Corrosion Handbook

Theory and practical advice for corrosion measurements

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Compact Electrochemical Interfaces

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1 List of Symbols

[A]	concentration of A
$ß_{anodic}$	Tafel slope for oxidation
$ß_{cathodic}$	Tafel slope for cathodic
$\frac{\partial x}{\partial y}$	derivative of x with respect to y
ε_0	electric field constant
ε_r	relative permittivity
Φ	phase shift
ϕ	CPE parameter: 0 Resistor, 1 Capacitor
τ	time constant of a capacitor (τ = RC)
a	activity
a_{Ox}	activity of the oxidized species
a_{Red}	activity of the reduced species
A	area
c	concentration
c^b	bulk concentration
c_{Ox}	concentration of the oxidized species
c_{Red}	concentration of the reduced species
C	capacitance
C_C	coating capacitance
C_{dl}	double-layer capacitance
CE	counter electrode
d	distance
E	potential
E^0	standard potential
$E^{0'}$	formal potential
E^C	charging potential applied to a capacitor
E_{corr}	corrosion potential
E_{pp}	primary passivation potential
E_{step}	step potential during DPV and SWV
E_T	transmission potential for the passivation film
f_{Ox}	activity coefficient of the oxidized species
f_{Red}	activity coefficient of the reduced species
F	Faraday constant
I	electric current
I^0	current at t = 0
I_{cap}	capacitive charging current
I_{corr}	corrosion current
I_{crit}	critical passivation current
I_{pas}	passive current/current for passivated material
k	reaction rate
K_L	solubility product
n	amount of substance/order of reaction
Ox	an oxidized species
Q	charge
r	reaction rate
R	resistance or universal gas constant
R_{por}	pore resistance
R_{sol}	Solution resistance
R_U	uncompensated resistance
RE	reference electrode
Red	a reduced species
t	time
$t_{interval}$	time between two points of measurement
T	temperature
U	voltage
v	scan rate
vs	versus
WE	working electrode
z	electrons transferred per molecule
Z	impedance
Z_{CPE}	impedance of the CPE
Z_W	Warburg impedance

2 Introduction

2.1 Corrosion and Electrochemistry

Wikipedia delivers the following definition of corrosion: "Corrosion is a natural process, which converts a refined metal to a more chemically stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment." Since electrochemical reactions are the cause of many corrosion processes, electrochemistry seems to be an appropriate means to study corrosion processes and mechanisms.

Electrochemistry is a versatile discipline that has applications in various fields of research and industry. Corrosion research develops methods to save millions of Euros that are needed to remove the damage done by corrosion. Combining these two disciplines delivers insights into the processes causing corrosion. Electrochemistry can investigate means to prevent corrosion in hours instead of weeks. Although these experiments cannot replace the long-term test under real conditions, they can provide the knowledge for a fast pre-selection of approaches that should be investigated more closely.

In the last 20 years, electrochemical impedance spectroscopy has been opening new possibilities in corrosion and coating research. This strengthened the electrochemical research in the field of corrosion.

2.2 Goals

This handbook explains some basic knowledge of corrosion research with a focus on Linear Polarization Curves and Electrochemical Impedance Spectroscopy (EIS). Furthermore, it should afterward be possible to have a general idea of what can be read from the Tafel plot and the EIS spectrum. Some typical shapes of curves and spectra will be shown, to develop some feeling for possible phenomena and indicators.

2.3 Literature

Everyone has a different way of explaining and everyone has different ways to learn. Usually, it is smart to consult multiple literature sources, so one can decide which is more helpful and suitable according to their background knowledge and experiences. To create this handbook some books and white papers were used. Our main sources were the following:
Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Edition, 2001, ISBN: 978-0-471-04372-0
Robert G. Kelly, John R. Scully, David W. Shoesmith, *Electrochemical Techniques In Corrosion Science and Engineering*, 2003, ISBN: 978-0-8247-9917-5
Andrzei Lasia, *Electrochemical Impedance Spectroscopy and its Applications*, 2014, ISBN: 978-1-4614-8932-0
Mark E. Ozrazem, Bernard Tribollet, Electrochemical Impedance Spectroscopy, 2008, ISBN: 978-0-470-04140-6

3 Potentiostats

3.1 What Is a Potentiostat Good for?

A voltmeter measures the potential difference between two points. To do so, the circuit needs to be closed, but a very tiny current is usually flowing. This way you can see the potential difference between the two points with almost no disturbance to the investigated system.

Knowing the potential between two points is useful, but manipulating potential is even better. This is what a power source does. In all households, batteries are the most common example of DC power supplies: a power supply having constant non-alternating potentials. They are used for flashlights, mobile phones, clocks, etc. In electrochemical applications DC power supplies are used for galvanization (the deposition of metals on conducting materials, often other metals). Another well-known application is the electrolysis of compounds.

A well-known industrial example is the chloralkali process where salt (NaCl) and water (H_2O) are split into chlorine (Cl_2), hydrogen (H_2), and sodium hydroxide (NaOH). The disadvantage is that you cannot investigate a single electrode and thus a single event. The current flows through the anode (electrode where oxidation happens) and the cathode (electrode where reduction takes place). So, both these electrodes influence the measured current and the current limiting process cannot be determined. This is especially an issue in analytical chemistry.

An electrochemical analysis that can be used easily with a power supply is electrogravimetry. An electrode's weight is determined and all the metal in a defined sample volume is reduced, which leads to the precipitation of the metal on the electrode. The weight is measured again and thus the amount of metal in the sample volume will be determined. Although this method works fine, it has some disadvantages. The process takes time, e.g. 30 min plus drying and weighting for copper, nickel, or lead oxide. In the given potential window only the analyte metal should be reduced. Hazardous side products may be produced. The solution needs to be heated and stirred to decrease the concentration polarization and to make the conversion of the analyte complete. The metal layer must stick to the electrode properly, otherwise, a precise weighting of the electrode is not possible. To use other electroanalytical methods a potentiostat is needed.

A potentiostat uses three electrodes and a feedback loop to control the potential and measure the current flowing at just one of these electrodes, the working electrode. The potential will be measured to a fixed reference point and thus a lot of information about the event happening at the working electrode can be gathered.

> The potentiostat controls the potential of an electrode **while measuring the current flowing through that electrode.**

3.2 How Does a Potentiostat Work (in a Nutshell)?

As just mentioned in the previous chapter, a potentiostat controls the potential of the working electrode and measures the current flowing through it by using three electrodes.

Why not just two electrodes? One of the reasons is that we cannot measure the potential of the working electrode against a fixed point when we just have two electrodes. Imagine a two-electrode system that consists of the already mentioned working electrode and the electrode, which potential should be our fixed reference point, the reference electrode. We apply a certain potential between these electrodes and an electrochemical reaction happens at the working electrode, but since the circuit needs to be closed and current needs to flow, a reaction that is inverse to the reaction at the working electrode must occur, that is if an oxidation occurs at the working electrode, a reduction must take place at the reference electrode. If a current flows at a constant potential, an electrochemical reaction must happen according to Faraday's law:

$$Q = n \cdot z \cdot F \tag{3.1}$$

This equation says that the charge Q flowing through an electrode is proportional to the amount n of a species that took or gave z electrons at the electrode. F is the Faraday constant and represents the charge of 1 mol electrons. The current I is the charge Q per time t flowing through the electrode:

$$I = Q/t \tag{3.2}$$

The equations 3.1 and 3.2's combination shows that the current I flowing is connected to the reaction happening at the electrode via the amount n:

$$I = \frac{n \cdot z \cdot F}{t} \tag{3.3}$$

Imagine now that the current is flowing at the reference electrode. At this electrode, a species' amount of n is converted. This conversion leads to a change of the surface or the concentration of the solution surrounding the electrode. The Nernst equation shows a clear correlation between the potential E of an electrode and its surrounding:

$$E = E^0 + \frac{RT}{zF} ln \frac{a_{Ox}}{a_{Red}} \tag{3.4}$$

E^0 is the standard potential of the redox couple Red and Ox. R is the gas constant and T the temperature. The activity of the oxidized and reduced forms of the species a_{Ox} and a_{Red} in the surrounding solution is not always easy to predict. This often leads to a simplification of the equation:

$$E = E^0 + \frac{RT}{zF} ln \frac{c_{Ox} f_{Ox}}{c_{Red} f_{Red}} = E^0 + \frac{RT}{zF} ln \frac{c_{Ox}}{c_{Red}} + \frac{RT}{zF} ln \frac{f_{Ox}}{f_{Red}} = E^{0'} + \frac{RT}{zF} ln \frac{c_{Ox}}{c_{Red}} \tag{3.5}$$

The two activity coefficients f_{Ox} and f_{Red} are included in the resulting potential $E^{0'}$, which is called the formal potential. Since it contains parameters that depend on the environment, such as temperature and activity coefficients, $E^{0'}$ cannot be listed but needs to be determined for each experiment, if necessary. Most experiments in analytical chemistry are performed at room temperature (295 K). This makes another simplification possible. Out of convenience also the ln will be transferred to the log.

$$E = E^{0'} + \frac{RT}{zF} 2.3 \log \frac{c_{Ox}}{c_{Red}} = E^{0'} + \frac{0.059\ V}{z} \log \frac{c_{Ox}}{c_{Red}} \qquad 3.6$$

For practical application, equation 3.6 is the most used form of the Nernst equation. For many applications, one can assume that E^0 is roughly the same as $E^{0'}$, because both activity coefficients are close to one. In this form (equation 3.6) the correlation between the surrounding of an electrode and its potential is visible more easily.

As mentioned before all the simplifications at equation 3.4 were performed: The change of the solution surrounding the reference electrode, due to a flowing current, leads to a change of the reference electrode's potential, but the reference electrode is supposed to be our fixed reference point. We cannot limit the current flow through the reference electrode (RE) because all limitations should be caused by the process that we want to investigate, that is the process at the working electrode (WE). The solution to this problem is a third electrode. At this counter electrode (CE), also known as the auxiliary electrode, the counter-reaction to the working electrode's reactions takes place. The current is flowing between the working and the counter electrode. The potential is controlled between the working and the reference electrode (see Figure 3.1).

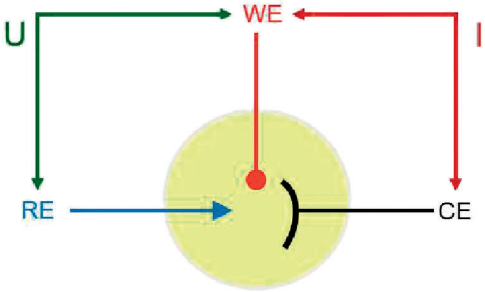


Figure 3.1: A schematic three electrode system

The potential between the counter and the reference electrode is adjusted in such a way that the current flowing through the working electrode at a certain potential between the working and reference electrode is satisfied. There are limits to the potential a potentiostat can apply between RE and WE (DC potential range) and between CE and WE (compliance voltage). Since you control the potential between RE and WE it is easy to stay within the limitation of the DC potential range.

The CE must be bigger than the WE because the compliance voltage cannot be controlled by the user. A bigger surface at the same potential leads to a higher current, so the CE should provide enough current without running into the compliance voltage. A rule of thumb suggests that the area of the CE should be 100 times bigger than the WE. For many experiments, this may not be necessary, but for a good praxis, you should ensure that the CE is big enough so that it does not limit the current flowing at the WE.

Usually, the distance between CE and WE is big enough, so the reactions of the two electrodes do not influence each other. Thus, the counter-reaction can be ignored, but sometimes, in small volumes for example, it can be helpful to know which reaction happens at the counter electrode.

> The potential is applied between the reference and working electrode, while the current flows through the working and counter electrode.
> **This way a constant reference point for the potential is maintained.**

3.3 Electrodes

While the potentiostat is the heart of an electrochemical experiment, modern potentiostats need little effort to set up and operate. The average electrochemist will spend a lot more time with their electrodes. Electrodes need to be polished, maybe modified, and sometimes it is rather challenging to fix them all in the right place. For this reason, we will first talk about the three different electrodes, before we take a closer look at the potentiostat again.

3.3.1 Working Electrode

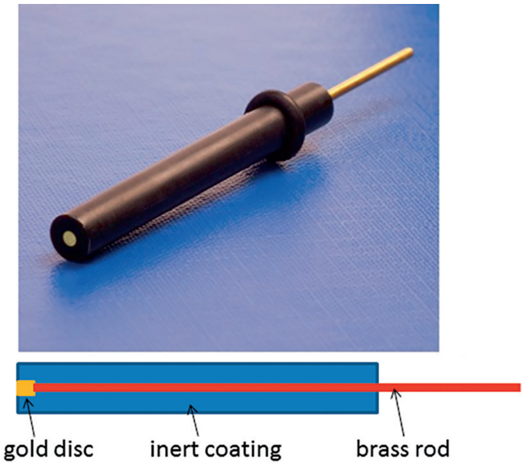


Figure 3.2: A gold disc working electrode in a Kel-F (Teflon) coat; photo and scheme.

The working electrode is the place where the reaction happens that we want to control or investigate. Consequently, this electrode should be carefully and reproducible prepared. The most common working electrodes are disc electrodes. For example, a metal cylinder or a metal wire is surrounded by Teflon or PEEK, and the cross-section is exposed. The metal disc is connected to a wire at the other end of the coating, so it can be connected (see Figure 3.2). Common materials in electrochemistry for working electrodes are platinum and gold as well as a variety of carbon phases. Very popular due to its conductivity and reusability is glassy carbon.

In corrosion research, the working electrode is usually the surface or material that is to be studied. Therefore, most cells or sample holders focus on exposing a defined area to the solution in which the measurement is performed as well as providing an electrical connection to the sample (see Figure 3.3).

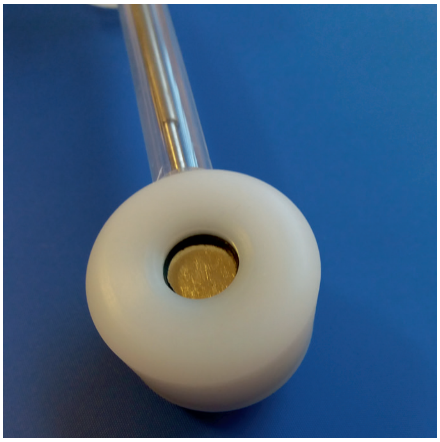


Figure 3.3: A metal coupon in a Teflon holder for corrosion experiments.

Another option to setup your sample is the Stern-Makrides arrangement. The sample has a cylinder shape and a hole with a screw thread. A Teflon cone is used to make the connection to the metal rod watertight (Figure 3.4). Many other cells allow the insulation of different parts of samples. You can find cells for metal sheets or cells that are like a scanning droplet cell, where an electrolyte-filled tip is pressed to the surface and turns thus the part in contact with the liquid into a working electrode.

Rough surfaces will lead to high currents due to the charging of the interface, which will be explained in chapter 4.5 (page 27). Dirty surfaces can show artifacts in the measurements or dirt can be the cause that not the whole active surface has access to the electrolyte. So, cleaning an electrode is an important step in electrode preparation. A clean surface also increases the reproducibility of your measurements. – We recommended wearing disposable gloves when assembling the samples and the holder.

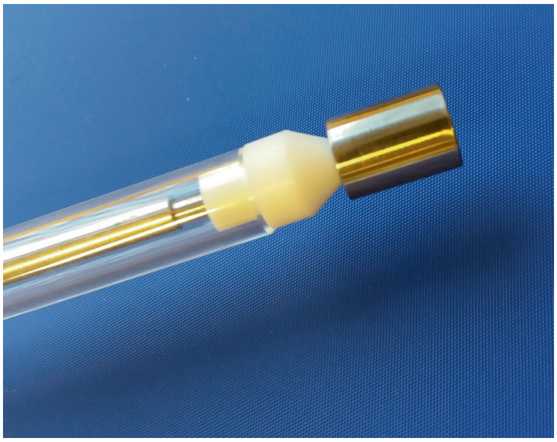


Figure 3.4: A steel cylinder in the Stern-Makrides arrangement.

> The working electrode is the electrode where the investigated processes occur.
> **It needs to be carefully prepared so that the surface is reproducible and known.**

3.3.2 Reference Electrode

The reference electrode should deliver a constant potential. A current flowing through an electrode leads to an electrochemical reaction that will change the composition of the electrode's environment and thus the potential. Therefore, there should be as little current as possible flowing through the reference electrode.

To establish and keep a constant potential an electrode of the second type is often chosen. Their potential usually depends indirectly on the concentration of a single anion. The electrodes of the first type are just metal surfaces in an electrolyte. According to Nernst's law (see equation 3.6) the potential depends directly on the surrounding solution. An electrode of the second kind is usually a metal surrounded by a hardly soluble salt of itself. This electrode is then immersed into a solution containing the anion of that salt. Usually, the anion has a high concentration to make sure that the metal salt is not dissolving fast and that small changes in the concentration have a low impact on the potential. A common reference electrode is the silver/silver chloride electrode (see Figure 3.5). A silver wire is coated with a film of silver chloride. This wire is immersed in a potassium chloride solution.

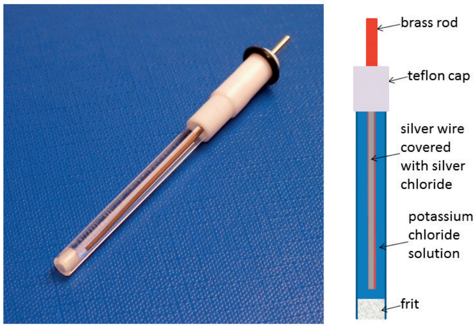


Figure 3.5: Photo and scheme of an Ag/AgCl/3 M KCl reference electrode.

The potential of the silver wire depends on the silver ions dissolved in the potassium chloride solution.

$$E = E^{0'} + \frac{0.059\ V}{z} log \frac{[Ag^+]}{[Ag]} \tag{3.7}$$

Since it is a solid material the concentration of silver is 1 M. The concentration of the silver ions depends on the concentration of chloride, as the solubility product K_L (equation 3.8) shows.

$$K_L = [Ag^+] \cdot [Cl^-] \tag{3.8}$$

If 3.7 and 3.8 are combined and all constants are summarized in $E^{0'}(Ag/Ag^+)$ the result is:

$$E = E^{0'}(Ag/Ag^+) + \frac{0.059\ V}{z} log[Cl^-] \tag{3.9}$$

If the chloride concentration is kept constant, a good reference electrode is created. This is usually achieved by separating the measuring solution from the solution surrounding the reference electrode using a porous frit. Small concentration changes due to diffusion through the frit or evaporation have little impact on the concentration if the concentration of chloride is high. The frit also prevents silver ions from diffusing into the measuring solution. The silver/silver chloride electrode is one of the two most popular chloride-containing reference electrodes.

Another one is the calomel electrode. This reference electrode contains mercury in contact with mercury(II) chloride in a chloride-containing solution often saturated with chloride. This is a quite common reference electrode for corrosion cells. The saturation of the solution means, that solid potassium chloride is inside the glass body. If the electrode's solution is losing chloride, a part of the solid chloride will go into the solution and keep the concentration constant.

You should always indicate clearly versus which reference electrode the potentials were applied or measured if you publish results or want to compare them to other measurements. Often you find this information in the axis label e.g. "E / mV vs Ag/AgCl" or "E / mV vs SCE" (SCE = Saturated Calomel Electrode).

If the currents are within the nA range, it is possible to immerse the wire with the hardly soluble salt coating in the measurement solution. This is called a pseudo reference electrode. The reference and counter electrode can also form a short circuit and you can work with a two-electrode system. If your currents are higher, you want to perform a long-term experiment, for example overnight or need a very stable potential, a three-electrode system with a proper reference electrode is necessary.

Positioning of the reference electrode is often not important if you have a well-conducting solution. If you have a solution with low conductivity, you might experience an Ohmic drop. The Ohmic drop is the amount of potential that is lost on the way from the reference electrode to the working electrodes. Since this potential is lost, it isn't felt by the working electrode. This means, if you apply 1 V between the reference and working electrode and have 200 mV of Ohmic drop, the working electrode will behave as if the driving force is 800 mV and not 1 V. The Ohmic drop is a result of the Ohmic resistance between the reference electrode and the working electrode. The resistance depends on the distance between the electrodes, the conductivity of the solution, and the frits used. The frits are fixed and can't be influenced by the user. The conductivity of the solution is often dictated by the experiments. In a solution of 100 mM KCl, the conductivity is sufficiently high, that for most purposes the Ohmic drop is negligible. Corrosion studies sometimes require that the solution is chosen according to the real environment the sample will be exposed to. This could mean a low-conducting solution. Here Ohmic Drop could be important.

The distance between the reference electrode and the working electrode is variable in many setups. Unfortunately, a reference electrode that is very close to the working electrode might block the diffusion of species to or from the electrode, creating an artificial crevice. Furthermore, the salt concentration in the reference electrode body is usually quite high. Since a frit is not 100% tight, a bit of the solution in the electrode's body will leak into the measurement solution. This will lead to increased concentrations of ions in front of the reference electrode. To avoid all this a Luggin capillary, or salt bridge, is used. A Lugging capillary is a glass body where the reference electrode is entered into one end and the other end is close to the working electrode. The capillary's narrow opening limits diffusion, but not as much as a frit. As a result, the resistance is lower than the one of a frit, but if the narrow part of the capillary increases the resistance again. Another advantage of the capillary is its small size. The capillary can be approached close to the working electrode with very little disturbance of the diffusion. Another option is to use a salt bridge. A salt bridge is delivered with ItalSens' corrosion test cell. It allows close positioning to the working electrode, has a frit, and is filled with the cell solution.

> The reference electrode keeps the system stable.
>
> **The reference electrode should be checked first if the system behaves unexpectedly.**

3.3.3 Counter Electrode

The counter electrode usually needs the least maintenance. It is just some inert metal or carbon species with a large surface. For people who work with many different materials, platinum is a good counter electrode due to its inertness towards most solutions. A larger surface area is achieved by a mesh structure, but often a platinum wire has already a surface area several magnitudes bigger than the working electrode. Platinum is also very easy to clean. A hand torch is usually enough for making the platinum glow and removing all stains.

The counter electrode should have a large surface area, to enable a high current flow even with low potentials. This way water splitting, gas production, or the production of aggressive radicals is avoided. If this kind of reaction is happening in a small volume of solution, it will no longer be negligible. A large surface area will lead to high capacitive currents (see Chapter 4.5). At the counter electrode, capacitive currents provide a current flow without changing the chemical composition of the solution.

> The counter electrode should not limit the current or influence the working electrode.
>
> **Popular electrodes are platinum wire or platinum mesh electrodes.**

3.4 About Potentiostats History

Knowing the history of a device is helpful to understand certain terminologies or identify obsolete parts of a device that are still used because this is how it was always done. Jaroslav Heyrovský developed the first polarographic instrument in 1922 for use with a dropping mercury electrode (see Figure 3.6). He received the Nobel Prize for Chemistry in 1959.

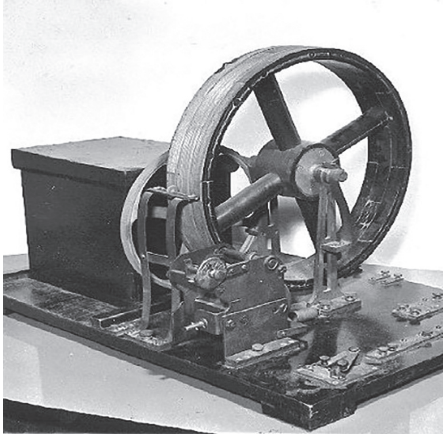


Figure 3.6: a polarograph designed by Jaroslav Heyrovský.

A more versatile instrument is the polarograph's successor, the potentiostat. A three-electrode setup became possible and the most potentiostats can also be used as galvanostats, that is either the potential or the current can be controlled, and the other component measured. Until the 1980's potentiostats were bulky instruments. The instruments were built using quite complicated analog electronics and had a front panel with switches, multi-turn potentiometers, and one or two meters for the potential and current. At the rear panel, some inputs (for additional potential control) and outputs (for potential and current) were found. These outputs could be used for an X-Y recorder. Before computers were commonly available, the X-Y recorder was often a plotter. This machine was drawing the measuring results on scaled paper with a felt tip.

Figure 3.7: modern analog potentiostat.

For specific applications analog instruments are still being used (Figure 3.7). Nowadays computer and analog-digital/digital-analog (AD/DA) converters are used for recording the results of a measurement, but the potentiostat itself is still a very bulky instrument. Furthermore, the necessary cable connections are vulnerable to noise by acting as antennas, and bad connections due to damaged cables can occur.

In the 1980s digital potentiostats became available. These instruments were initially still quite big. The development of digital electronics was and still is progressing at high speed and the advantages of digital signals (noise reduction and fewer connections) were beneficial to the measurements.

The first digital instruments required many different digital and analog components. Nowadays, a new general-purpose, low-power instrument, can be made on a single PCB (Printed Circuit Board) with a size of 30 mm x 18 mm (see Figure 3.8). By far the largest component is the connector needed to make connections to the working, reference, and counter electrodes.

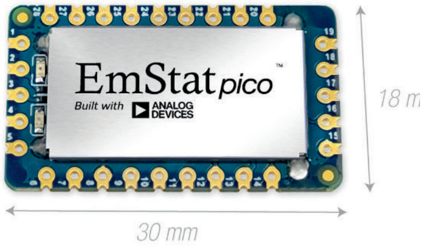


Figure 3.8: EmStat Pico digital potentiostat module by PalmSens BV.

Since the measuring device itself, the potentiostat, and the means to record the measured values, a computer, shrunk the electrochemical workplace shrunk too. Due to this development, the area of research and the number of applications for electrochemistry is growing. In 2001 a battery-powered potentiostat controlled by a pocket PC was introduced by PalmSens BV, at that time still named Palm Instruments BV. In 2014, more than 10 years later, this idea of a truly mobile electrochemical device led to the release of PStouch, an Android App to control PalmSens BV's potentiostats. Electrochemistry has unplugged itself from the lab and is taking more and more steps into the world of point-of-care devices.

> In less than a hundred years the basic equipment for electrochemical analysis was invented **and shrunk from the size of a big coffer to pocket size.**

3.4.1 Troubleshooting

Here are some general comments on troubleshooting that are valid for any experiment. We made this list, to enable even not very experienced users to find the sources of trouble as soon as possible to keep the frustration level for you and your coworkers as low as possible.

1. When you observe strange behavior, especially only a random zigzag line, first check if all your electrodes or your sensor are connected properly. Especially croc clips tend to slip off the electrode if not placed properly.
2. Make sure all electrodes are immersed into the electrolyte solution. See if bubbles in front of electrodes are insulating the electrode surface.
3. Check if the potential of your reference electrode is still correct. This is easily done by using a second reference electrode. Measure the potential difference between the two electrodes. After a few seconds, it should be a stable value. If the other reference electrode is the same kind of reference electrode, for example, two Ag/AgCl electrodes, the difference between them is supposed to be zero, if the difference between them exceeds 20 mV the reference electrode should be replaced. A good way to test reference electrodes is to put both reference electrodes in the same electrolyte and connect the electrodes to a voltmeter or multimeter.
4. Maybe the working electrode is dirty, and an insulating layer was formed on it. Polishing the electrode should remove any stains.

5. If you suspect a malfunction of the potentiostat, check first if the LEDs light up correctly. The blue LED indicates the USB connection provides power and control. It should light up as soon as the EmStat is connected to the PC. The red LED should light up as soon as the cell is switched on. This usually happens when a measurement is started. The cell is switched off at the end of the measurement. For the PalmSens4, you can check the information on the screen.
6. A good way to check if the potentiostat and the cable are operating correctly is to perform the standard measurements described. Just connect the dummy cell, which was delivered together with the device, use the WE B, and load the method PSDummyCell_LSV.psmethod. If this measurement does not look as shown in Figure 3.9, try to change the cable and perform the measurement again. If the problem is solved, the cable is the source of trouble. If the curve looks even with a different cable not as expected, it seems your EmStat or PalmSens is malfunctioning. Please contact info@palmsens.com to solve this issue.
7. If a higher level of noise is your issue, the solving strategies are rather numerous, but the sources of noise are also numerous. Here we describe the most successful and common methods for noise reduction.
    a. Your power grid is usually using an alternating current. This undulating current influences the measured currents. PSTrace and PStouch have a filter for this mains frequency. Check in the *Tools* menu under *General Settings* if the mains frequency is set correctly.
    b. Our environment is filled with electrical fields. Some of them are created by devices around us as side effects or in the case of wireless communication on purpose. Although it is a bad idea to measure directly next to an electric arc furnace, it is usually not possible to have a workspace free of electrical fields, especially not during point-of-care measurements. A Faraday cage is usually sufficient to create a field-free environment. A metal box or cage out of metal mesh is a good Faraday cage. Even a shield out of aluminum foil can help. Place your electrochemical cell inside the Faraday cage and connect the cage to the ground lead (green) of the potentiostat. The cable delivered with your EmStat or PalmSens has an inbuilt shield and should protect your signal outside the Faraday cage. This is one of the most effective methods to reduce noise.
    c. Cables should not be unnecessarily long, since they act as antennas for noise, but the cable delivered with your EmStat or PalmSens has an inbuilt shield and if you use the original cable, there is little reason to worry about cable-induced noise.
    d. Ground your measurement equipment. The best way to connect your equipment is with all parts connected to the ground at the same point. In an electrochemical lab, that point is usually one small space of the Faraday cage. This way earth loops that induce noise are avoided.
    e. Check if the contacts are corroded. If so, remove the stains, for example with sandpaper.
8. If you encounter problems that you cannot solve, please contact PalmSens BV (info@palmsens.com).

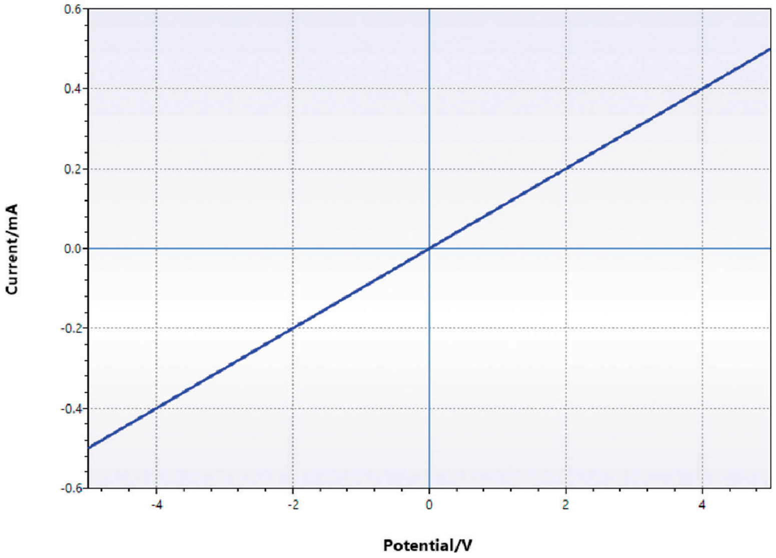


Figure 3.9: A typical linear sweep of the dummy cell's WE B.

4 Basic parameters

4.1 Origins of Electrochemical Potentials

Most readers will have a rough idea of electrochemical potentials, noble and non-noble metals. However, a small recap of this knowledge seems suitable to understand the processes happening at the electrodes or corroding metals better.

If you immerse two blank metal sheets made from different materials, e.g. iron and copper, into the same conducting solution and connect them with a device that can measure the potential difference or voltage between these two metal sheets, the device will show a characteristic voltage difference between the two metals. They have different potentials. Why is that so? When a metal gets in contact with a solution some metal ions will be emitted by the metal. When the positive metal ions, cations, leave the metal solid phase, they leave their electrons behind. The electrons charge the metal negatively. This means that the metal ions are attracted again by the metal sheet. This results in a flux of metal ions from the metal and back to the metal. A dynamic equilibrium is reached and the amount of charge in the metal is characteristic for each metal.

As we know, the potential of a metal sheet can be actively influenced by a potentiostat. If the potential is changed to a more negative (cathodic) potential, the metal ions will be pulled toward the electrode. If we change the potential to a more positive (anodic) potential, the metal will release more ions and dissolve.

> Anode and cathode as well as anodic and cathodic potentials are for electrochemistry beginners not always very intuitive terms. The anode is where the oxidation happens and the cathode is where the reduction happens. Anodic potentials are potentials with more oxidizing properties and cathodic potentials are potentials with more reducing properties.
>
> **A good way to remember this is:**
> **Oxidation and anode start with a vowel.**
> **Cathode and Reduction start with a consonant.**

If any change of potential leads to a change in the direction of the reaction, i.e. from reduction to oxidation or vice versa, the system is at its formal potential. If the formal potential is measured under standard conditions (activity of all components is 1, 298.15 K, 1 bar) it is called standard potential. With the standard potential and the Nernst equation (s. equations 3.4 and 3.6), the resulting potential can be calculated.

4.2 Corrosion Potential

The electrochemical potential can be measured. Technically it is only possible to measure the difference in potential between two points. If two metals are immersed in an electrolyte (conducting solution), a voltmeter connected to both will show their potential difference. If the two metals are connected with a cable, for example, electrons flow from the metal with the lower potential to the metal with a higher potential. As a result, the potential difference between the two metals will get smaller.

Another dynamic equilibrium will be created between the processes leading to the electrochemical potential and the electron flow, which leads to a new potential difference depending on the current flowing. The higher the current flow is the lower the potential difference. Due to this reason usually the open circuit potential (OCP) or open circuit voltage (OCV) is especially interesting. It is the potential where no current is flowing because the circuit is open. Between two metals in the same solution, the OCP is the highest potential difference possible without applying a potential from the outside. Measuring the OCP is also non-invasive because no current is flowing.

For most applications, the OCP and other potentials will be measured versus a reference electrode. Since potentials are additive, one can easily calculate what the potentials would be versus other reference electrodes. There is no absolute potential, but electrochemists have agreed that the standard potential of the standard hydrogen electrode (SHE) is by convention 0 V. This makes it easy to identify noble metals. All metals with a positive standard potential versus SHE are noble metals. They are resistant to acid corrosion, because to corrode the protons of the acid need to be reduced to hydrogen. And for that to happen the potential of the metal would need to be lower (more cathodic) than the potential of the proton reduction.

Is the OCP the same as the corrosion potential? Yes, it is, despite the definition sounding slightly different: The corrosion potential is the potential a sample has when no external current is applied. A current can still flow inside the sample to enable two reactions, one oxidation, and one reduction. For example, a steel sample in contact with an acid solution will oxidize (depending on the steel composition) and protons will be reduced at the surface. If you connect a voltmeter and a reference electrode, the measured OCP is the corrosion potential of the steel-proton reaction.

Observing the OCP or corrosion potential allows you to monitor corrosion processes as well. High corrosion potentials are good. The system will rather take up electrons than lose electrons, so a reduction is more likely. If the corrosion potential is dropping, it means that the sample is oxidizing, and negative charges are accumulating in it.

4.3 Corrosion Current

What most scientists are interested in is the corrosion rate, so how fast the sample is destroyed. This depends on the corrosion current, so the amounts of electrons per time that are transferred inside the system. In the example of the steel in an acid solution from the previous chapter, this would be the electrons that are transferred from the steel to the protons to form hydrogen. The knowledge of the corrosion current allows calculating the amount of material that is corroding per time unit. The corrosion current flows between the two reactions in the system, e.g. hydrogen evolution and steel oxidation, and can't be measured directly.

Both reactions must provide the same current, so they can exchange this current, i.e. all electrons donated by the steel need to be accepted by the protons to form hydrogen. Donation and uptake of electrons happen at the corrosion potential as discussed in the previous chapter. This means the corrosion current is flowing at the corrosion potential and at the corrosion potential the electrons donated by the oxidation and the electrons accepted by the reduction are equal.

4.4 Tafel Plot and Evans Diagram

As usual, it would be great, if we can predict the corrosion current or corrosion potential. Julius Tafel studied the Hydrogen Evolution Reaction (HER) in early 1900. HER is a common reaction in corrosion because all water contains protons. He found that there is an exponential relationship between the applied current at a platinum surface and the potential. This is also true the other way around. A convenient way of plotting this relationship was to plot the potential versus the logarithm of the current lg I because using the logarithm leads to a linear plot.

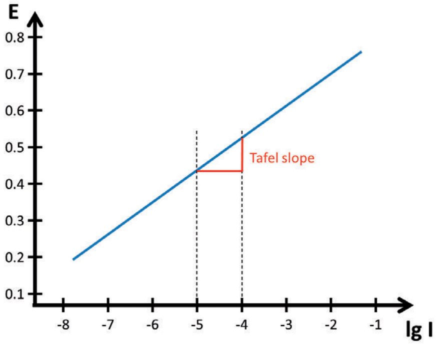


Figure 4.1 Tafel plot scheme with arbitrary scale and an indication of the Tafel slope.

In Figure 4.1 the slope of the line is called the Tafel slope. It is usually expressed in the unit mV/decade. This approach is the ideal case. For many reasons, real reactions often deviate from this behavior.

Very common reasons are passivation and diffusion limitation. The influence of passivation will be discussed later (see Chapter 5.4). Diffusion limitation leads to a potential independent current. The amounts of available species for conversion, for example in the oxygen reduction reaction (ORR) the oxygen, are depleted within reach of the electrode. The reaction can only continue, and thus a current can only occur if new oxygen diffuses toward the electrode. The current no longer depends on the potential, but on the transport of oxygen in the solution, so the Tafel plot will no longer be linear (see. Figure 4.2)

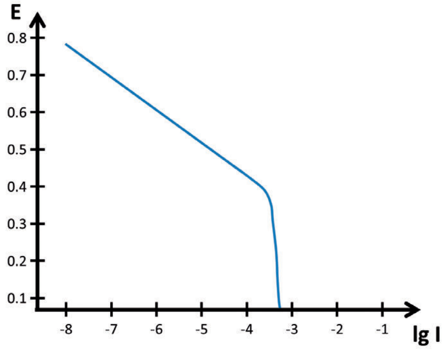


Figure 4.2 Tafel plot of a diffusion limited system.

Up to now, we have only looked at the reduction or the oxidation, but we need to combine a reduction and an oxidation for corrosion to occur. This is also the situation in real environments. If the Tafel plot of both side reactions is known, one can use the two Tafel plots to find the theoretical corrosion current and corrosion potential. This is possible due to two facts:

1. An immersed conducting sample has one potential at any instant and thus all reactions must happen at that potential.
2. The conversion of charge demands that all electrons donated need to be accepted, i.e. the reactions have to happen at the same rate which implies the same current.

From these two conditions, it can be derived that the corrosion current and the corrosion potential are determined by the point where the two Tafel plots of the reduction reaction and oxidation reaction meet. Plotting the two Tafel plots (or more) into one plot is an Evans diagram (see Figure 4.3). It is helpful to estimate what influence a change in the oxidation or reduction rate has on the corrosion rate. Also, the potential and corrosion current of a galvanic couple can be predicted.

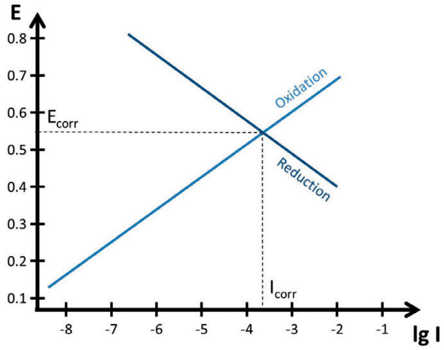


Figure 4.3: Evan's Diagram.

Unfortunately, Evan's diagram is most of the time only used for qualitative estimations. The number of influences and missing quantitative data usually make it necessary to evaluate the system with an experiment. This is done quite often with a polarization curve. To record such a curve a linear potential sweep is applied to the sample and the current is recorded. The recorded current is the difference between the current of the oxidation and the reduction reactions in the sample. This means that the measured current at the corrosion potential is 0. Since the plot is made on a logarithmic scale a 0 would correspond to a minus infinite (∞), which a potentiostat can't measure. A scheme of a polarization curve is shown in Figure 4.4.

The goal of recording a polarization curve is usually to extract the corrosion potential E_{corr} as well as the corrosion current I_{corr}, but as the previous paragraph discussed the point of interest, the intersection of the two Tafel plots, is not directly visible in the polarization curve. Further away from the corrosion potential the polarization curve is mainly influenced by only one of the reactions. At very cathodic potentials the reduction dominates and at very anodic potentials the oxidation. Due to this, the linear parts of the polarization curves can be used for extrapolation of the Tafel slopes and thus the corrosion potentials as well as corrosion current.

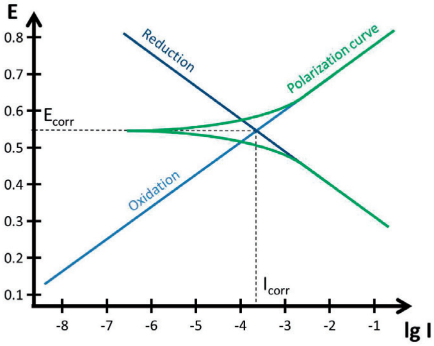


Figure 4.4 Polarization curve (green) with Evan's diagram (blue).

For a reliable extrapolation, the linear behavior over a few decades is ideal and at least for one decade necessary. The more decades show the linear behavior the better the extrapolation. According to the theories we have looked at up to now, the curves should stay linear in the Tafel plot when the potential difference to E_{corr} is increased. Unfortunately, some limitations will lead to deviation from this behavior. We have already seen an example in Figure 4.2, where some reaction partners are limited by diffusion. Other examples can be the onset of another reaction or the passivation of the surface. In the section about polarization curve processing alternatives to the extrapolation via Tafel slope fitting will be presented (see Chapter 5.3).

4.5 Capacitive Current

Usually, electrochemists are interested in the Faraday current which is the current caused by an electrochemical reaction; the capacitive current, caused by physics, is an unwanted side effect. The cause of this current is ions accumulating in front of the electrode. These ions and the electrode's charged surface form a capacitor. A capacitor will store a charge Q depending on the potential E and its capacitance C:

$$C = \frac{Q}{E} \qquad 4.1$$

What does this mean for measurements? If the potential of the electrode is changed, for example during a potential step, a current will flow that has no chemical but only a physical meaning. This is the current that charges or discharges the capacitor also known as capacitive charging current or short capacitive current. This current decays exponentially with time *t* as known from electronics (see Equation 4.2).

$$I = \frac{E^C}{R} e^{-\frac{t}{RC}} = I^0 e^{-\frac{t}{RC}} \quad 4.2$$

E^C is the charging potential or voltage, I^0 is the starting current, *R* is the resistance of the circuit around the capacitor, and C is the capacitance of the capacitor. This decay is much faster than the decay of Faraday current if the sufficient reactant is present. It is well known that for reactions involving a free diffusing species in solution the Faraday current decays with $t^{-½}$. This means that the capacitive current decays much faster than the Faraday current. The difference between the decay of capacitive current and the Faraday current of a free diffusing species is shown as a scheme in Figure 4.5.
During linear sweep voltammetry or cyclic voltammetry (also known as linear polarization and cyclic polarization), the potential of the electrode is changed continuously during the whole measurement. This means during a linear sweep a constant capacitive current is flowing. This can be deducted from the definition of current *I*, which is charge *Q* per time *t*, and Equation 4.1:

$$I = \frac{\partial Q}{\partial t} = C \frac{\partial E}{\partial t} \quad 4.3$$

Equation 4.3 shows the higher the capacitance C is, the higher the capacitive current. The capacitance C for a plate capacitor can be calculated with Equation 4.4:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \quad 4.4$$

Where ε_0 is the electric field constant, ε_r is the relative permittivity of the medium between the plates, *d* is the distance between the two plates and *A* is the surface area of the two plates.

Most factors influencing the capacitance cannot be altered in an electrochemical experiment. The constant ε_0 cannot be changed. The distance *d* and the relative permittivity ε_r can only be changed by changing the solution because *d* is defined by the distance between the electrode's surface and the layer of ions. Area *A* is influenced by surface roughness. The rougher a surface is the higher its area. If a reusable electrode is used, proper polishing that leads to a smooth surface can reduce capacitive current drastically.

Fortunately, digital potentiostats don't provide a true linear sweep. The linear increase of potential is done step-wise. These small steps are approximately a line. However, this means capacitive current behaves under these conditions according to Equation 4.2 and not Equation 4.3. Only the last quarter of each step is used for the measurement and most of the capacitive current is already decayed at that point. Measurements with digital potentiostats that don't offer a true linear option will always show a significantly smaller capacitive current than the theory predicts. The disadvantage is that digital potentiostat can't perform measurements where the exact capacitive current needs to be measured.

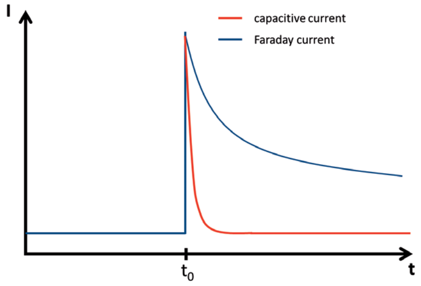


Figure 4.5: Scheme of the capacitive and Faraday current through time.

5 Polarization Curves

5.1 Setup your Measurement

Polarization curves are made by making a linear sweep of the sample's potential over time. In analytical research fields of electrochemistry, this technique is called Linear Sweep Voltammetry (LSV), which is the same name PSTrace uses for this technique in Scientific Mode. In Corrosion Mode, this technique is labeled Linear Polarization.

Before the measurement's parameters will be discussed, the setup for the measurement is described. The sample is installed (see Figure 3.3) in the holder. The cell is filled with electrolyte. The cell can be filled with 1 L of solution. Suitable are various salt solutions. Which one is chosen depends on the application and the real environment the sample is exposed to. A common electrolyte is sodium chloride solution (NaCl). The concentrations vary, but a common concentration is 0.5 M NaCl. Conducting solutions like NaCl or KCl are making it easy for electrochemistry to happen, but that also means that corrosion happens more easily. Low salt concentrations reflect sometimes the behavior of a sample in the real environment better, but they cause an IR-drop. The IR-drop is part of the applied potential that the working electrode or sample doesn't feel. This missing potential is caused by the electrolyte between the reference and the working electrode acting as an ohmic resistor with the resistance R_u. The IR-drop is calculated by multiplying the flowing current I and R_u according to Ohm's law. In 2018 PalmSens released a module for the PalmSens4, which allows compensation of the IR-drop during the measurement. For that purpose, R_u must be known. It can be determined by Electrochemical Impedance Spectroscopy, for example.

Before or after filling the cell, the counter electrodes are inserted into the cell. Usually both types of counter electrodes, platinum or graphite, will work fine. If nothing special is required, the graphite rods are a good choice. They have a large surface area and are inexpensive. The platinum electrodes are sensitive to mechanical stress, especially the connection between the wire and the sheet, but they are quite chemically inert and will also resist oxidizing solutions, which might attack graphite. The counter electrode's task is to deliver enough current for the working electrode. When the area of the counter electrode is large enough the capacitive current of the electrode will suffice, and only very few chemical changes are caused by the counter electrode. To turn the two counter electrodes into one big one, just short-circuit both counter electrodes with a cable.

The working electrode or the sample should be placed in the center opening. The reference electrode is a bit more delicate, and it is recommended to read the manual of the reference electrode. When a reference electrode is not used, it should be stored with the frit's end in 1 M (or higher) KCl. Your set also contains a salt bridge for your reference electrode. The bridge has a fitting top for the reference electrode and the bottom can be covered with a Teflon cap. This cap has a ceramic sand core. When the measurement solutions have a low salt concentration, they have a high resistance. A high resistance and/or a high current can lead to a significant IR-drop, i.e. there is a difference between the applied potential and the potential felt by the working electrode. In such a situation the salt bridge can decrease the resistance between the reference and working electrode. The bridge is filled with a well-conducting solution, e.g. 0.5 M NaCl, and covered with the Teflon cap. The Teflon cap is placed close to the working to reduce the distance the current travels through the high-resistance solution. Placing the Teflon cap close to the working electrode can lead to an artificial crevice formation, so the placement needs to be done carefully. If a well-conducting solution is used, the salt bridge does not need the Teflon cap. However, don't forget to fix the position of the reference electrode with the ball and socket clamp.

The gas inlet is needed if a certain gas needs to be removed or added to the solution. For example, oxygen can be added to reduce diffusion limitation or oxygen can be removed by nitrogen flow to study the reaction in the absence of oxygen. After connecting all the electrodes to your potentiostat, the cell is ready for the measurements.

5.2 Recording Polarization Curves

In the previous chapter, the setup of the cell was discussed and now it will be described how to measure a polarization curve with a potentiostat by PalmSens. As previously mentioned, to record a polarization curve with our software PSTrace the technique Linear Polarization (Corrosion Mode) or Linear Sweep Voltammetry (Scientific Mode) needs to be chosen.

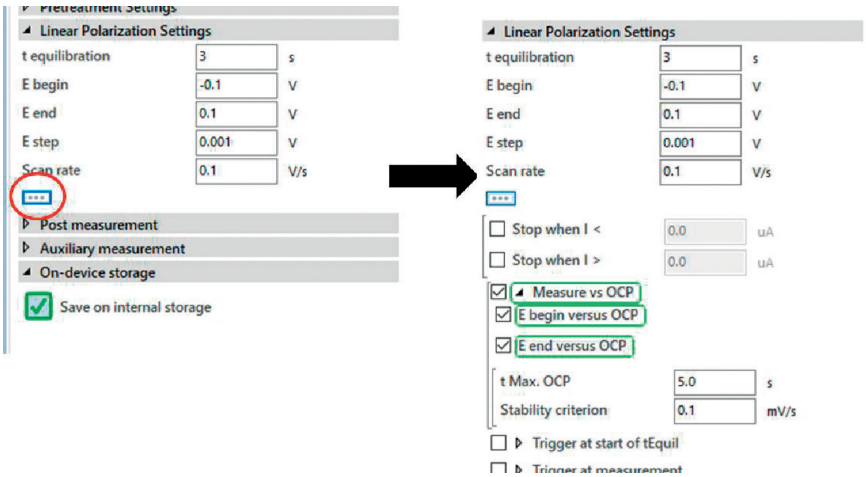
If a sample's polarization curve is unknown, all current ranges can be made available, i.e. all current ranges are blue. After the first measurements, current ranges higher than the maximum current should be switched off. Please, keep in mind that the maximum current a PalmSens4 can measure in each current range is 6 times the current range, and 30 mA for the highest (10 mA) current range. The lower current ranges allow a better current resolution for lower currents. Unfortunately, the changing of current ranges during a measurement can induce some artifacts to a measured curve. Should a curve show a spike or a step that can be associated with a current range change, it is advised to only use a single current range for the measurement.

If no specific potential needs to be applied to the sample before the measurement, the *Pretreatment Settings* are not important. Check if *t deposition* and *t condition* are set to 0 and close this section by clicking on the small arrow.

In the section for the *Linear Polarization Settings,* the *t equilibrium* is the time that elapses while the starting potential is applied but no values are recorded. This is quite useful to exclude the initial capacitive current of a measurement. The capacitive current is the result of the electrochemical double layer. Positive or negative charges (depending on the polarization) accumulate at the electrode surface during a potential step. Ions of opposing charge are attracted to the electrode and form a layer in front of the electrode. This form of charge separation is in principle a capacitor and indeed the behavior of an electrode in a solution of inert ions is the same as that of a capacitor.

Each measurement begins with switching on the cell, which leads to a potential step from the corrosion potential to the set potential for the start. This often leads to a capacitive current that decays exponentially. This is one reason why often the first 3 to 8 s of the measurement are not used, i.e. the *t equilibration* is 3 to 8 s. Another reason is that the potentiostat's auto-ranging has time to choose the proper current range.

E begin and *E end* are the potential where you want to start and end your polarization curve. Please note that the potentials are all versus the reference electrode. It is quite common in corrosion research to measure potentials in relation to the corrosion potential. This option can be easily changed manually, and the potentials will be versus the OCP or respectively the corrosion potential E_{corr}. If the option isn't visible on your screen, click on the button with "..." and it will appear (see Figure 5.1).



Pretreatment Settings

Linear Polarization Settings
t equilibration 3 s
E begin -0.1 V
E end 0.1 V
E step 0.001 V
Scan rate 0.1 V/s

Post measurement
Auxiliary measurement
On-device storage
☑ Save on internal storage

Linear Polarization Settings
t equilibration 3 s
E begin -0.1 V
E end 0.1 V
E step 0.001 V
Scan rate 0.1 V/s
☐ Stop when I < 0.0 uA
☐ Stop when I > 0.0 uA
☑ Measure vs OCP
☑ E begin versus OCP
☑ E end versus OCP
t Max. OCP 5.0 s
Stability criterion 0.1 mV/s
☐ Trigger at start of tEquil
☐ Trigger at measurement

Figure 5.1 Applied potential versus reference electrode or OCP / $E_{corr.}$

When the boxes are checked the PalmSens will measure the OCP / E_{corr} before the measurement and set that value as an internal 0. A -0.1 V in the field *E begin* means that the measurement will start 100 mV more cathodic than the E_{corr}. You can choose the maximum amount of time the measurement of the OCP will take (*t Max. OCP*). If you expect the OCP to be quite unstable, you want this time to be longer (up to a few minutes). If you have already reached a rather stable situation, a few seconds (ca. 5 s) will suffice. The *Stability criterion* defines a change in mV per s and if the measured change of the E_{corr} is lower than the Stability criterion, the E_{corr} measurement is finished. According to the literature a change of less than 5 mV per 10 minutes, so 8.4 µV/s is regarded as a stable state.

The starting and end potentials should be chosen in a way that the measurement starts at least 50 to 100 mV below and ends 50 to 100 mV above the corrosion potential. You can use a broader potential window if you like. A longer linear part in your Tafel plot will increase the accuracy of the measurement, but more extreme potentials induce more changes to the surface. A broader potential window doesn't guarantee a longer linear part because the potential for another reaction, passivation, or diffusion limitation might be reached.

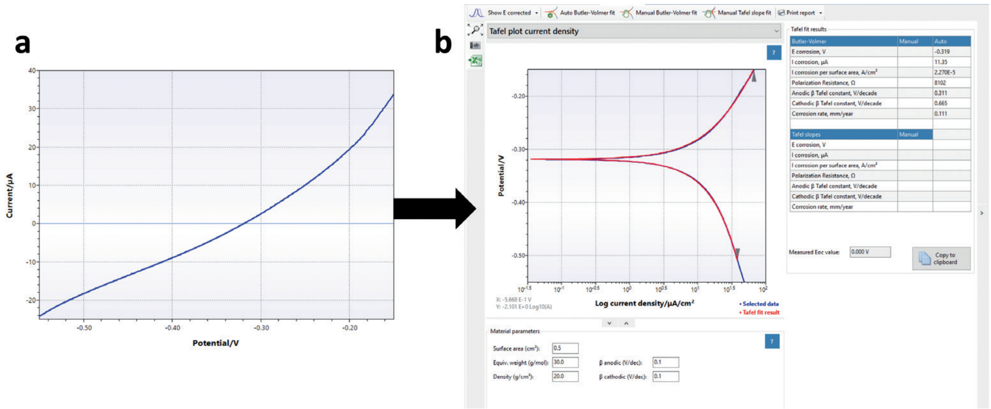
E step defines the potential difference between each point of the measurement, which is the resolution of the measurement. A digital potential cannot perform truly linear changes of the potential. The linear sweep is simulated by small steps of the potential. When *E step* is increased, the potentiostat has more time for one step if the *scan rate* is constant. This means the potentiostat takes more samples at this potential step and averages them to output a data point. The more values are averaged, the more noise is averaged out, because usually noise is equally distributed around the real value. A decrease in *E step* makes the measurement more noise sensitive but increases resolution. For most measurements, a value between 1 and 5 mV is chosen.

The *Scan rate* has some critical influences on the measurement. It is from the discussion of *E step* clear that the *Scan rate* has the opposing influence on the noise sensitivity. The lower the scan rate, the more samples can be averaged for a data point and more noise is averaged out. More importantly, the *Scan rate* defines the time scale of the experiment. This can be used to research the kinetics of electrochemical reactions. For corrosion measurements usually, low *Scan rates* are chosen. This has two reasons. First, you want the reactions that are happening to be at a steady state for the corresponding potential. Second, you want to measure the current caused by the oxidation and reduction, not the capacitive current, which was discussed previously in the paragraph about *t equilibration*.

If we are looking at the basic equations for a capacitor, it is easy to see that the capacitive current depends linearly on the *Scan rate* (see Chapter 4.5). Despite this isn't true for a digital potentiostat, which works with potential steps during which most capacitive current decays, usually a low *Scan rate* is chosen. According to the literature values of 4 to 20 mV/s should be fine. After all parameters are set, the measurement can be performed by pressing the *Run* button. The raw data will look like Figure 5.2 a).

5.3 Processing Polarization Curves

After recording the curve, you can extract the corrosion current easily from the curve in the *Corrosion Mode*. Just choose the *Corrosion* tab above the plot, while the polarization curve is the active curve (blue highlighted in the legend). The polarization curve and an automated fit will appear on the screen. Right to the plot is a small table showing the results of the plot (see Figure 5.2 b).



Tafel fit results

Butler-Volmer	Manual	Auto
E corrosion, V		-0.319
I corrosion, µA		11.35
I corrosion per surface area, A/cm²		2.270E-5
Polarization Resistance, Ω		8102
Anodic β Tafel constant, V/decade		0.311
Cathodic β Tafel constant, V/decade		0.665
Corrosion rate, mm/year		0.111
Tafel slopes	**Manual**	
E corrosion, V		
I corrosion, µA		
I corrosion per surface area, A/cm²		
Polarization Resistance, Ω		
Anodic β Tafel constant, V/decade		
Cathodic β Tafel constant, V/decade		
Corrosion rate, mm/year		

Measured Eoc value: 0.000 V

Material parameters

Surface area (cm²): 0.5
Equiv. weight (g/mol): 30.0
Density (g/cm³): 20.0
β anodic (V/dec): 0.1
β cathodic (V/dec): 0.1

Figure 5.2 a) typical polarization curve b) automated Tafel plot and fit with extrapolated values.

If the curve of the fit matches the measurement and the values in the table are realistic, you are already done. However, we are offering more options.

The following analysis techniques are supported for the estimation of the corrosion rate based on linear polarization measurements:

- Auto Butler-Volmer fit: Fitting the Butler-Volmer model over an automatically detected range.
- Manual Butler-Volmer fit: Fitting the Butler-Volmer model over a manually selected range.

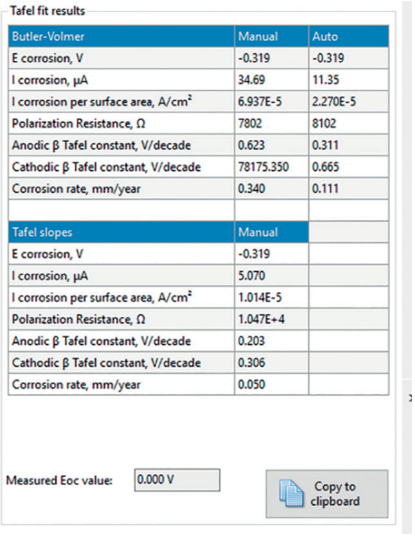
- Manual Tafel slope fit: Fitting Tafel slopes in the linear regions of the anodic and cathodic slopes.
  For all these options you should note that to achieve an accurate estimation of the corrosion rate it is recommended to use a measurement with at least one linear Tafel slope that ranges over one decade in current density. Additionally, the distance between the Tafel slope and the corrosion potential should at least be 50 mV.
  In chapter 4.4 the Tafel slopes were already discussed. The option to do a *Manual Tafel slope fit* allows you to choose a cathodic linear part and an anodic linear part of the curve. Linear fits will be performed on these, and a Tafel Analysis is performed. These fits are quite sensitive and easily an error of factor 5 or even completely unrealistic values can be the result of badly chosen linear parts. It needs experience to choose the correct linear parts of these curves and see the influence of diffusion limitation.

Another approach is the *auto Butler-Volmer fit*. The Butler-Volmer fit uses the theoretical prediction of a polarization curve according to the Butler-Volmer equation (equation 5.1). It creates a relation between applied potential E, the measured current *I*, the corrosion potential E_{corr}, corrosion current $I_{corr,}$ and the Tafel slopes for the anodic and cathodic reaction $ß_{anodic}$ and $ß_{cathodic}$, also known as Tafel constants.

$$I = I_{corr}\left(e^{\frac{2.303(E-E_{corr})}{\beta_{anodic}}} - e^{\frac{-2.303(E-E_{corr})}{\beta_{cathodic}}}\right) \tag{5.1}$$

This does not require a very long linear range of the polarization curve, because the fit is made to the central part of the polarization curve. Of course, interferences with the middle part might have an impact on the quality of the fit.

The *Manual Butler-Volmer fit* allows you to select the range of the curve, which should be used for the fit. This allows you to exclude parts where other effects than the oxidation or reduction itself have an impact. The results of these analysis techniques are presented in the Tafel fit results table (Figure 5.3).



Tafel fit results

Butler-Volmer	Manual	Auto
E corrosion, V	-0.319	-0.319
I corrosion, µA	34.69	11.35
I corrosion per surface area, A/cm²	6.937E-5	2.270E-5
Polarization Resistance, Ω	7802	8102
Anodic β Tafel constant, V/decade	0.623	0.311
Cathodic β Tafel constant, V/decade	78175.350	0.665
Corrosion rate, mm/year	0.340	0.111
Tafel slopes	**Manual**	
E corrosion, V	-0.319	
I corrosion, µA	5.070	
I corrosion per surface area, A/cm²	1.014E-5	
Polarization Resistance, Ω	1.047E+4	
Anodic β Tafel constant, V/decade	0.203	
Cathodic β Tafel constant, V/decade	0.306	
Corrosion rate, mm/year	0.050	

Measured Eoc value: 0.000 V

Figure 5.3 Table with values extrapolated from a polarization curve.

Various parameters appear in this table. The corrosion potential and the corrosion current have been discussed before. In some research fields, it is quite common to calculate the current density, which is the current per surface, to make measurements with different samples comparable.

When plotting the current versus the potential the polarization curve is approximately linear close to E_{corr} (±10 mV range). The slope of a line in a voltammogram (current versus potential plot) is resistance. The slope close to E_{corr} is called the polarization resistance R_{pol}. The polarization resistance is of interest to corrosion researchers because it is inversely proportional to the corrosion current, assuming that the Tafel slopes are constants. This is described by the Stern-Geary equation (equation 5.2).

$$I_{corr} = \frac{\beta_{anodic}\beta_{cathodic}}{R_{pol}2.3(\beta_{anodic} + \beta_{cathodic})} \qquad 5.2$$

The corrosion rate in mm/year can be calculated according to the standard practice described in the ASTM Standard G 102. To calculate an estimation of corrosion the corrosion current as well as the following material parameters are needed: equivalent weight *EW* in g/mol, the density ρ in g/cm^3, and the sample area *A* in cm^2 of the study sample. Combined with a constant (*K*) defined by the ASTM (3272 mm/(A*cm*year*mol)) this information is used to determine the corrosion rate in mm/year according to equation 5.3.

$$Corrosion\ Rate = \frac{I_{corr} \cdot K \cdot EW}{\rho A} \qquad 5.3$$

K is the summary of a few constants. Equation 5.3 is derived from Faraday's law (equation 3.1) by introducing the equivalent weight *EW*. For an atomic species (pure metals) the equivalent weight *EW* is the atomic weight *AW* divided by the number of electrons needed for conversion z (equation 5.4). *AW* corresponds here with the more commonly used, molecular weight *M*.

$$EW = \frac{M}{z} \tag{5.4}$$

The equivalent weight *EW* of alloys is more complex to determine. If an alloy is corroding homogeneously, the *EW* is the weighted averaged molecular *M* of the alloy's components. The weighting factor is the mole fraction of each component. Many alloys do not dissolve homogeneously. If you want to calculate a corrosion rate for them anyway, you need to measure in which mole fraction the alloy dissolves, for example by investigating the solution in contact with the alloy before and after a corrosion event.

There are some implications in the corrosion rate and its calculation. One of the most prominent ones is the assumption that the surface corrodes homogeneously. We calculate the converted mass, and from that the volume of that mass, and that volume we spread evenly across the area of the sample to get the corrosion rate. This is often not true. Events like pitting corrosion appear, alloys corrode faster around phase boundaries, crevices corrode faster, etc.

The corrosion rate is still a great parameter to compare the behavior of different materials in certain environments, but the values should be taken with a pinch of salt. How to use the interface of the corrosion analysis in PSTrace can be read in detail, if you click on the ?buttons.

5.4 Features of Polarization Curves

Polarization curves often give indications of what is happening at the surface. One visible effect is Diffusion, which was already discussed before (see Chapter 4.4). It is not always easy to recognize and differentiate between a rather slow reaction and a diffusion-limited reaction. Since the sample itself is usually the oxidizing partner, which is available in abundance, diffusion limitation is usually in the reductive part of the polarization curve. Often the reduction is the reduction of oxygen, which is free diffusing in the solution and thus can be depleted. The effects of a diffusion limitation are visible in Figure 4.2. Unfortunately, the transition is in a real polarization curve from the linear part to the diffusion-limited part quite hard to see.

Pitting corrosion can create misleading features as well. The onset is often characterized by a decrease of the Tafel slope, but if pitting corrosion appears already close to the E_{corr} it is difficult to recognize that pitting corrosion occurs.

The influence of other substances can sometimes be isolated by choosing a different measurement solution or choosing a different electrode. An iron electrode in an alkaline sulfide solution will show sulfide oxidation next to the iron oxidation current. This can be identified with a platinum electrode because platinum does not oxidize in this potential range, so all measured currents can be attributed to sulfur.
Quite interesting polarization curves are the ones of passive alloys or metals. There are two types of passive metals: thick and thin film. A thick film metal shows corrosion resistance even when there is a driving force for corrosion (sufficient potential). Evan's diagram of such a system is shown in Figure 5.4 a. Other metals or alloys show a decrease in the current density if the potential is increased towards anodic potentials. These metals form a thin protective layer after reaching a critical potential. Evan's diagram can be seen in Figure 5.4 b.

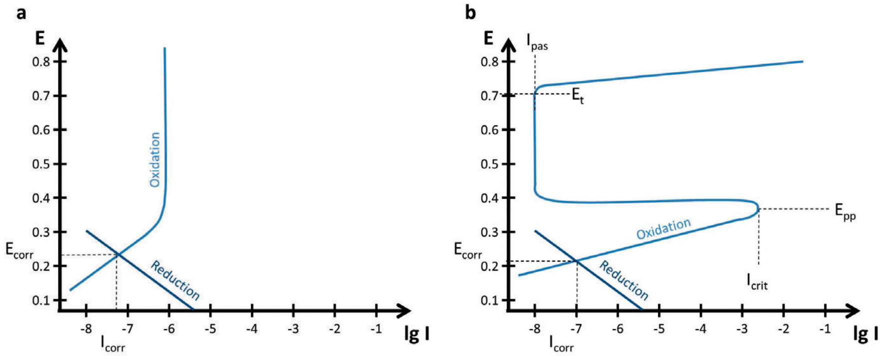


Figure 5.4 Evan's diagrams of (a) a thick film passive sample and (b) a thin film passive sample.

Important parameters are the primary passivation potential E_{pp}, the critical passivation current I_{crit}, the passive current I_{pas}, and the transmission potential E_t. At E_{pp} and I_{crit} the oxidation is strong enough to form a dense layer that protects the sample. The current drops to I_{pas} instead of the expected current predicted by a Tafel plot. At the potential E_t oxidative processes can happen through the thin film and will quite likely lead to the destruction of the protective layer. This behavior can cause quite some interesting effects on the polarization curves (see Figure 5.4 b). The processes below E_{pp} cause a polarization curve as we know it from the previous chapters, but the anodic part would not show a Tafel behavior for potential above E_{pp}.

If the cathodic reaction has its intersection with the anodic reaction in the region of the passivation (above E_{pp} below E_t), the corrosion current I_{corr} is significantly lower than without passivation see Figure 5.5 a. If you want to estimate I_{corr} without the passivation for this figure, just extend the linear part of the oxidation curve below E_{pp} until you have the intersection with the reduction. That I_{corr} would be in the µA range in Figure 5.5 a.

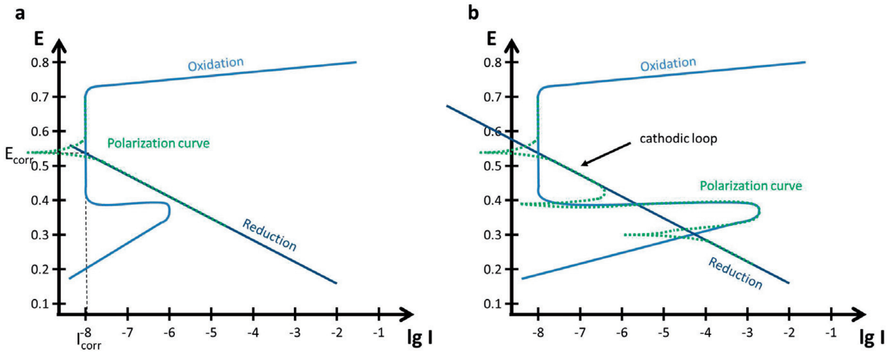


Figure 5.5 Schematic Evan's diagrams with resulting polarization curve of (a) a through passivation protected surface and (b) a cathodic loop caused by three intersections of the anodic and cathodic curve.

A more complex polarization curve occurs, if the reduction Tafel plot and the oxidation Tafel plot have multiple intersections as shown in Figure 5.5 b. Despite a more anodic potential suddenly a reductive current appears since the surface is now passive. In such a case the E_{corr} of the sample is usually the highest or lowest of the three intersections.

Film formation can also be studied using cyclic polarization also known as cyclic voltammetry. The film formation can be observed during an anodic scan followed by a cathodic scan, which then shows the cathodic loop. Or it would be possible to investigate the repassivation potential. If, during the anodic scan, the film was destroyed due to very high anodic potentials, the film won't be reestablished immediately. The potential needs to drop below a certain threshold, the repassivation potential, for the formation of a stable protective layer.

5.5 Pitting and Crevice Corrosion

These are two quite complex topics, which will only be discussed here briefly. Both are local processes, which can lead to corrosion of the whole surface.

Pits are small spots where corrosion appears. Instead of spreading wide most of them penetrate the surface and then spread. This way a coating is undermined. During an anodic scan, a sudden increase in the Tafel slope might indicate corrosion pitting. If this high Tafel slope is used for calculating the corrosion rate and the whole surface area of the sample is used, the corrosion rate is significantly underrated.
Passivated metals often show metastable pitting corrosion before the real pitting corrosion starts. The metastable pitting corrosion creates some current spikes in the polarization curve, which can be easily confused with noise. These spikes are the result of pit formation, and these pits passivate again, so the pits have only a short lifetime.

Pits of a certain depth and crevices have the same problem. The diffusion inside the pits and crevices is quite limited. Mechanisms developed for steel corrosion are widely accepted as the foundation for the general process of local corrosion. The first reduction of oxygen is happening everywhere at the surface, but the oxygen in the crevice is depleted after a while and diffusion is too slow to replenish significant amounts. This means that inside the crevice the oxidation of the metal occurs, but the whole surface area is reducing oxygen. This separation of the anode and cathode is the initial step that triggers local corrosion. The electrons taken from the crevice anode are compensated by a flux of chloride ions into the crevice. Metal complexes are formed inside the crevice, which are hydrolyzed and release protons this way. The pH in the crevice is dropping and thus the solution inside the crevice becomes more aggressive. This process is self-sustaining creating a critical crevice solution (CCS), which is strong enough to remove the passive film.

6

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) gained a lot of attention in the last 20 years. It is for multiple reasons quite popular. One reason is that EIS allows separating the influences of different components, meaning the contribution of the electron transfer resistance, double layer capacity, etc. Another one is that EIS is very surface sensitive and reveals many changes that other techniques don't detect, for example, changes in polymer layers due to swelling, surface changes due to protein adsorption, or penetration of corrosion protection layers. As a result, EIS is interesting for analytical electrochemistry, because molecules can be detected without a redox-active marker.

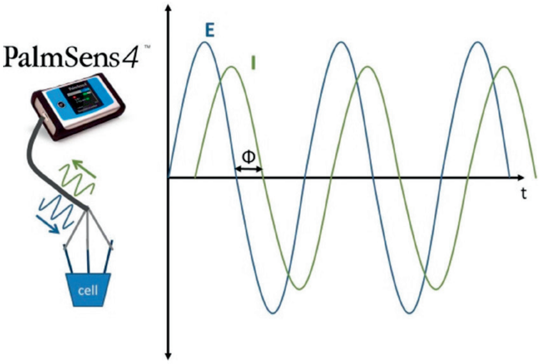


Figure 6.1 Schematic representation of the potential excitation and current response in the measurement setup (left); potential and current waves over time (right).

While resistance is the ratio of voltage or potential and current for a DC (direct current) system, impedance is the ratio of voltage or potential and current for AC (alternating current) systems. The wave nature makes it necessary to define the impedance with two parameters. The first is the total impedance *Z* and the second is the phase shift *Φ*. If you consider the two periodic waves of current and voltage, the waves have the same frequency, because one wave causes the other. There is a constant time shift between the two waves, which is called the phase shift *Φ*. Its unit is degrees (°) because in general waves are vectors in a polar coordinate system or a sine function (see Figure 6.1). The total impedance is the ratio of the potential's amplitude and the current's amplitude. The resulting impedance is a complex number. This number can be expressed in the complex plane in polar coordinates by using *Z* as the length of the vector and *Φ* as the angle. With the common knowledge of calculations for complex numbers, the impedance can also be expressed as the real part of the impedance *Z'*, which is the resistance, and imaginary part *Z''* (see Figure 6.2). The two notations are the origin of the two most popular plots for impedance spectra: the Bode plot and Nyquist plot. More information will be given in Chapter 6.1.

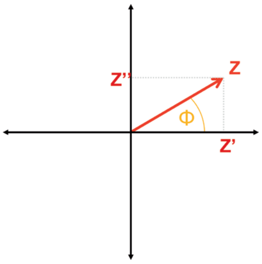


Figure 6.2 Impedance Z, phase shift Φ, real part Z' and imaginary part Z'' of the impedance in the complex plane.

A potentiostat measures the impedance by applying a potential wave to the working electrode and records the resulting current wave. From these two waves, the potentiostat calculates Z, Φ, Z', and Z''. The spectrum is made by measuring these parameters for potential waves with different frequencies. A fixed number per decade is usually chosen because most plots have a logarithmic axis. For example, a measurement from 10 000 Hz to 100 Hz with 10 points per decade has 10 frequencies between 10 000 Hz and 1000 Hz and 10 between 1000 Hz and 100 Hz. These frequencies are usually equidistant on a logarithmic scale. PSTrace allows you to choose if you want to define the total number of points through the whole spectrum or the number of points per decade. Whichever option you choose, you can always see a list of the chosen frequencies.

6.1 Bode and Nyquist Plot

As mentioned in the previous chapter, there are two main ways to plot an impedance spectrum. One is the Bode plot. This plot is two plots in one. The abscissa is a logarithmic scale of the frequency, and one ordinate is the logarithm of the impedance Z while the second ordinate is the phase shift Φ. The advantage of this plot is that all information is visible. A capacitor in parallel to a resistor, which is an important circuit for electrochemical impedance spectroscopy, is visible in this spectrum as a peak in the phase shift. The spectra of single components can be understood more easily in the Bode plot.

The Nyquist plot is more complex to understand, but due to practical reasons is more popular in electrochemistry. One reason is that the Nyquist plot is very sensitive to changes. Another is that for the most common circuits, some parameters can be read directly from the plot. To get a Nyquist plot the negative imaginary impedance $-Z''$ versus the real part of the impedance Z'.

In the following paragraphs, some simple components' effects on a Bode plot and Nyquist plot will be shown. This is useful because it is common to create an electronic circuit that represents the electrochemical system under investigation. A fit of the spectrum based on this equivalent circuit is made to identify the contribution of the single components.

The simplest component is the resistor, which just follows Ohm's law:

$$R = \frac{U}{I} \tag{6.1}$$

This is true for DC and AC currents. As a result, there is no phase shift ($\Phi = 0$ °), and the impedance Z, which is equal to R in this case, is independent of the AC frequency. This is visible in the Bode plot by two constant parallels to the abscissa (see Figure 6.3). In the Nyquist plot, a single point with $Z'' = 0$ and $Z = R$ is visible (see Figure 6.3).

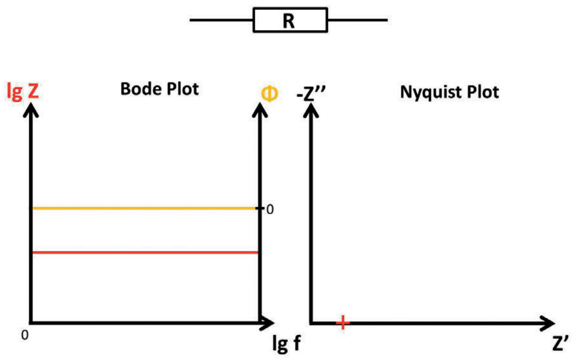


Figure 6.3 EIS of a Resistor in a schematic Bode and Nyquist plot.

Another common element that is often utilized for experiments is the capacitor. Capacitors store charge. A simple capacitor is a plate capacitor. It comprises two conducting parallel plates that are not in contact with each other. If a power source is connected to the plates, a current flows that is exponentially decaying until it is insignificant. A current flows because one plate is charged negatively and the other positively. The separation of charges means current flows. At some point, the plates cannot store any more charge and the current stops flowing. The current decays over time according to

$$I = \frac{E^C}{R} e^{-\frac{t}{RC}} = I^0 e^{-\frac{t}{RC}} \tag{6.2}$$

E^C is the charging potential or voltage, I^0 is the starting current, R is the resistance of the circuit around the capacitor, t is the time, and C is the capacitance of the capacitor. The capacitance is a property of the capacitor and is defined as the charge Q that can be stored per applied potential E or as an equation:

$$C = \frac{Q}{E} \tag{6.3}$$

Usually, U is used for voltage, but since these equations need to be transferred to electrochemical experiments, it is useful to start with the potential E instead of the voltage U. These two are not synonymous but in this context, it is fine to exchange them.

Assuming that the electrochemical double layer, i.e. the ions in front of the electrode and the electrons (or their deficiency) in the electrode, behaves exactly like a plate capacitor, the two equations 6.2 and 6.3 show three important facts:

1. The capacitive current decays exponentially with the time t. The higher the resistance R and capacitance C are the slower it will decay. The product of resistance R and capacity C is often called the time constant .
2. The charge Q that can be stored is proportional to the applied potential. Every time the charge Q that can be stored changes a current I flows until the charge Q is adjusted. The charge Q that can be stored changes if the potential E is changing. This is expressed in equation 6.4:

$$I = \frac{\partial Q}{\partial t} = C\frac{\partial E}{\partial t} \tag{6.4}$$

3. In equation 6.2 it is shown implicitly and in 6.4 explicitly that the higher the capacitance C is the more capacitive current will flow if the potential changes.

These insights were gained by looking at a DC system but can be transferred to an AC system. Equation 6.4 shows that changing the potential at higher frequencies will result in higher currents flowing, which means the impedance *Z* is low. Reducing the frequency of the AC potential will lead to a higher *Z*. This means that at a very high frequency, a capacitor has no contribution to *Z*, and at very low frequencies *Z* goes towards infinite. The phase shift *Φ* of an ideal capacitor is 90 ° and the impedance Z is calculated according to:

$$Z_{cap} = \frac{1}{2\pi f C} \tag{6.5}$$

As a result, the Bode plot shows a constant *Φ* of 90 ° and a linear curve with a negative slope and the Nyquist plot shows a straight line along the ordinate (see Figure 6.4). From this example, it is clear that in the Nyquist plot, the frequency at which a value was recorded is not visible.

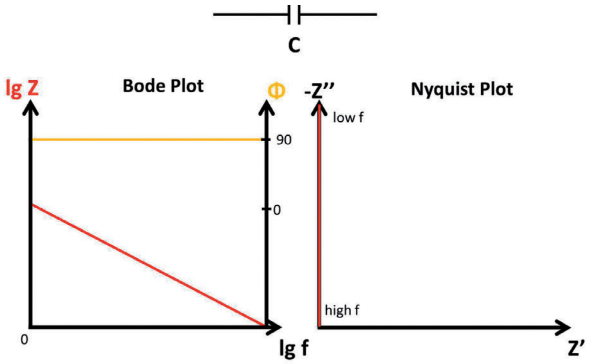


Figure 6.4 EIS of a Capacitor in a schematic Bode and Nyquist plot.

Capacitors are easily formed in an electrochemical experiment. The electrochemical double layer forms a capacitor with a huge impact on electrochemical measurements. Unfortunately, parallel cables, crocodile clips, and other electronic components can form a capacitor as well. This happens at high frequencies and leads to stray capacitance. The PalmSens4 negates the impact of capacitors that form between the cables in the cell cable and the shield of the cell cable by using an active shield. Still, it is advisable to avoid cables parallel at short distances from each other.

A resistor and a capacitor can be combined in different ways with rather different effects. If the connection is serial, which resembles a perfect coating as will be discussed later, the impedance *Z* can't be smaller than *R*. The capacitor's impact decreases with increasing frequency. The resulting Nyquist and Bode plots can be seen in Figure 6.5.

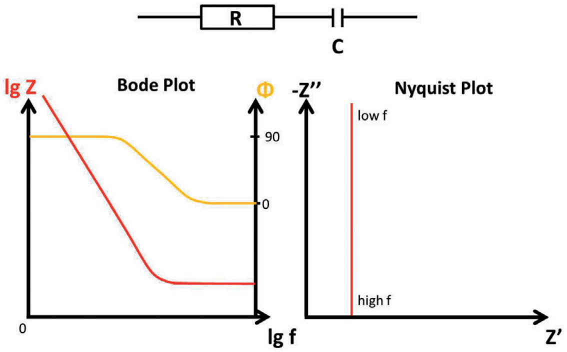


Figure 6.5 EIS of a serial Resistor and Capacitor in a schematic Bode and Nyquist plot.

A more interesting effect is observed when the resistor and the capacitor are parallel. The current chooses the path of the lowest impedance, no matter if it is AC or DC. The impedance of the capacitor is frequency dependent, as discussed, which means the path the current choose will change. At high frequencies, the impedance of the capacitor will be very low, and most of the current will flow through the capacitor. With decreasing frequencies, the impedance of the capacitor increases, and a bigger fraction of the current flows through the resistor. When most of the current flows through the resistor, the total imaginary resistance *Z''* will drop as the real part *Z'* increases.

These processes lead in the Bode plot to a gradual change in the Φ curve from 90 ° to 0 ° and in the Nyquist plot to a semicircle (see Figure 6.6). Note that the Nyquist plot represents the complex plane, and each value is a complex number, so the axes should have the same scale. Under this condition, an ideal capacitor in parallel with a resistor leads to a semicircle.

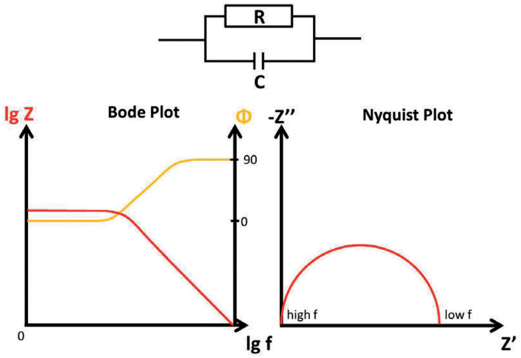


Figure 6.6 EIS of a parallel Resistor and Capacitor in a schematic Bode and Nyquist plot.

This circuit is already quite close to a real system. The capacitor represents the electrochemical double layer, which can only store charge and ion movement. The resistor represents the charge transfer resistance. This is the resistance opposed to an electron being moved from one phase to another, e.g. from the electrode into the solution or to be more precise to a species solved in the solution. These are two ways for current to pass through the electrode-solution interface. All cell current must pass through the solution, which acts as an Ohmic resistor. The resulting circuit is seen in Figure 6.7 and is called the simplified Randles circuit.

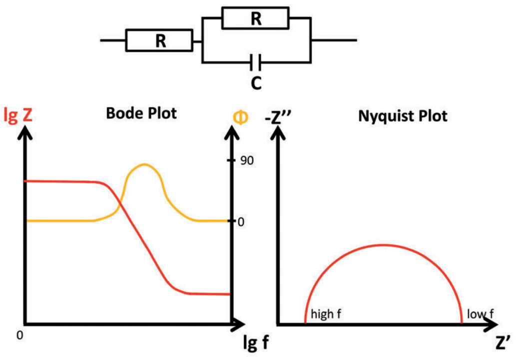


Figure 6.7 EIS of a simplified Randles circuit in a schematic Bode and Nyquist plot.

The resulting EIS shows a peak in *Φ*. Similar to the difference between Figure 6.5 and Figure 6.4, the Nyquist plot has a shift to higher real impedance values compared to Figure 6.6. The influence of every component can be explored by simulation. An interactive EIS of the Randles Circuit can be downloaded together with the free Wolfram Alpha Player here: http://demonstrations.wolfram.com/ElectrochemicalImpedance/

Unfortunately, the real-life examples are not behaving as nicely as circuits constructed from the ideal components presented in this chapter. The following chapter will deal with models for real measurements. Nevertheless, the Randles circuit nicely shows why the Nyquist plot is so popular. At high frequencies, C_{dl} is close to 0 and the main contribution comes from the R_{sol}. So, the beginning of the semicircle equals R_{sol}. At low frequencies the C_{dl} has very high impedance and all the current goes through R_{ct}. As a result, the impedance contribution at the point where the right end of the semi-circle would hit the 0 of the y-axis is $R_{sol} + R_{et}$. Due to this R_{sol} and R_{et} can easily be estimated just by looking at the semi-circle. Furthermore, the C_{dl} could be calculated from the frequency at the highest point of the semi-circle (maximum of Z'') f_{max} using equation 6.6.

$$C_{dl} = \frac{1}{R_{et} 2\pi f_{max}} \quad 6.6$$

6.2 Equivalent Circuit Fitting for Corrosion Measurements

From the previous chapter, a basic understanding of the Bode and Nyquist plot is gained. These plots have been explained using elements known from electronics. This is quite a common technique in EIS. A circuit is created, and each electrical component represents a part of the electrochemical system. This equivalent circuit should create the same impedance spectrum as the real electrochemical system. With suitable software, a fit is done to match the spectrum calculated from the circuit and the measured spectrum. The values (capacitance, resistance, etc.) for each electronic component used in the equivalent circuit are then displayed. This way the contribution of the single elements to the whole impedance is identified. For example, you can follow the changes in the charge transfer resistance without the solution resistance or the double-layer capacitance interfering.

It was observed that some effects occur in EIS that can't be modeled with classic electronic components, so new components were introduced. One component is the Warburg impedance. The Randles circuit (Figure 6.7) is quite close to an electrochemical experiment. As mentioned before, the solution resistance R_{sol} is the serial resistor. All current needs to go through the solution. The current can go through the interface of the working electrode by capacitive current caused by the electrochemical double Layer, represented by the double layer capacitance C_{dl}, or by Faraday current caused by an electrochemical reaction, which requires an electron transfer and therefore needs to go through the charge transfer resistance R_{ct}. Up to here, the expected EIS would be a semi-circle just as for the simplified Randles circuit.

However, if a free diffusing species is converted at the electrode, this behavior isn't observed. At low frequencies oxidizing or reducing potentials are held long enough so that depletion of the species in front of the electrode becomes relevant. The depletion of species in front of electrodes is well understood and described by the Cottrell equation. Due to the lack of species in front of the electrode, fewer species are converted, and less current flows while the same potential is applied. During an EIS measurement, this is recorded as an increase in impedance. This increase is represented by the Warburg element *W* or Z_W, which is a virtual electronic component only used to make equivalent circuits for electrochemical experiments. The Warburg element's impedance is calculated by:

$$Z_W = \frac{\sigma}{\sqrt{2\pi f}} - j\frac{\sigma}{\sqrt{2\pi f}} \tag{6.7}$$

Z_W is the impedance of the Warburg element and σ is the Warburg coefficient also known as A_W. It has the unit $\Omega/s^{½}$ and can be extracted from measurement data or it can be calculated according to

$$\sigma = \frac{RT}{Az^2F^2\sqrt{2}}\left(\frac{1}{\sqrt{D_O}c_O^b} + \frac{1}{\sqrt{D_R}c_R^b}\right) \tag{6.8}$$

where *R* and *F* are the Gas and Faraday constant, *D* is the diffusion coefficient and c^b is the concentration of the species in the bulk. The indices O and R indicate the oxidized and reduced species.

The Warburg Impedance is visible in the Nyquist plot as a straight line with a 45° angle to the abscissa. As mentioned before, the depletion has a significant effect on the impedance at lower frequencies. The moment it becomes visible depends on the double-layer capacitance. A schematic representation of a full electrochemical system's EIS is shown in Figure 6.8.

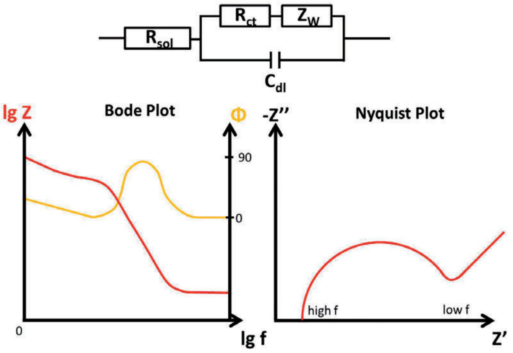


Figure 6.8 EIS of a Randles circuit including a Warburg element in a schematic Bode and Nyquist plot.

As mentioned before, the Randles circuit contains a free diffusing species. The presence of such a species is typical for analytical electrochemistry but is not necessarily true for corrosion experiments. An example where this equivalent circuit works quite nicely is a non-porous electrode (e.g. platinum disc electrode) and a reversible redox couple in solution (e.g. ferrocyanide and ferricyanide). Two examples are shown in Figure 6.9.

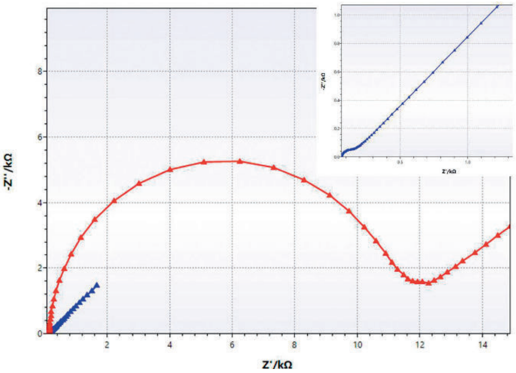


Figure 6.9 EIS of a Pt disc electrode (blue) and an IS-1 SPE (red curve) with a carbon ink working electrode in $K_3[Fe(CN)_6]$ + $K_4[Fe(CN)_6]$ solution; Insert: Zoom in on blue curve.

The platinum electrode (blue curve) has a very low charge transfer resistance, leading to a dominance of the Warburg impedance at very low resistances, while the carbon electrode by ItalSens (red curve) shows a significantly higher charge transfer resistance, leading to the expected semi-circle. These two examples are found in your PSData folder after installation of PSTrace. There are many different equivalent circuits and often more than one can deliver a good fit for the spectra. One must try to find a circuit where every component represents a real process or element of the electrochemical system. It is good practice to try to keep the number of elements in the circuit low.

Some equivalent circuits are quite common in the field of corrosion. The simplest one is already shown in Figure 6.5. The capacitor would be the coating with the capacity C_C. A perfect coating wouldn't allow any Faraday current, because the coating blocks any transfer of electrons. However, the electric field of the electrode can still create a double layer. A resistor and capacitor in series describe this system. Since no coating is perfect, usually one can see at lower frequencies some deviation from the perfect straight line tending towards a semi-circle with a large diameter.

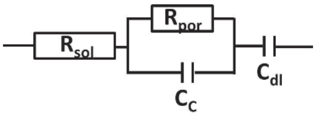


Figure 6.10 Equivalent circuit for a real coating

Unfortunately (or fortunately if you make a living from corrosion research), most coatings are not perfect or don't stay perfect for an unlimited amount of time. A real coating will have a different thickness at different places or pores. This leads to a slightly more complex equivalent circuit (see Figure 6.10) including R_{sol}, C_{dl}, C_C as well as the pore resistance R_{por}. Just like a thinner cable means a higher resistance, a narrow tunnel for ions to flow through does as well. This is the cause of the R_{por}.

The system gets even more complex when corrosion starts. Current travels through an opening and either passes through a very thin layer of coating or is in contact with the metal. This means that in series to the just introduced R_{por} there will be a parallel RC system (see Figure 6.11). The capacitance is the double-layer capacitance C_{dl} and the resistance is the charge transfer resistance R_{ct}.

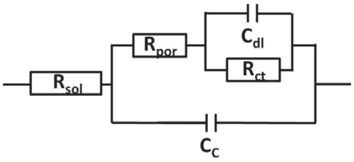


Figure 6.11 Equivalent circuit for a coating with corrosion.

A further increase in complexity needs to be done when disbonding starts. Disbonding means that suddenly there are a lot of places where the metal surface has direct contact with the solution, but the solution travels through a pore or opening to the spot of disbonding. Furthermore, these places can have significant resistance between each other. If they don't, the situation gets simpler, because the whole area of disbonding can be treated as one big electrode. Another problem during disbonding is that EIS theory is based on stationary systems. In the time scale of the EIS recording the changes happening in the system should be negligible.

Despite all the above these processes can be expressed in equivalent circuits. The circuit for the disbonding with significant resistance between the disbonding sites (under film resistance R_{uf}) needs a series of RC elements connected by resistors to each other, each representing a site of disbonding or rather a collection of equal sites (see Figure 6.12). This circuit especially has a lot of components and variables for a fit. With enough variables, almost every curve gets a good fit, but that doesn't mean that the equivalent circuit represents the system well. One should try to use the least complex equivalent circuits first before trying more complex ones.

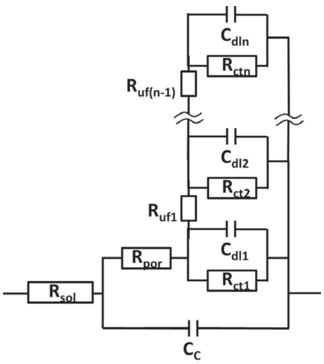


Figure 6.12 Equivalent circuit for a disbonding coating with significant resistance under the film.

If the resistance between the disbonding sites is negligible, the circuit is simplified again and looks just like the regular corroding surface (see Figure 6.11).

Another problem the equivalent circuits must face is that nature doesn't act as a perfect capacitor in most situations. The reasons for this aren't quite clear. It is often mentioned that the rough nature of real surfaces needs to be considered, but in other publications, the dispersion of impedance at the solid interface is mentioned. Using an empirical correction for a non-ideal capacitor doesn't require a complete understanding of the reasons for non-ideal behavior. If the semi-circle in a Nyquist plot is depressed and doesn't show a constant radius before the Warburg impedance dominates the spectrum, the use of a constant phase element (CPE) in the equivalent circuit should be considered. The CPE has a frequency-independent constant phase shift, just like a capacitor. The impedance is calculated by 6.9.

$$Z_{CPE} = \frac{1}{T(j2\pi)^{\phi}} \qquad 6.9$$

The ϕ is not the phase shift here, but the degree to which the CPE is a resistor or capacitor. If ϕ is 0, the CPE is just a resistor and if it is 1 the CPE is a capacitor. All values in between represent a state between two extremes. ϕ can't have values below 0 or above 1. What *T* stands for depends on ϕ. For ϕ = 1, T is capacitance and for ϕ = 0, it is conductance. Accordingly, the units of *T*, which are shown in equation 6.10, seem quite unusual. If you want to work with CPEs in your equivalent circuit, just replace the corresponding capacitor with a CPE.

$$[T] = \frac{F}{cm^2} s^{\phi - 1} = \frac{s^{\phi}}{\Omega cm^2} \qquad 6.10$$

This is a brief introduction to equivalent circuit fitting, and it should help you to get started with corrosion research, but there is a lot more to discover. Many books on this topic are published, which sometimes even have contradictory content. Furthermore, it requires some experience to recognize some typical shapes or behaviors for your systems.

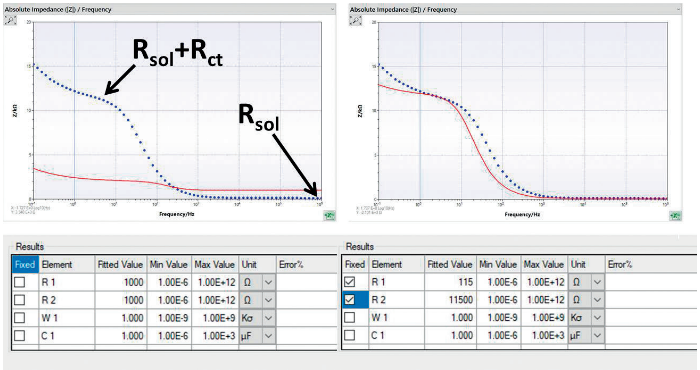
6.3 Tips for Equivalent Circuit Fitting

Often a fit will be pretty good with the first iteration. Sometimes, a fit just won't deliver a curve that overlaps with the measurement. This is due to the way a fit is calculated. The computer tries to find values for the variables that deliver a curve with the smallest difference to the measurement (Least Square fitting). A drawback of the Complex Non-linear Least Squares fitting algorithm is that starting with initial values for parameters that are too far off, can lead to getting stuck in a local minimum and returning a suboptimal fit instead of finding the absolute minimum.

Unfortunately, the default initial values of PSTrace for the resistors and capacitors are sometimes too far off from the optimal values for some systems. The default values have been selected to be optimal for the most common types of electrochemical cells.

To obtain a correct fit when modeling coatings/corrosion with equivalent circuits the following steps are recommended if a clear RC system is visible (semi-circle in Nyquist plot).

1. In the fitting window, switch the view to the absolute impedance over frequency.
2. The solution resistance R_{sol} can be read from the right side of the plot (high frequency). Enter this value into the fitting parameters. The plot is directly updated after editing a value. You can, of course, also read this value from the Nyquist plot (start of the semi-circle).
3. For estimating the charge transfer resistance R_{ct} use the value of the impedance at the left side of the plot (low frequencies), where the slope of the curve is suddenly decreasing. Enter this value into the fitting parameters. The plot is directly updated after editing a value. You can, of course, also read this value from the Nyquist plot (end of the semi-circle) (see Figure 6.13).



Results

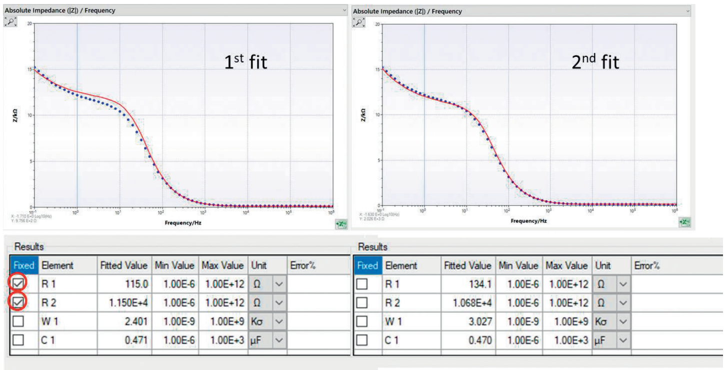
Fixed	Element	Fitted Value	Min Value	Max Value	Unit	Error%
☐	R 1	1000	1.00E-6	1.00E+12	Ω	
☐	R 2	1000	1.00E-6	1.00E+12	Ω	
☐	W 1	1.000	1.00E-9	1.00E+9	Kσ	
☐	C 1	1.000	1.00E-6	1.00E+3	µF	

Results

Fixed	Element	Fitted Value	Min Value	Max Value	Unit	Error%
☑	R 1	115	1.00E-6	1.00E+12	Ω	
☑	R 2	11500	1.00E-6	1.00E+12	Ω	
☐	W 1	1.000	1.00E-9	1.00E+9	Kσ	
☐	C 1	1.000	1.00E-6	1.00E+3	µF	

Figure 6.13 Step-by-Step Fitting Part 1.

4. The capacitance of the constant phase element or the capacitor can then be lowered, 0.001 µT/µF for instance is a good value. Whether or not your change of capacitor's value was suitable will become clear when the plot is updated.
5. Next, press "fit" to obtain the fit with the correctly fitted values of the resistors and the constant phase element.



Results

Fixed	Element	Fitted Value	Min Value	Max Value	Unit	Error%
☑	R 1	115.0	1.00E-6	1.00E+12	Ω	
☑	R 2	1.150E+4	1.00E-6	1.00E+12	Ω	
☐	W 1	2.401	1.00E-9	1.00E+9	Kσ	
☐	C 1	0.471	1.00E-6	1.00E+3	µF	

Results

Fixed	Element	Fitted Value	Min Value	Max Value	Unit	Error%
☐	R 1	134.1	1.00E-6	1.00E+12	Ω	
☐	R 2	1.068E+4	1.00E-6	1.00E+12	Ω	
☐	W 1	3.027	1.00E-9	1.00E+9	Kσ	
☐	C 1	0.470	1.00E-6	1.00E+3	µF	

Figure 6.14 Step-by-Step Fitting Part 2.

6. Sometimes it is necessary to fix the known values before the first fit, then release them and fit again. The first fit will bring the unknown values close to the optimum and the second one will optimize all parameters (see Figure 6.14).

Although these steps have been quite specific for RC systems, they can be used in an analog way for other circuits. First, values are estimated from the measurement and afterward, a fit with these parameters fixed is performed to determine the values of the other parameters. Afterward, a fit with no fixed parameters is performed.

6.4 Constant Potential vs OCP or Reference Electrode

As mentioned before, during EIS an AC voltage is applied, and the current answer is measured. The AC voltage should be applied in a potential region, where a small potential change induces a strong answer in current. This means, that if we plot the current versus the potential, we want to choose a potential range where the slope of the reaction we are interested in is high. A simple system to demonstrate this is a platinum electrode in a solution containing $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. The non-diffusion limited voltammogram of this species clearly shows that the biggest current changes are induced around the formal potential of the species (see Figure 6.15), which is in agreement with the Nernst Equation (equation 3.5, page10). If a DC potential, which corresponds to the formal potential, is applied, the AC potential will have good sensitivity.

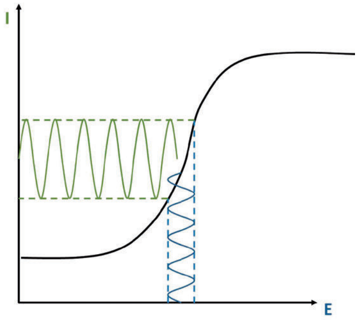
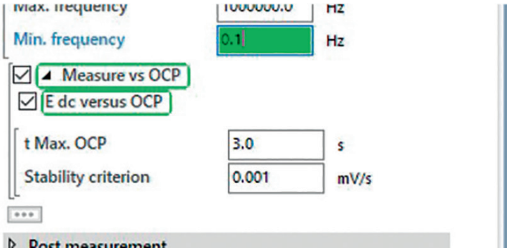


Figure 6.15 I-E curve according to the Nernst-Equation and the effect of an AC voltage close to the formal potential.

For the example of a $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ solution, the formal potential can be looked up in a table or measured by a linear sweep voltammetry. This value can be entered as *E dc* in the corresponding field of PSTrace. Another method is to use a 1-to-1 ratio of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. The immersed electrode potential (OCP) will be the formal potential of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. This has two advantages: Identification of the right potential and keeping a steady state. The right potential is the OCP. Even if an unusual reference electrode is used, the potential to be applied is clear. It can easily be determined by a short open circuit potential (OCP) measurement also known as corrosion potential. Furthermore, the system will not be disturbed when the measurement starts. If you move the potential away from the OCP, the environment of the electrode will react, the system won't be in a stable state, and a diffusion layer will grow. If the measurement happens at the OCP of the electrode, this means the electrode had the potential before the measurement already. As a result, only the AC potential will "wiggle" at the equilibrium.

For corrosion measurements, it is very common to measure at the E_{corr}, which corresponds to the OCP, of the sample. This potential usually represents a stable state in the time scale of the EIS measurement. If the sample wouldn't change at all over time, no corrosion would occur, and the measurement would be unnecessary in the first place. This means, if a sample is observed over a long time, the E_{corr} will change. If before each EIS measurement the E_{corr} is determined and used as the *E dc*, the measurements will still be comparable and deliver sensitive measurements.

In PSTrace you have the option to measure EIS with the applied *E dc* versus the OCP. You just need to check the checkbox *Measure vs OCP* and *E dc versus OCP*. The first checkbox triggers an OCP measurement directly before the EIS recording is performed. The second checkbox changes the reference point for the *E dc*. In electronics only potential differences can be measured, so the potentiostat needs to have a 0-reference point. This is usually the reference electrode, so 0.25 V in the field *E dc* usually means 0.25 V more anodic than the reference electrode. If the checkbox *E dc versus OCP* is checked, a 0.25 V in E dc means 0.25 V more anodic than the E_{corr}. Other techniques allow the OCP to be the reference point, for example, polarization curves. The two additional parameters that are displayed define the duration of the OCP measurement (see Figure 6.16). The *t Max. OCP* is the longest time the OCP measurement is performed. If the OCP measurement reaches this duration, it will be stopped, and the last measured value is used as OCP. The OCP measurement can be shorter if the *Stability criterion* is met. If the change of the OCP per second is lower than the *Stability criterion*, the OCP is considered stable and the OCP measurement is stopped. The last recorded value is used as OCP.



Max. frequency 1000000.0 Hz
Min. frequency 0.1 Hz
☑ Measure vs OCP
☑ E dc versus OCP
t Max. OCP 3.0 s
Stability criterion 0.001 mV/s

Figure 6.16 Checkboxes to measure versus OCP (respectively E_{corr}).

7

Rapid Electrochemical Assessment of Paint

“Rapid” is a relative term. Rapid Electrochemical Assessment of Paint (REAP) includes an overnight step, which for example for the common spectroscopist will seem like a long time, but for a corrosion scientist, it is a rather short amount of time. During REAP a series of measurements with multiple samples is performed and the long-term stability is extrapolated. Electrochemical Impedance Spectroscopy (EIS) and cathodic disbonding are the central techniques for the REAP, which allow us to estimate the time to failure.

This description is based on the ASTM G01.11 subcommittee on Electrochemical Measurements in Corrosion, which offers more details than this application note. REAP was originally suggested in Kending et al, J. Coatings Tech., 1996, 68, p. 39 – 47, which is available through Research Gate. During this procedure, the corrosion potential, the water uptake of the coating, and the disbonding rate will be determined. With these three parameters, an estimation of the Time to Failure (TTF) can be obtained.

7.1 Sample

REAP requires pairs of samples, which leads to an even number of samples. Usually, a minimum of three measurements is recommended. Half of the samples stay pristine, and the other half is scribed. The scribed samples should have a right-angle cross with both lines 2 cm long. If you want to make sure you keep to the ASTM standards, you can look up how to scribe a sample in ASTM B117. Before the REAP both samples should have a cured and dried coating.

For the measurement, 0.5 M NaCl solution is used. Two setups will be needed to keep both samples immersed for 24 h. The setup should allow you to connect your sample to the potentiostat’s working electrode lead while exposing a defined area to the measuring solution like the Corrosion Cell Kit from ItalSens does.

7.2 REAP First Step: Corrosion Potential

The first parameter, which will be determined, is the corrosion potential E_{corr} of the pristine sample because it is necessary for the following measurements. The E_{corr} should be measured in a short time after the sample’s immersion, so we recommend setting up the measurement parameters first before pouring the measurement solution (0.5 M NaCl) into the cell.

The technique *Corrosion Potential* (in *Corrosion* mode) also known as *Open Circuit Potentiometry* (in *Scientific* mode) is performed with *t run* 200 s and one value every 0.5 s (*t interval*). If you don’t know how to perform this measurement with PSTrace, it will be explained in the following paragraph.

You don’t have to perform this measurement in the *Corrosion Mode* of PSTrace, although this explanation will assume you are in *Corrosion Mode*. You can change the mode in the upper left corner of your PSTrace window.

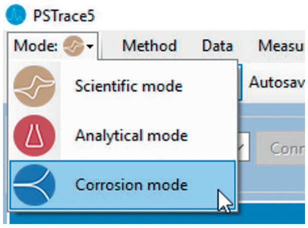
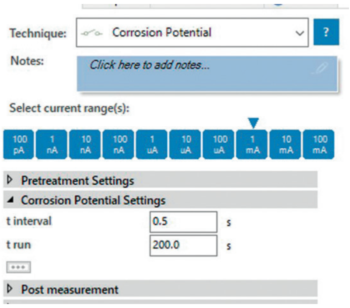


Figure 7.1 Choosing the mode in PSTrace.

Choose from the techniques list the *Corrosion Potential*. Please note: If you don't know what a specific technique does, just choose the technique in the drop-down menu and press the *?*-button. You can activate all the current ranges for this technique, so all current ranges should be marked blue. Into the field *t interval* enter 0.5 s and into *t run* 200 s.



Technique: Corrosion Potential

Notes: Click here to add notes...

t interval 0.5 s

t run 200.0 s

Figure 7.2 Parameters for the Corrosion Potential Measurement.

Position the sample in the measurement solution or position the sample first and then pour the solution in. Make sure there aren't any air bubbles trapped at the surface of the sample. Connect your potentiostat to the counter, reference, and working electrode. Press the *Run*-button. After recording the E_{corr} you can save it. You can set the dropdown menu next to the *Run*-button on *Overlay* if you want to save all the different measurements performed during your REAP in one pssession file.

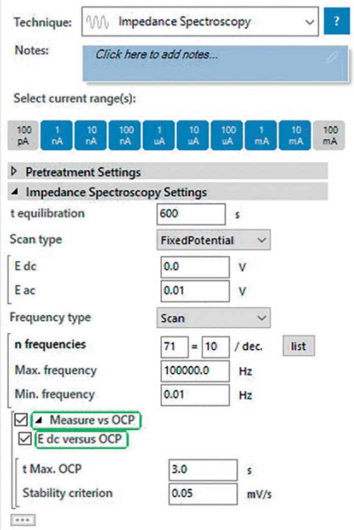
There is the possibility that your coating is very good and will behave close to an ideal capacitor. As a result, you might not get a stable E_{corr} with no indication of a trend of reaching a constant potential. While this is inconvenient for our measurements, it means you produced a proper coating. For the next steps of the REAP E_{corr} is required. If you can't get a stable measurement of E_{corr}, the literature suggests that you assume an E_{corr} of 600 mV.

7.3 Step 2: Determine the Coating's Capacitance without Swelling

The goal of this step is to determine the capacitance of the pristine sample coating. Later the coating's capacity after immersion in water for 24 h will be determined. The change in the capacity is caused by water penetrating the coating. With the two capacitances, the water uptake can be calculated.

The reference and counter electrode, as well as the sample, should still be connected from Step 1. Change the technique in the dropdown list to *Impedance Spectroscopy*. Set a *t equilibration* of 600 s. The dropdown menu should show *Fixed Potential*. If your previous measurement delivered a stable OCP during step 1, you could set *E dc* to 0 V and check the checkboxes *Measure vs OCP* and *E dc versus OCP* below. This way the *E dc* indicates the potential difference to the OCP. A short OCP measurement is performed before the EIS measurement to determine the OCP. This measurement will last until the time *t Max. OCP* is elapsed or until the *Stability criterion* is met. If you didn't get a stable OCP, uncheck the check boxes *Measure vs OCP* and *E dc versus OCP*. Try an *E dc* of 600 mV vs SCE, which is now versus the reference electrode. If you don't know how much 600 mV vs SCE is versus the reference electrode in your setup, visit this website: http://www.consultrsr.net/resources/ref/refpotls3.htm

Set an *E ac* of 10 mV. Select in the *Frequency Type dropdown menu Scan. A Max. frequency* of 100 kHz should be sufficient. The *Min. frequency* is set to 0.01 Hz. Start your measurement (see Figure 7.3).
The analysis is done via an equivalent circuit fit, but this will be discussed in step 4 after the second impedance spectrum is acquired.



Technique: Impedance Spectroscopy

Notes: Click here to add notes...

Select current range(s):

Pretreatment Settings

Impedance Spectroscopy Settings

t equilibration	600	s
Scan type	FixedPotential	
E dc	0.0	V
E ac	0.01	V
Frequency type	Scan	
n frequencies	71 = 10	/ dec.
Max. frequency	100000.0	Hz
Min. frequency	0.01	Hz

☑ Measure vs OCP

☑ E dc versus OCP

t Max. OCP	3.0	s
Stability criterion	0.05	mV/s

Figure 7.3 Parameter settings for step 2.

7.4 Step 3: Disbonding Rate

During disbonding the coating peels off the substrate. The goal of this step is to find the disbonding rate of the coating. This will be measured in distance from the initial scratch per time dx/dt, so how fast does the disbonded area expand.

A proper coating won't allow disbonding, so we need to use the scribed sample. The pristine sample stays in the NaCl solution for 24 hours, to perform step 4, so you will need a second setup or at least a holder and vessel to keep the sample immersed in the NaCl solution.

The scribed sample still disbonds rather slowly, so this process is accelerated by applying a potential to the scribed samples for 24 h while the sample is immersed in NaCl solution. This potential is very cathodic, so hydrogen will form during the time under this potential. This should increase the rate of disbonding, so the disbonding rate can be evaluated within 24 h.

Prepare a cell with NaCl solution and insert a reference and counter electrode. The scribed sample is immersed in the cell as well. Change the technique to *Chronoamperometry*. Set *t equilibration* to 600 s and *E dc* to 1.05 V vs SCE. *t interval* can be set to 30 s and *t run* to 86400 s. Start the measurement.
Although the recorded current is not needed to determine dx/dt, we recommend that you save the data for future reference. There is a correlation between the current and the disbonding rate, so a measurement with a high current should have a high disbonding rate.

After 24 h take the sample out of the solution and rinse it with demineralized water to prevent further reaction. Dry the sample with a cloth or paper towel. Use a piece of the adhesive tape to remove the loose coating around the scratch. Take a sharp object to check if all loose material has been removed. Use a ruler to measure the width w of the area around the scribed line as shown in Figure 7.4. The disbonding rate dx/dt is usually expressed in mm/h, despite being rather in the range of μm/h. These low rates require a very precise ruler to measure the width w. The border of the disbonded area isn't always as sharp as one would like, so the width should be measured multiple times and averaged. The disbonding rate, so how fast the border between disbonded and proper coating is progressing, can be calculated by taking half the width, which is the distance between the original scratch and the border of the uncoated area *x*, and dividing it by the time *t*. This is expressed in equation 7.1:

$$\frac{dx}{dt} = \frac{w}{2t} = \frac{x}{t} \tag{7.1}$$

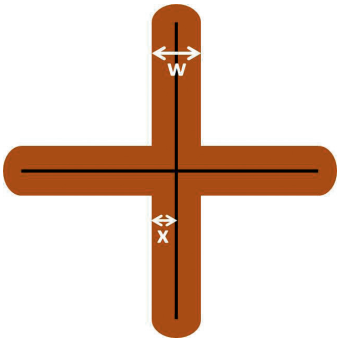


Figure 7.4 Scheme of the scratched sample after the 24 h cathodic disbonding; black is the original scratch; brown is the disbonded area.

7.5 Step 4: Determine the Coating's Capacity with Swelling

The pristine sample's coating will have taken up some water after 24 h of immersion in the NaCl solution. To determine this water uptake the coating capacity needs to be determined. Water has a dielectric constant, which is at least a magnitude higher than the constants of the organic compounds in the coating.

The measurement is analog to the measurement from step 2. First, the cell with the pristine sample is connected (reference, counter, and working electrode). Then the EIS measurement from step 2 is repeated. If you used the OCP as *E dc* before, you should use it again. Otherwise, enter the same potential as during the first measurement. If you want you can save the Method file of the measurement from step 2 and just reuse it, so you set up your experiment in an easy way. Just click in the top menu under *Method* the option *Save method* and later *Load method* to load the parameters. With PSTrace, it is easy to determine the coating capacity before and after the 24 h immersion from the two spectra.

In Chapter 6.2 the use of equivalent circuits was discussed thoroughly. For the REAP a model like the one in Figure 6.11 has proven useful. Just the capacitor for the substrate solution interface has been replaced with a constant phase element (CPE) to take the non-ideal character of the coating capacitor into consideration. This model is shown in Figure 7.5.

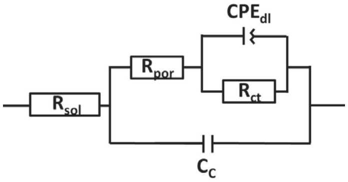


Figure 7.5 Equivalent Circuit for water uptake determination during REAP.

The hints from Chapter 6.3 should be taken into consideration when fitting the data. When a satisfactory fit for both curves is achieved, the water uptake of the coating in volume percentage %V can be calculated using the capacity before and after immersion. Maybe the C_C must be replaced with a CPE as well to achieve a proper fit. The capacity of the CPE has the unit T, but can for this experiment be used in an analog way as a capacitance in F. Equation 7.2 delivers %*V*.

$$\%V = 100 \frac{\log \frac{C_{C,wet}}{C_{C,dry}}}{\log 80} \tag{7.2}$$

7.6 Step 5: Determine R_{corr}

From the fit in step 4 also the corrosion resistance R_{corr}, labeled as R_{ct}, can be extrapolated. Just read the value from the fit of the EIS after 24 h of immersion.

7.7 Step 6: Estimation of the Time to Failure (TTF)

The TTF can be calculated if the corrosion resistance R_{corr}, the water uptake in *%V*, and the disbonding rate *dx/dt* are known. Equation 7.3 is suggested in the literature:

$$TTF = -830.1 + 118 \cdot log\, R_{corr} - 169.2 \cdot log\, \frac{dx}{dt} - 48.03 \cdot \%V \tag{7.3}$$

From equation 7.3 it is visible that an increase of R_{corr} will increase the TTF, and an increase of *dx/dt* or water uptake *%V* will decrease the TTF. This equation contains several empirical constants based on measurements with mild steel under the same conditions. Other metals might have different constants and it is not entirely clear which other influences might have an impact on these measurements. By using other methods for the TTF estimation and a series of REAP measurements, the constants for other systems can be obtained. Collecting all this data requires time and effort. However, the values obtained from the equation above make it possible to compare two coatings measured under the same conditions even when they aren't applied to mild steel.

An intensive discussion of all the REAP aspects would exceed the frame of this handbook.
If a deeper understanding is required, we recommend looking at the already-mentioned publications:
ASTM G01.11 and Kending et al, J. Coatings Tech., 1996, 68, p. 39 – 47.

8 Coating Research in Food Industry

Coating for food storage containers or other objects that get in contact with food is important to prevent spoiling or contamination of the food, as well as, to protect the container itself from the corrosive properties of the food. Tins are still quite common as food containers because the food is protected from air and light for a long time. Tins are conducting surfaces, which allow electrochemical studies of themselves and their coatings.

In an ideal case, the expiration date stored in a food container can be predicted. Possible obstacles for prediction are the different reaction rates of the components in the food during spoiling, which are not always constant. Often the reaction rate is linear or a parable. Furthermore, the storage temperature might be different, for example, if the food is exported to different countries.

As discussed in previous chapters, a high polarization resistance or the resistance added by the coating means low corrosion of the can, which means a longer shelf life for the food contained in it. The resistance of the coating is also influenced by the temperature and the storing time. To make a proper prediction of the shelf life, measurements performed at different temperatures and storage times will be needed.

EIS, as a non-destructive technique with high sensitivity for interface changes, is a suitable method to investigate coatings for food cans. It is assumed that you are familiar with the principles explained in previous chapters.

Most coatings will have a behavior like an ideal coating directly after filling the can, which means that the matching equivalent circuit is a resistor and capacitor in series (see Figure 6.5). More complex behavior will be developed over time due to water penetrating the coating. If corrosion hasn't started, the EIS will look like a simplified Randles circuit (Figure 6.7). The serial resistor would stay the R_{sol}, but the charge transfer resistor R_{ct} would be replaced by the pore resistance R_{por} and the double layer capacity C_{dl} by the coating capacitance C_C. When the water reaches the metal interface, corrosion can appear. This situation is reflected by the equivalent circuit in Figure 8.1. Corrosion can lead to gas formation under the coating, leading to blisters and disbonding. If the blister is closed, the solution inside a blister can be quite different from the bulk solution. The corrosion reactions often lead to a low pH value.

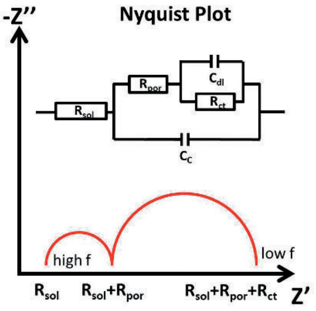


Figure 8.1 Equivalent circuit and Nyquist plot of a corroding coated surface.

8.1 Testing the Shelf Life

First cans are coated and packed as usual for your food products. The cans are divided into three groups and stored at three different temperatures, for example, 35 °C, 45 °C, and 55 °C. The cans are tested after certain periods, for example, 1 day, 1 week, 1 month, 4 months, and 12 months.

If the product in the can is conducting, the measurement can be performed in the product, which acts as an electrolyte. Otherwise, the product needs to be replaced with 0.5 M NaCl solution. Keep in mind that a fat or oil film on the can coating might act as an additional film, but there is also the possibility that strong detergents for removing the fat film will change your coating.

The can is connected as the working electrode to the potentiostat. The reference and counter electrode are immersed in the can's solution. Electrochemical Impedance Spectroscopy is performed and the spectra for the different storage times are compared. It is expected that R_{por} will decrease over time when the quality of the film decreases.

As stated previously there is a correlation between the quality of a coating and the rate of food spoiling. It seems there is a connection between the pore or coating resistance and the reaction rate *r* of the spoiling substances. The reaction rate *r* is defined as the negative change in the reactant's concentration. The change depends on the concentration of the reactant to the power of n and the reaction rate constant *k*. Common values for *n* are 0, 1, or 2 (see equation 8.1).

$$r = -\frac{dC}{dt} = -kC^n \tag{8.1}$$

Using the Power law, we can exchange the concentration C for the pore resistance R_{por} (Equation).

$$r = -\frac{dR_{por}}{dt} = -kR_{por}^n \tag{8.2}$$

If *n* and *k* are determined, the reaction rate after long periods can be extrapolated. Determining n and k is done best by transforming the differential equation for each of the three common *n* (0, 1, and 2) into a linear relationship. Sample data is plotted according to these linear relations and via a linear fit, it is determined which order fulfills best the linear criteria.
Solving the zero-order equation results in

$$R_{por} - R_{por}^0 = -kt \tag{8.3}$$

R^0_{por} is the pore resistance at day 0. If the difference between R_{por} and R^0_{por} is plotted versus the time *t* and a linear relationship is visible, the reaction is 0 order (*n* = 0) and the slope of this curve is $-k$.
The solution of the 1st order (*n* = 1) delivers

$$ln\left(\frac{R_{por}}{R_{por}^0}\right) = -kt \tag{8.4}$$

A plot of the ratio's logarithm versus the time t should deliver a linear curve with a slope of –*k* if the reaction is of 1st order. Analog to previous orders the 2nd order (*n* = 2) solution is

$$\frac{1}{R_{por}} - \frac{1}{R^0_{por}} = kt \quad (8.5)$$

In case the reaction is of 2nd order a plot of the inverse's difference versus the time *t* will deliver a linear curve, but this time the slope is k (not –k). The fit with the best correlation coefficient R^2 is made with the correct *n*. This way the reaction order as well as the reaction rate can be determined. With the values from the linear fit, the time t it takes to reach a certain R_{por} can be calculated. The linear fit result is described by equation 8.6.

$$y = ax + b \quad (8.6)$$

With the slope *a*, and the intercept *b*. If you keep in mind that for this case *x* is *t*, the equations needed to calculate *t* for the different *n* are:

n = 0

$$y = R_{por} - R^0_{por} = at + b \quad (8.7)$$

n = 1

$$y = ln\left(\frac{R_{por}}{R^0_{por}}\right) = at + b \quad (8.8)$$

n = 2

$$y = \frac{1}{R_{por}} - \frac{1}{R^0_{por}} = at + b \quad (8.9)$$

If the time *t*, where the can isn't acceptable anymore needs to be determined, a threshold value for R_{por} needs to be defined, for example, 300 Ω. With the R^0_{por} from the measurements and the afterward determined *n* and *k*, the time *t*, until the non-acceptable Rpor is reached, can be calculated. After a and b have been determined from the linear fit, the corresponding equation (8.7, 8.8, or 8.9) is rearranged for t.

With this method, the behavior over time for a fixed temperature can be predicted if several values at different points in time are known. If the reaction rates for multiple temperatures are known, the reaction rates and shelf lives for other temperatures can be extrapolated. However, the extrapolations are to be taken with a pinch of salt. Changing the temperature might change other factors that influence the reaction rate *k*.

Phase transitions can cause these changes, for example. In food packaging the glass transition is an important influence. Readers, who want to determine from reaction rate or pore resistance measurement the shelf life for a temperature that wasn't used in the measurements, should consult the corresponding literature.

9 Postface

This handbook was written to help corrosion researchers to enter the field of electrochemistry or help electrochemists to enter the field of corrosion research. This handbook cannot provide the depth necessary to understand corrosion processes in detail or analyze completely unknown processes. However, if there is a request for a deeper understanding, textbooks as well as white literature offer a broad knowledge and with the knowledge from this handbook, the literature should be easier to understand. We hope that we have provided a starting point for your electrochemical corrosion research and are looking forward to your successful products or publications.

Notes

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