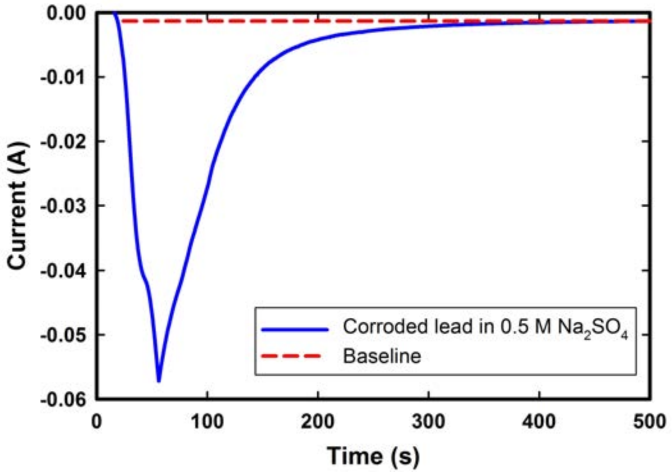

Figure 9. Current versus time for the potentiostatic reduction of corroded lead at −1.3 V vs. SSE in 0.5 M Na_2SO_4. The counter electrode was platinum mesh. The solid line shows the changing current as the lead corrosion is reduced. The dashed line, extrapolated from the region where the current has dropped to a steady value of −1.3 mA, is used as a baseline in calculating the area between it and the solid line for coulometric calculations.

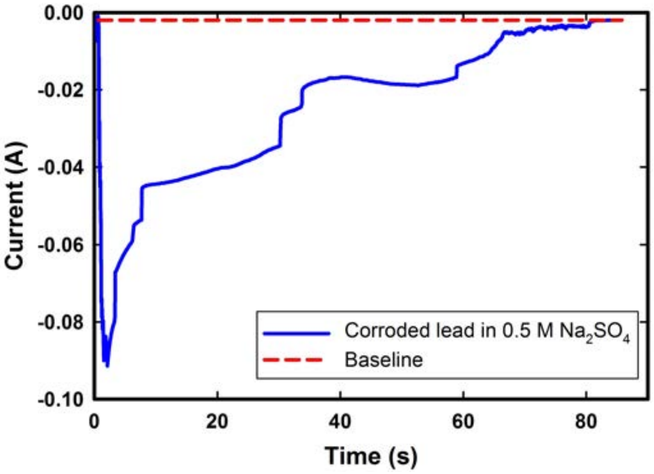

Figure 10. Current versus time for the potentiostatic reduction of corroded lead in 0.5 M Na_2SO_4 using a power supply. The counter electrode was platinum mesh. The solid line shows the current versus time for the lead sample, recorded using a data-logging program. The dashed line, a background current of −1.96 mA, is used as a baseline in calculating the area between it and the solid line for coulometric calculations.

Procedure Using Power Supply – for Treating Iron

Early conservation treatments of iron with electrolysis used two electrodes (the object and the counter electrode). In some treatments a hole was drilled into a corroded object to attach a wire to the metal core; in others, wire was wrapped around the object to form a conducting cage. The wire to the object was connected to a power supply along with another wire connected to the counter electrode. The potential was adjusted until bubbles of hydrogen began to form.[39,40] At this point, the setting of the power supply could be increased to generate even more bubbles, or else decreased back to a value just before the appearance of bubbles. An alternative to watching for bubbles is to measure the current-voltage curve with two electrodes and to estimate the onset of hydrogen gas from the potential setting at which the current increases suddenly.[3] It is important to note that the appearance of bubbles alone is not a sign that the power supply is connected properly. If the power supply is connected backwards, bubbles may still appear on the object, but they will be bubbles of oxygen gas (from water being oxidized), not hydrogen gas (from water being reduced), and the object will be corroded further.

As mentioned above, an excess of hydrogen bubbles can lead to embrittlement. When a reference electrode is added, the potential of the object can be measured and controlled, and excessive hydrogen can be avoided. Treatment conditions can be presented on a Pourbaix diagram. **Figure 11** shows a partial Pourbaix diagram[41] for iron with potentials recommended for treatment of archaeological iron.[17] The line separating iron(III) oxyhydroxide (FeOOH) and magnetite (Fe_3O_4) has been calculated using E^0 from **Appendix I**, and for convenience, the potential scale versus SSE has been added on the right.

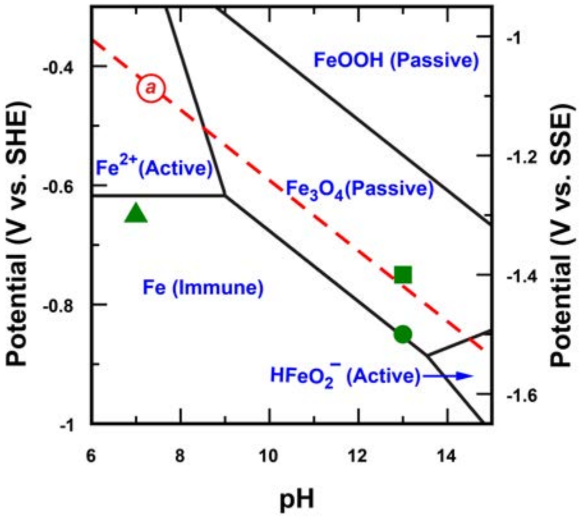

Figure 11. Portion of Pourbaix diagram for iron, showing position of recommended treatment potentials:[17] circle pH 13, −1.5 V vs. SSE, square pH 13, −1.4 V vs. SSE and triangle pH 7, −1.3 V vs. SSE. Below the dashed line (labelled a), water is reduced to hydrogen gas. Regions between the solid lines are labelled to indicate the dominant species present and the expected state of corrosion (Active, Passive, Immune).

The lower potential at pH 13, −1.5 V vs. SSE, is chosen if hydrogen bubbles are to be used initially to loosen concretion. After the concretion has been removed, the potential is then set to −1.4 V vs. SSE to minimize the formation of bubbles. During this phase of the treatment, the electrolyte is changed regularly to encourage diffusion of Cl^- ions out of the pores, and the concentration of Cl^- ions is monitored until a suitably low value is reached, such as 5 mg/L.[42] The container should be covered to keep carbon dioxide from reacting with hydroxide ions and reducing the pH, especially for large objects where the electrolyte is not changed often.[43] Finally, during rinsing to remove residual electrolyte at a pH near 7, the potential is held at −1.3 V vs. SSE, in the immune region of the Pourbaix diagram. Note that measurement of the potential becomes more difficult in the final step as the conductivity of the solution becomes lower with repeated washing.

In contrast to silver tarnish or copper corrosion, where the reduction produces silver or copper metal, iron corrosion cannot be reduced all the way to iron metal except in special circumstances. Iron(III) corrosion products can be reduced to Fe_3O_4 or Fe^{2+} ions, but generally not to Fe metal,[44,45] except possibly at highly negative potentials.[46] The potential for reduction of Fe_3O_4 to Fe is close to the potential for reduction of water to hydrogen (**Appendix I**), so the two reactions compete.

The reduction of FeOOH to Fe_3O_4 opens up pores in the corrosion layer, because FeOOH takes up more room than Fe_3O_4. The molar volume per mole of Fe is 20.9 cm^3 for FeOOH but only 14.9 cm^3 for Fe_3O_4.[47] When the pores open, Cl^- ions can diffuse out more rapidly. In addition, some of the current in the electrolysis is carried by Cl^- ions, giving an added boost to the chloride ion removal, although it has been argued that this is not a significant effect.[8] If marine iron is allowed to dry out after excavation, then the lepidocrocite (γ-FeOOH) that forms initially may convert to goethite (α-FeOOH), which is harder to reduce.[48]

Studies of removing Cl^- ions from corroded iron have compared electrolysis to simple soaking in sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), or in alkaline sulfite, which is a mixture of sodium hydroxide and sodium sulfite (Na_2SO_3). These studies were done with a limited number of samples and with mixed results. In some cases, electrolysis and soaking in NaOH or Na_2CO_3 removed about the same amount of Cl^- ions and at similar rates[49,50] for both wrought iron and cast iron, although electrolysis was faster than soaking in NaOH in one case.[50] Another study of cast iron found that electrolysis was faster and removed more Cl^- ions than soaking in KOH or alkaline sulfite.[51] Electrolysis was found to remove more Cl^- ions than soaking in NaOH or alkaline sulfite from marine iron objects that had been allowed to dry.[4]

Procedure Using Local Treatments

Local electrochemical treatments have been developed so that electrochemical reduction can be applied without immersing the object in an electrolyte. The counter electrode is housed in a cylinder, which can be held like a pencil.[52] The electrolyte is contained in an absorbent material such as foam or cotton at the end of the cylinder. When the counter electrode and the working electrode (the object) are connected to a power supply and the absorbent material pressed against the object, the area wet by the electrolyte can be reduced by electrolysis.

In the simplest design, the reference electrode is eliminated.[52] A reference electrode can be added in a separate beaker of electrolyte; cotton thread is run from the beaker to the absorbent material and kept wet with electrolyte.[53] It is easier to keep the thread wet if the beaker with the reference electrode is elevated above the object. Flat cotton stay tape, also called tailor's stay tape, with a 5 mm width also works well, because it takes longer to dry out than cotton thread. Once the best setting for the power supply has been found, by a potentiostatic scan or by trial and error on a small region of the object, the thread can be removed and the treatment continued without the reference electrode. A more sophisticated system is being developed,[37,54] where the reference electrode (glassy carbon) and counter electrode (platinum) are packaged together in a cylinder. The cylinder also houses tubes that supply fresh electrolyte to the foam pad and remove contaminated electrolyte from the pad.

One difficulty in these local methods is the high resistance of the electrolyte in the foam or cotton. This causes the peaks in the potentiodynamic scan to be broadened and shifted to more negative potentials, and these shifts must be considered in setting the treatment potential.[54]

Cathodic Protection

A second role of electrolysis in conservation is to protect an object from corroding while Cl^- ions are being removed. When an object is corroding, its potential, E_{corr}, is a corrosion potential or mixed potential, set by the balance between oxidation (of the metal) and reduction (usually of dissolved oxygen). When the potential is forced below E_{corr} by a power supply or potentiostat, the oxidation reaction slows down and the reduction reaction speeds up. Thus the rate of corrosion decreases at the expense of increasing the rate of oxygen reduction. This approach to decreasing corrosion rate is called cathodic protection. Cathodic protection can also be accomplished by connecting the iron object to a sacrificial metal, such as zinc (Zn) or aluminum (Al).[55] Cathodic protection was used in the treatment of the Hunley submarine.[5,56] The side effect of increased oxygen reduction is an increase in local pH, which can allow corrosion products such as iron(II) hydroxychloride (β-$Fe_2(OH)_3Cl$) to release their Cl^- ions, a process that occurs at high pH.[57] If cathodic protection is done in seawater, which contains calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}), then the increase in pH can cause calcium carbonate ($CaCO_3$) to precipitate.[58]

Constant Current (Galvanostatic Technique)

In the galvanostatic technique (also called chronopotentiometry) the current is set to a constant value, and the potential is recorded as a function of time. The potential stays roughly constant while a given type of corrosion is being reduced, producing a plateau in a plot of potential as a function of time, then changes when that reduction is finished. The current is switched off when the potential has fallen below the value of the plateau. Whereas the potentiodynamic scan of a corroded material shows a series of peaks, this technique shows a series of plateaus near the same potentials where the potentiodynamic peaks would be.

Figure 12 shows the potential as a function of time for galvanostatic reduction of a tarnished silver sample in 0.1 M KCl. The measurement was done with a potentiostat, using a current of 0.25 mA or 0.00025 A and an SCE reference electrode. The choice of current depends on the size of the object (6.8 cm^2 in this case); typically it is chosen so the corrosion is reduced reasonably quickly but the plateaus remain distinct. Each plateau corresponds to the reduction of a specific compound (or reduction of water to hydrogen). The duration of a plateau can be used to calculate the amount of material reduced during the plateau, as discussed below. This technique is generally used to characterize corrosion, rather than for treatment.[29,59]

Calculation of Amount of Material Reduced (Coulometry)

In electrolysis, a current produces a chemical reaction. From the size and duration of the current for each chemical reaction, the amount of material that reacted can be calculated. This measurement and calculation is called coulometry.

Coulometry can be used to estimate the amount of corrosion on a sample. If samples of some metal are deliberately corroded in different environments, the amount of corrosion that forms reveals how corrosive the environment is for that metal. In this way, coulometry has been used to characterize indoor air quality in museums.[11,12]

This section reviews this calculation for the three techniques discussed above: galvanostatic, potentiostatic and potentiodynamic. The calculation of the amount of material reduced has two parts: determination of the charge reduced, and conversion of the charge to a mass or thickness.

Determination of the Charge

Electric current I (in units of amperes, A) is the flow of electric charge Q (in units of coulombs, C) over time t (in units of seconds, s). A charge of 1 coulomb corresponds to a current of 1 ampere flowing for 1 second (1 C = 1 A s).

The simplest calculation of charge Q for the methods discussed above is that for the constant current technique (galvanostatic). If a given plateau in the potential lasts for a time t, the charge is given by $Q = It$. It is assumed that only one reaction is contributing to the current during a given plateau. Any reduction of oxygen will lead to an overestimate of Q, so if high accuracy is needed, the experiment should be done under nitrogen rather than air. For example, the plateau in **Figure 12** lasts about 1000 sec at 0.25 mA, corresponding to $Q = (2.5 \times 10^{-4}\text{ A})\ (1000\text{ s}) = 0.25\text{ C}$.

In the potentiostatic technique, the charge Q for a given reaction is the area under the curve of current I plotted versus time t. Areas can be calculated with most modern software packages for plotting data. In the potentiostatic measurements in **Figure 9** and **Figure 10**, the areas to be calculated are between the data (solid line) and a dashed baseline. The baseline is intended to correct for the reduction of dissolved oxygen gas and is extrapolated from the current flowing at long times. The correction is only approximate, because it assumes that this extra current is independent of time. The area in **Figure 9** is 4.0 A s which corresponds to $Q = 4.0$ C. Similarly the area in **Figure 10** gives a charge of $Q = 115$ C.

In the potentiodynamic method, the charge Q for a given reaction is proportional to the area under the corresponding peak in the graph of current I versus potential E. **Figure 13** shows an example peak for the reduction of tarnished silver. The area is calculated only for the peak, to eliminate as much as possible any contributions to the current from the reaction associated with the background (reduction of oxygen or of water). If current is plotted in amperes and potential in volts, the area will have units of ampere-volts. This can be converted to charge Q (in units of coulombs) by dividing this area by the scan rate (in volts per second). In **Figure 13**, the area between the peak and the baseline is 5.8×10^{-5} A V and the scan rate is 1 mV/s (i.e., 1×10^{-3} V/s), giving a charge of $Q = 0.058$ C.

Determination of the Mass and Thickness

Once the charge Q is estimated, the mass and thickness of the material reduced can be calculated from Q using Faraday's law of electrolysis.[60] For tarnished silver, the mass m (in units of grams, g) of tarnish converted to metal is related to Q by

$$m = \frac{Q \cdot M}{z \cdot F}$$

where z is the number of electrons needed to reduce each formula unit back to metal ($z = 2$ for Ag_2S); F is Faraday's constant (96,487 C/mol); and M is the molecular mass of the tarnish (247.8 g/mol for Ag_2S).

From the mass m, the thickness h (in units of centimetres, cm) is given by

$$h = \frac{m}{s \cdot d}$$

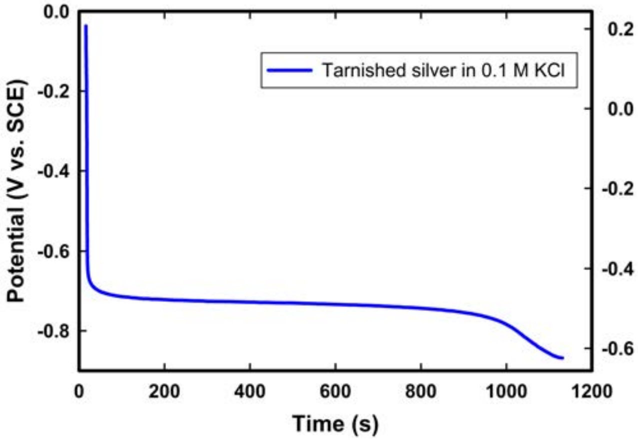

Figure 12. Potential versus time for the galvanostatic reduction of tarnished silver in 0.1 M KCl at a current of 0.25 mA. The counter electrode was platinum mesh.

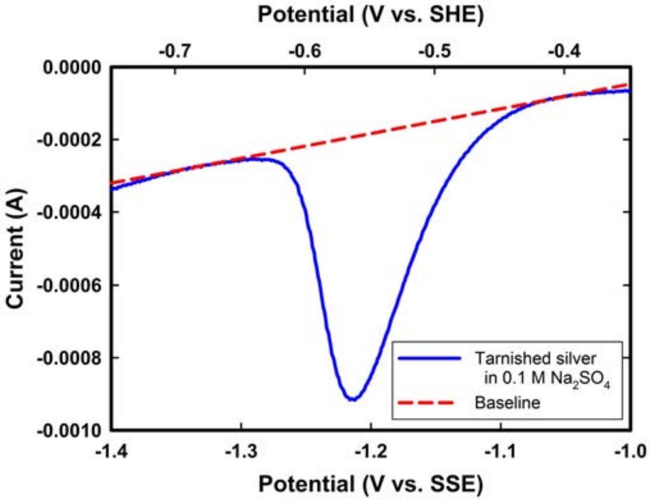

Figure 13. Expanded view of current versus potential from **Figure 6** showing the reduction peak (solid line) at −1.2 V vs. SSE. This peak is due to the reduction of silver sulfide to silver metal. The dashed line is a baseline used in calculating the area between it and the solid line.

where s is the surface area where the tarnish was reduced (in units of square centimetres, cm^2) and d is the density (in units of grams per cubic centimetre, g/cm^3). The density of Ag_2S is $d = 7.234$ g/cm^3.[61] The formula directly relating h to Q (bypassing the intermediate calculation of m) is

$$h = \frac{Q \cdot M}{z \cdot F \cdot s \cdot d}$$

For **Figure 13**, where the sample area exposed to the electrolyte was 3 cm^2 and the charge was 0.058 C, the calculated thickness h is 3.4×10^{-6} cm (34 nm) of Ag_2S.

For the reduction of lead carbonate hydroxide, where $z = 2$, $M = 777.67$ g/mol and $d = 6.14$ g/cm^3,[62] the thickness h is 3.3×10^{-4} cm (3.3 μm) for **Figure 9** (where $s = 8$ cm^2 and $Q = 4.0$ C) and 5.9×10^{-3} cm (59 μm) for **Figure 10** (where $s = 12.8$ cm^2 and $Q = 115$ C).

Oxidation Reactions on the Working Electrode

The examples provided above are based on reduction reactions on the working electrode. Electrochemical techniques can also be used to oxidize the working electrode. One technique that has been used in conservation is called voltammetry of microparticles (VMP).[6,63,64] A graphite electrode is rubbed over a metal object to pick up a small amount of metal. Particles of metal that adhere to the graphite electrode are then oxidized in an electrochemical cell by scanning the potential of the electrode in the positive direction. This is the opposite direction to that used in the reduction techniques discussed until now. The potential of peaks in the potentiodynamic scan is used to identify what metals are present in the sample. Peaks identified as zinc, silver, lead, copper and tin (Sn) in a study of archaeological materials[6] are within 0.1 V of the values for E^0 given in **Appendix I**.

On gilded silver objects where silver sulfide tarnish covers the gold (Au), a two-step electrolytic treatment to clean the surface has been developed.[65] This treatment uses 0.1 M sodium nitrate ($NaNO_3$) buffered at pH 5 with equal concentrations (10^{-4} M) of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa). The first step is reduction (potentiostatic mode at −1.3 V vs. SSE) which converts the dark tarnish back to white silver metal that obscures the yellow gold. The second step is oxidation (potentiodynamic scan to 0.25 V vs. SSE) which forces the reduced silver metal to corrode and dissolve into the electrolyte, thus uncovering the gilding.

CONCLUSIONS

This paper has provided basic information on using electrochemical techniques that involve the flow of electric current, to supplement the information in Part I on measuring the potential of metal objects. Most of the examples given involved reduction, either to treat objects or to identify the potentials needed for treatments. The use of oxidation in characterizing alloy composition and in removing reduced silver from gilded surfaces was discussed briefly.

Electrochemical processes are the basis of corrosion, so conservators treating metal artifacts are constantly dealing with the negative consequences of electrochemistry. The goal of this paper and Part I is to help conservation professionals to see the positive aspects of electrochemistry and to encourage them to consider using electrochemical techniques more widely. The detailed, practical information is intended as a resource that will be helpful to conservators and conservation scientists who are just getting started in setting up and using electrochemical equipment appropriate for conservation.

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 or treatments.

Connectors, cables and clips: It is useful to have an assortment of adaptors, cables and clips. In general, the connectors on potentiostats accept BNC plugs, whereas the connectors on power supplies and voltmeters accept banana plugs. Reference electrodes can have BNC plugs, banana plugs or pin tips. Cables are needed for the different types of connectors, as well as adaptors to switch between them. Clips are needed to attach to objects. Alligator clips (also known as crocodile clips or spring clips) are useful for this and come in styles that can accept banana plugs. Larger alligator clips, useful for attaching to large objects, are available with coated handles (e.g., SureGrip, Fluke AC285).

Pomona Electronics <www.pomonaelectronics.com/> is one manufacturer of these components and part numbers for some adapters and connectors are provided for ease of searching on the internet for images and other manufacturers. Some useful adapters are BNC to banana plug (e.g., Pomona 1894), BNC to binding post jacks (e.g., Pomona 1296), banana plug to pin tip (e.g., Pomona 1432), and pin tip to banana plug (e.g., Pomona 1809). Some useful banana connectors are banana plugs (e.g., Pomona 1325) and banana plug splices (e.g., Pomona 1829). Useful cables, also called test leads or patch cords, are ones with multi-stacking banana plugs on either end (e.g., Pomona B-36-2 which has a 36 inch (~1 m) cable).

A selection of electronic suppliers includes: Allied Electronics <www.alliedelec.com/>; Digi-Key Electronics <www.digikey.com/>; Fluke <www.fluke.com/>; McMaster-Carr <www.mcmaster.com/>; Newark element14 <www.newark.com/>

Electrochemical cell accessories (cells for use with inert gases): Gamry Instruments <www.gamry.com/>; Radiometer Analytical <www.radiometer-analytical.com/>

Platinum mesh electrodes: Alfa Aesar <www.alfa.com/en/>

Potentiostats (e.g., Solartron Analytical and Princeton Applied Research, PAR): Ametek <www.ametek.com/>; Gamry Instruments <www.gamry.com/>

Power supplies: Keysight Technologies (formerly part of Agilent Technologies) <www.keysight.com/>; Keithley (now part of Tektronix) <www.tek.com/>

Stainless steel hardware: a broad selection is available from McMaster-Carr <www.mcmaster.com/>

APPENDIX I. STANDARD POTENTIALS

Table I gives standard potentials, E^0, for some reactions involved in the reduction of corrosion products. Values have been calculated from free energies[62,66,67] using standard methods.[68] In **Table I**, ions are on the right-hand side of the reactions. If the reactions are being driven to the right (reduction), then these ions will be produced in the reaction, and their concentration will build up near the surface of the object. The concentration near the surface will be unknown, but if it is taken to be 1 M as a rough estimate, then the potential of the reaction will be equal to E^0 through the Nernst equation. In an acid solution, where the OH^- ions will react with H^+ from the acid, this will give a poor estimate for potential. For reduction in an acid, it is better to rewrite the reactions in terms of H^+ rather than OH^-. Standard potentials for reactions can be written both ways, either involving H^+ ions or OH^- ions.[69] The water is assumed to be pure except for the ions in the reaction and their counter ions. The counter ions are assumed to be unreactive.

One trend in **Table I** should be noted. For a given metal ion, E^0 for the sulfide is more negative than for other compounds of the same metal ion, such as chlorides or oxides. This reflects the low solubility of the sulfides. In fact, there is a direct connection between E^0 and solubility.[70]

Table II shows the standard potentials for metal ions. These values of E^0 can be compared to potentials measured during the characterization of metals by voltammetry of microparticles, where small samples of metal are oxidized (reactions going from right to left).[6] The reaction involving oxygen has been added to the list as an estimate of the potential at which water can be expected to be oxidized to oxygen. When water is

Table I. Standard Potentials for Water, Oxygen and Selected Corrosion Products

Reaction	E^0 (V vs. SHE)	E^0 (V vs. SSE)
Water/Oxygen		
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	0.401	−0.250
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.828	−1.479
Copper		
$CuCl_2 + e^- \rightleftharpoons CuCl + Cl^-$	0.783	0.132
$CuCl + e^- \rightleftharpoons Cu + Cl^-$	0.118	−0.533
$2CuO + H_2O + 2e^- \rightleftharpoons Cu_2O + 2OH^-$	−0.171	−0.822
$Cu_2O + H_2O + 2e^- \rightleftharpoons 2Cu + 2OH^-$	−0.371	−1.022
$Cu_2S + H_2O + 2e^- \rightleftharpoons 2Cu + HS^- + OH^-$	−0.923	−1.574
Silver		
$Ag_2SO_4 + 2e^- \rightleftharpoons 2Ag + SO_4^{2-}$	0.653	0.002
$Ag_2O + H_2O + 2e^- \rightleftharpoons 2Ag + 2OH^-$	0.343	−0.308
$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.222	−0.428
$Ag_2S + H_2O + 2e^- \rightleftharpoons 2Ag + HS^- + OH^-$	−0.687	−1.338
Lead		
$PbCl_2 + 2e^- \rightleftharpoons Pb + 2Cl^-$	−0.267	−0.918
$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$	−0.355	−1.006
$PbO + H_2O + 2e^- \rightleftharpoons Pb + 2OH^-$	−0.578	−1.229
$PbCO_3 + 2e^- \rightleftharpoons Pb + CO_3^{2-}$	−0.506	−1.157
$Pb_3(CO_3)_2(OH)_2 + 6e^- \rightleftharpoons 3Pb + 2CO_3^{2-} + 2OH^-$	−0.589	−1.240
$PbS + H_2O + 2e^- \rightleftharpoons Pb + HS^- + OH^-$	−0.988	−1.639
Iron		
$3FeOOH + e^- \rightleftharpoons Fe_3O_4 + OH^- + H_2O$	−0.608	−1.259
$3Fe_2O_3 + H_2O + 2e^- \rightleftharpoons 2Fe_3O_4 + 2OH^-$	−0.650	−1.301
$Fe_3O_4 + 4H_2O + 8e^- \rightleftharpoons 3Fe + 8OH^-$	−0.911	−1.562
$Fe_3O_4 + H_2O + 2e^- \rightleftharpoons 3FeO + 2OH^-$	−0.941	−1.592
Other metals		
$HgS + H_2O + 2e^- \rightleftharpoons Hg + HS^- + OH^-$	−0.739	−1.390
$SnO_2 + 2H_2O + 4e^- \rightleftharpoons Sn + 4OH^-$	−0.935	−1.586
$ZnO + H_2O + 2e^- \rightleftharpoons Zn + 2OH^-$	−1.260	−1.911

Table II. Standard Potentials for Water and Selected Metals

Reaction	E^0 (V vs. SHE)	E^0 (V vs. SSE)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.229	0.578
$Ag^+ + e^- \rightleftharpoons Ag$	0.799	0.148
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$	0.796	0.145
$Cu^+ + e^- \rightleftharpoons Cu$	0.518	−0.133
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.340	−0.311
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.126	−0.777
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.141	−0.792
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.409	−1.060
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.762	−1.413

oxidized, the concentration of H^+ will build up near the surface of the electrode (reaction driven to the left), so if the concentration of H^+ is taken to be 1 M as a rough estimate, then the potential for that reaction will be equal to E^0. In a basic solution, this will be a poor estimate of the potential because the H^+ ions will react with the OH^- ions in the solution.

REFERENCES

[1] 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.

[2] Costa, Virginia, "Electrochemistry as a conservation tool: an overview," in: *Conservation Science 2002*, edited by Joyce H. Townsend, Katherine Eremin and Annemie Adriaens (London: Archetype, 2003), pp. 88–95.

[3] North, N.A., "Conservation of metals," in: *Conservation of Marine Archaeological Objects*, edited by Colin Pearson (London: Butterworths, 1987), pp. 207–252.

[4] Guilminot, E., D. Neff, C. Rémazeilles, S. Reguer, F. Kergourlay, C. Pelé, P. Dillmann, P. Refait, F. Nicot, F. Mielcarek, N. Huet and J. Rebière, "Influence of crucial parameters on the dechlorination treatments of ferrous objects from seawater," *Studies in Conservation*, vol. 57, no. 4, 2012, pp. 227–236.

[5] Mardikian, Paul, "Conservation and management strategies applied to post-recovery analysis of the American civil war submarine *H.L. Hunley* (1864)," *The International Journal of Nautical Archaeology*, vol. 33, no. 1, 2004, pp. 137–148.

[6] Costa, V., K. Leyssens, A. Adriaens, N. Richard and F. Scholz, "Electrochemistry reveals archaeological materials," *Journal of Solid State Electrochemistry*, vol. 14, no. 3, 2010, pp. 449–451.

[7] Selwyn, Lyndsie and W. Ross McKinnon, "Practical Electrochemistry for Conservators and Conservation Scientists: Part I – The Basics of Potential Measurement," *Journal of the Canadian Association for Conservation*, vol. 42, 2017, pp. 3–15.

[8] North, N.A., "Electrolysis of marine cast iron," in: *Papers from the First Southern Hemisphere Conference on Maritime Archaeology: Perth, Western Australia, 1977* (Melbourne, Australia: Oceans Society of Australia, 1977), pp. 145–147.

[9] Schalm, Olivier, Amandine Crabbé, Patrick Storme, Rita Wiesinger, Arianna Gambirasi, Eva Grieten, Pieter Tack, Stephen Bauters, Christoph Kleber, Monica Favaro, Dominique Schryvers, Laszlo Vincze, Herman Terryn and Alessandro Patelli, "The corrosion process of sterling silver exposed to a Na_2S solution: monitoring and characterizing the complex surface evolution using a multi-analytical approach," *Applied Physics A*, vol. 122, no. 10, article 903, 2016, 16 pp.

[10] Schalm, Olivier, Patrick Storme, Arianna Gambirasi, Monica Favaro and Alessandro Patelli, "How effective are reducing plasma afterglows at atmospheric pressure in removing sulphide layers: Application on tarnished silver, sterling silver and copper," *Surface and Interface Analysis*, vol. 50, no. 1, 2018, pp. 32–42.

[11] Thickett, David and Virginia Costa, "The effect of particulate pollution on the corrosion of metals in heritage locations," 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 0907, 8 pp.

[12] `t Hart, Lucy, Patrick Storme, Willemien Anaf, Gert Nuyts, Frederik Vanmeert, Walter Dorriné, Koen Janssens, Karolien de Wael and Olivier Schalm, "Monitoring the impact of the indoor air quality on silver cultural heritage objects using passive and continuous corrosion rate assessments," *Applied Physics A*, vol. 122, no. 10, article 923, 2016, 10 pp.

[13] 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.

[14] Skoog, Douglas A., Donald M. West, F. James Holler and Stanley R. Crouch, *Fundamentals of Analytical Chemistry*, 9th edition (Belmont, CA: Brooks/Cole, Belmont, 2014), p. 611.

[15] Doménech-Carbó, Antonio, "Voltammetric methods applied to identification, speciation, and quantification of analytes from works of art: an overview," *Journal of Solid State Electrochemistry*, vol. 14, no. 3, 2010, pp. 363–379.

[16] Degrigny, C. and R. Le Gall, "Conservation of ancient lead artifacts corroded in organic acid environments: electrolytic stabilization/consolidation," *Studies in Conservation*, vol. 44, no 3, 1999, pp. 157–169.

[17] 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.

[18] MacLeod, Ian D. and Neil A. North, "Conservation of a composite cannon *Batavia* (1629)," *The International Journal of Nautical Archaeology*, vol. 11, no. 3, 1982, pp. 213–219.

[19] ASTM-G193, "G193-12d. Standard terminology and acronyms relating to corrosion," in: *Annual Book of ASTM Standards 2015, Volume 03.02 Corrosion of Metals; Wear and Erosion* (West Conshohocken, PA: American Society for Testing and Materials, 2015), pp. 833–856.

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

[21] Bard, Allen J. and Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edition (New York: John Wiley & Sons, 2001), pp. 228–239.

[22] Dean, John A., *Lange's Handbook of Chemistry*, 14th edition (New York: McGraw-Hill, 1992), pp. 8.124–8.139.

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

[24] Smith, J.M., J.C. Wren, M. Odziemkowski and D.W. Shoesmith, "The electrochemical response of preoxidized copper in aqueous sulfide solutions," *Journal of the Electrochemical Society*, vol. 154, no. 8, 2007, pp. C431–C438.

[25] Devaud, Charlotte, Elodie Guilminot, Sylvie Labroche and Gilles Baron, "Stabilization of iron/copper composites: an overview of treatment difficulties," in: *Metal 2016: Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group*, New Delhi, India, 26–30 September 2016, edited by Reghu Menon, Claudia Chemello and Achal Pandya (Paris: International Council of Museums Committee for Conservation, 2016), pp. 109–116.

[26] Capelo, S., P.M. Homem, J. Cavalheiro and I.T.E. Fonseca, "Linear sweep voltammetry: a cheap and powerful technique for the identification of the silver tarnish layer constituents," *Journal of Solid State Electrochemistry*, vol. 17, no. 1, 2013, pp. 223–234.

[27] Morel, Olivier and Christian Degrigny, "Mise au point d'un traitement électrolytique de nettoyage d'instruments de musique à vent," in : *Conservation et restauration d'objets métalliques*, Archéologie en Yvelines, Document de Travail, vol. 5 (Versailles, France: Conseil général des Yvelines, 1992), pp. 50–61.

[28] Vacquié, Cécile, Jean-Michel Blengino and Noël Lacoudre, "Traitement électrolytique de franges de drapeau ternies par la corrosion atmosphérique," *Les Cahiers Techniques de l'ARAAFU*, vol. 1, 1994, pp. 19–26.

[29] Lin, Huang, G.S. Frankel and W.H. Abbott, "Analysis of Ag corrosion products," *Journal of the Electrochemical Society*, vol. 160, no. 8, 2013, pp. C345–C355.

[30] Tran, T.T.M., C. Fiaud and E.M.M. Sutter, "Oxide and sulphide layers on copper exposed to H_2S containing moist air," *Corrosion Science*, vol. 47, no. 7, 2005, pp. 1724–1737.

[31] Graedel, T.E., J.P. Franey, G.J. Gualtieri, G.W. Kammlott and D.L. Malm, "On the mechanism of silver and copper sulfidation by atmospheric H_2S and OCS," *Corrosion Science*, vol. 25, no. 12, 1985, pp. 1163–1180.

[32] Graedel, T.E., "Corrosion mechanisms for silver exposed to the atmosphere," *Journal of the Electrochemical Society*, vol. 139, no. 7, 1992, pp. 1963–1970.

[33] Cottis, R.A., "Hydrogen embrittlement," in: *Shreir's Corrosion, Vol. 2: Corrosion in Liquids, Corrosion Evaluation*, 4th edition, edited by R.A. Cottis, M.J. Graham, R. Lindsay, S.B. Lyon, J.A. Richardson, J.D. Scantlebury and F.H. Stott (Amsterdam: Elsevier, 2010), pp. 902–922.

[34] Degrigny, C., M. Jerome and N. Lacoudre, "Surface cleaning of silvered brass wind instruments belonging to the Sax collection," *Corrosion Australasia*, vol. 18, no. 2, 1993, pp 16–18.

[35] Degrigny, Christian and Denise Witschard, "La châsse des enfants de Saint Sigismond de l'Abbaye de Saint-Maurice: traitements électrochimiques des reliefs d'argent en cours de restauration," in: *Medieval Reliquary Shrines and Precious Metalwork: Châsses-reliquaires et orfèvrerie médiévales*, edited by Kilian Anheuser and Christine Werner (London: Archetype, 2006), pp. 9–16.

[36] 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.

[37] Degrigny, Christian, Romain Jeanneret and Denise Witschard, "Local cleaning with the Pleco electrolytic pencil of the tarnished Saint Candide reliquary head at the Treasury of Saint-Maurice Abbey, Valais (Switzerland)," *e-Preservation Science*, vol. 12, 2015, pp. 20–27.

[38] Palomar, Teresa, Blanca Ramírez Barat, Emma García and Emilio Cano, "A comparative study of cleaning methods for tarnished silver," *Journal of Cultural Heritage*, vol. 17, no. 1, 2016, pp. 20–26.

[39] Hamilton, Donny L., "Conservation of cultural materials from underwater sites," *Archives and Museum Informatics*, vol. 13, nos. 3–4, 1999, pp. 291–323.

[40] Pearson, Colin, "Conservation of ethnographic metal objects," *Senri Ethnological Studies*, vol. 23, 1988, pp. 129–176.

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

[42] Rimmer, Melanie, David Watkinson and Quanyu Wang, "The impact of chloride desalination on the corrosion rate of archaeological iron," *Studies in Conservation*, vol. 58, no. 4, 2013, pp. 326–337.

[43] Sullivan, K., W. Ross McKinnon and L. Selwyn, "Carbon dioxide absorption in alkaline treatment solutions for archaeological iron," in: *Metal 2013: Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group*, Edinburgh, Scotland, 16–20 September 2013, edited by Ewan Hyslop, Vanesa Gonzalez, Lore Troalen and Lyn Wilson (Edinburgh: Historic Scotland, 2013), pp. 77–84.

[44] Schmuki, P., M. Büchler, S. Virtanen, H.S. Isaacs, M.P. Ryan and H. Böhni, "Passivity of iron in alkaline solutions by in situ XANES and a laser reflection technique," *Journal of the Electrochemical Society*, vol. 146, no. 6, 1999, pp. 2097–2102.

[45] North, N.A. and C. Pearson, "Methods for treating marine iron," in: *Preprints, 5th Triennial Meeting, ICOM Committee for Conservation*, Zagreb, Croatia, 1–8 October 1978 (Paris: International Council of Museums, 1978), 78/23/3, pp. 1–10.

[46] Schmuki, Patrik, Sannakaisa Virtanen, Alison J. Davenport and Carissima M. Vitus, "In situ x-ray absorption near-edge spectroscopic study of the cathodic reduction of artificial iron oxide passive films," *Journal of the Electrochemical Society*, vol. 143, no. 2, 1996, pp. 574–582.

[47] Selwyn, L., "Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge," 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, Australia: National Museum of Australia, 2004), pp. 294–306.

[48] Stratmann, M. and K. Hoffmann, "*In situ* Möβbauer spectroscopic study of reactions within rust layers," *Corrosion Science*, vol. 29, nos. 11/12, 1989, pp. 1329–1352.

[49] Drews, M.J., P. de Viviés, N.G. Gonzalez and P. Mardikian, "A study of the analysis and removal of chloride in iron samples from the 'Hunley'," 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, Australia: National Museum of Australia, 2004), pp. 247–260.

[50] Gonzalez, Nestor, Desmond Cook, Philippe de Vivies, Michael Drews and Paul Mardikian, "The effects of cathodic polarization, soaking in alkaline solutions and subcritical water on cast iron corrosion products," 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. 32–37.

[51] Coelho, J.C., C.M. Oliveira, M.D. Carvalho and I.T.E. Fonseca, "The efficiency of electrochemical methods for the removal of chloride ions from iron marine archaeological objects: a comparative study," *Materials and Corrosion*, vol. 65, no. 1, 2014, pp. 38–44.

[52] Aldaz, A., T. España, V. Montiel and M. Lopez-Segura, "A simple tool for the electrolytic restoration of archaeological metallic objects with localized corrosion," *Studies in Conservation*, vol. 31, no. 4, 1986, pp. 175–176.

[53] Degrigny, Christian, "Cleaning of CH artefacts: an overview," in: *Electrochemistry in Historical and Archaeological Conservation*, Lorentz Centre Workshop, 11–15 January, 2010 (Leiden, The Netherlands: Lorentz Center, 2010), <www.lorentzcenter.nl/lc/web/2010/364/presentations/Degrigny_cleaning.pdf>. Accessed June 2018.

[54] Jeanneret, Romain, Célia Fontaine, Denise Witschard, Antonin Tarchini and Christian Degrigny, "Using the Pleco: electrolytic treatment of metal components on artefacts," in: *Metal 2016: Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group*, New Delhi, India, 26–30 September 2016, edited by Reghu Menon, Claudia Chemello and Achal Pandya (Paris: International Council of Museums Committee for Conservation, 2016), pp. 228–234.

[55] 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.

[56] Meier, Craig K. and Paul Mardikian, "When corrosion science meets an icon of maritime history," in: *Corrosion 2004*, New Orleans, Louisiana, 28 March – 1 April 2004, paper 4317 (Houston: NACE International, 2004), 11 pp.

[57] Kergourlay, K., C. Rémazeilles, D. Neff, E. Foy, E. Conforto, E. Guilminot, S. Reguer, Ph. Dillmann, F. Nicot, F. Mielcarek, J. Rebière and Ph. Refait, "Mechanisms of the dechlorination of iron archaeological artefacts extracted from seawater," *Corrosion Science*, vol. 53, no. 8, 2011, pp. 2474–2483.

[58] North, N.A. and I.D. MacLeod, "Corrosion of metals," in: *Conservation of Marine Archaeological Objects*, edited by Colin Pearson (London: Butterworths, 1987), pp. 68–98.

[59] ASTM-B825, "B825-13. Standard test method for coulometric reduction of surface films on metallic test samples," in: *Annual Book of ASTM Standards 2015, Volume 02.04 Nonferrous Metals* (West Conshohocken, PA: American Society for Testing and Materials, 2015), pp. 988–995.

[60] Skoog et al., *Fundamentals of Analytical Chemistry*, 2014, p. 595.

[61] Dean, *Lange's Handbook of Chemistry*, 1992, p. 3.51.

[62] Greninger, Dorothy, Valerie Kollonitsch and Charles H. Kline, *Lead Chemicals* (New York: International Lead Zinc Research Organization, 197-), p. 214.

[63] Doménech-Carbó, Antonio, "Electrochemical techniques," in: *Analytical Archaeometry: Selected Topics*, edited by Howell Edwards and Peter Vandenabeele (Cambridge, UK: The Royal Society of Chemistry, 2012), pp. 210–241.

[64] Ottenwelter, E. and V. Costa, "Evidence of metallic plating on archaeological artefacts by voltammetry of microparticles," *Archaeometry*, vol. 57, no. 3, 2015, pp. 497–504.

[65] Degrigny, C., M. Wéry, V. Vescoli and J.M. Blengino, "Altération et nettoyage de pièces en argent doré," *Studies in Conservation*, vol. 41, no. 3, 1996, pp. 170–178.

[66] Dean, *Lange's Handbook of Chemistry*, 1992, pp. 6.60–6.106.

[67] Robie, Richard A., Bruce S. Hemingway and James R. Fisher, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures*, U.S. Geological Survey Bulletin 1452 (Washington, DC: United States Government Printing Office, 1978), pp. 12–29.

[68] Moore, Walter J., *Physical Chemistry*, 4th edition (Englewood Cliffs, NJ: Prentice Hall, 1972), pp. 520–549.

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

[70] Moore, *Physical Chemistry*, 1972, p. 538.