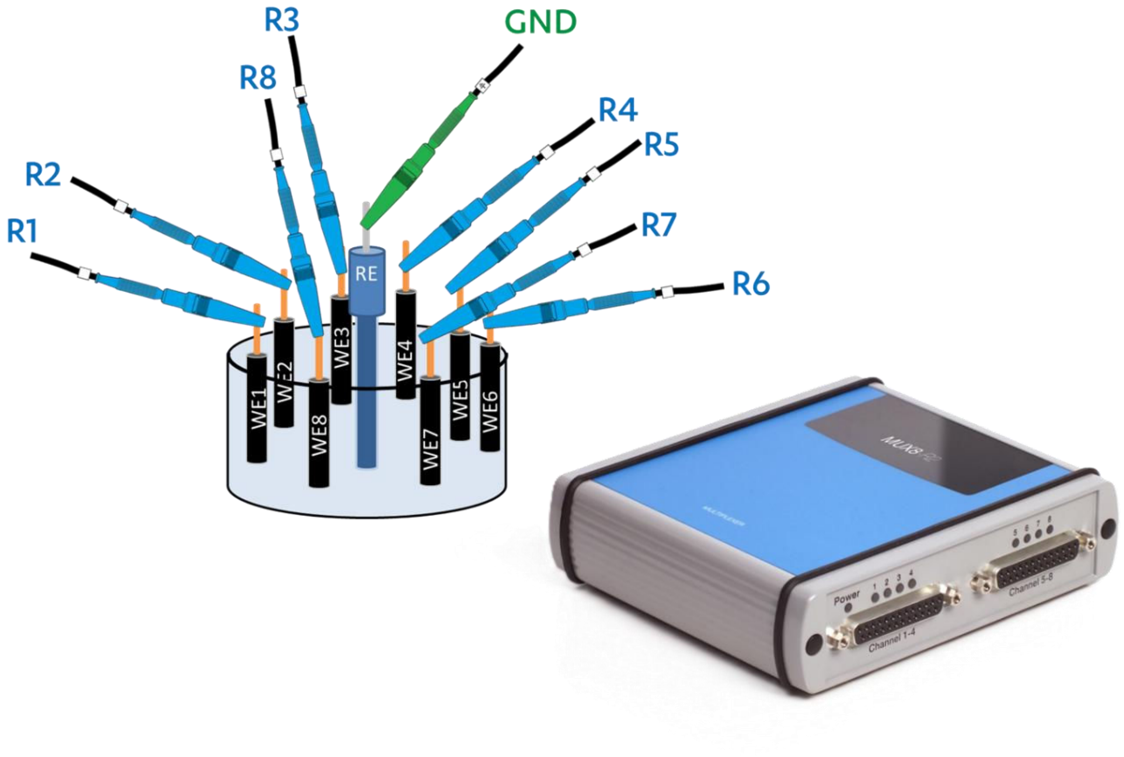
Open Circuit Potential measurements with a MUX8-R2



PalmSens

Application Note PSAN0401

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Contents

1 Open Circuit Potential

The Open Circuit Potential (OCP) or Open Circuit Voltage (OCV) is the potential between two points with no current flowing between the two points. Without an external potential source, this is usually the highest possible potential difference between these two points. If a current flows between these two points, the potential difference is reduced.

The OCP is often used to check if a system behaves as expected. In corrosion research the OCP of a sample is used to monitor the development of corrosion on the sample surface.

In general OCP measurements require high impedance measurement circuitry to avoid errors in the OCP due to leakage currents.

1.1 OCP of Galvanic Cell

To illustrate the OCP, we use the example of a Daniell Cell (see Figure 1). The setup is a galvanic cell consisting of two vessels. One vessel is filled with copper sulfate solution and a copper sheet is immersed in the solution. The other vessel contains zinc sulfate solution and a zinc sheet is immersed. The two vessels are connected via a salt bridge. The salt bridge is made of a salt, usually KCl, NaCl, K_2SO_4 or Na_2SO_4. If you measure the voltage between the two metal sheets, an OCP of 1.1 V under standard conditions is observed. The copper site is the nobler site, so the potential of the copper sheet is 1.1 V higher than the potential of the zinc sheet. If the two metal sheets are connected to each other so that electrons can flow between them, electrons will flow from the less noble zinc to the noble copper. As a result, the measured potential difference between the two metal sheets will decrease. As electrons are removed from the zinc sheet, zinc ions are generated into solution and the electrons of these ions replace the missing electrons in the zinc sheet. This results in a dissolution process of the zinc sheet. At the same time, the copper sheets gains mass by reducing copper ions. The rates of these processes, however, are not fast enough to maintain the original OCP. Finally, the salt bridge is necessary to maintain electro-neutrality in each compartment by promoting ion exchange.

A good analogy for the behavior of potentials and currents are connected vessels filled with different levels of water. The height difference of the water represents the potential and the water flowing from one vessel to another represents the current.

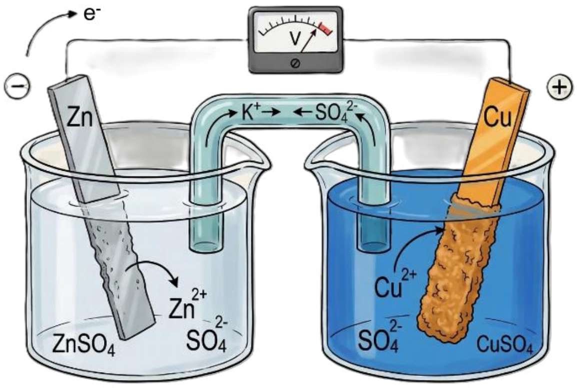


Figure 1 Illustration of the Daniell Cell

1.2 OCP in Analytical Chemistry

1.2.1 Chronopotentiometric Stripping

Chronopotentiometric Stripping is a technique where metal ions from the solution are reduced at the electrode. The metals formed from the ions adsorb to the electrodes surface. After this deposition, the OCP of the electrode is observed in the presence of an oxidation agent, e.g. oxygen. The least noble metal oxidizes first. During this oxidation process, the OCP stays approximately constant. If the metal is

used up, there will be a steep change of the OCP, because the first metal doesn't contribute to the OCP anymore. This way all immobilized metals get oxidized. In the resulting E vs t curve, the potential of a step correlate with the metal species and the step's width with the amount of immobilized metal.
For a better visualization you often find plots of dE/dt versus E, where the transitions between the different OCPs appear as peaks, whose height correlates with the amount of immobilized metal.

1.2.2 Ion Selective Electrodes

Ion selective electrodes (ISE) are electrodes whose OCP only depends on one ion species. The most common ISE is the pH electrode, which is sensitive to H^+ (protons). These electrodes allow measuring this specific ion without changing the solution, unlike amperometric sensors.

The Open Circuit Potential (OCP) is the potential between two points with no current flow

2 Multiplexers

Multiplexers are a great economic way to increase your efficiency. The MUX8-R2, MUX8, MUX16, EmStatMUX8, EmStatMUX16 and EmStatMUX8-R2 are multiplexer instruments made by PalmSens. While the first three are extensions for a PalmSens or an EmStat the latter are EmStats with an integrated multiplexer. The MUX8-R2 is the successor of the MUX8 and MUX16. The MUX8-R2 has a maximum of 8 cells, but the MUX8-R2 can be combined with another MUX8-R2 to create 16 cells. Actually, you can combine MUX8-R2s to up to 128 cells.
A multiplexer is like a multi-way switcher. One potentiostat is connected to this switcher and the switcher (the multiplexer) switches the connection of the potentiostat between the different channels. For most methods the switching is done after the experiment is finished (e.g. DPV, CV), but for time dependent methods like chronoamperometry (amperometric detection) or (open circuit) potentiometry the channel can be switched between each point of the measurement within a short interval of tens of milliseconds. This is we call **Alternate Mode**. Thus, virtually the measurement is done parallel. It doesn't matter if the electrode systems are in separated cells or share one solution, since only one set of reference electrode (RE), counter electrode (CE) and working electrode (WE) is active at a time.

A multiplexer is an economic solution to increase the efficiency of your sample throughput, but it never measures different electrodes at the exact same point in time.

3 Multiplexed OCP Measurements

3.1 Issues related to charge injection from switches

Multiplexing is an economical way to use arrays of small ion selective electrodes, but often such a setup does not deliver stable OCPs or it delivers unrealistic values. These issues are usually observed when the alternating mode of the potentiostat is used, that means the multiplexer changes the channel after a point of the measurement was recorded. If the consecutive mode is used, the results are fine. Consecutive mode means that the measurement is finished on one channel before the multiplexer switches to the next channel.

3.1.1 Why does it happen?

A multiplexer is a series of switches, which are used to connect the electrodes of the different channels to the lines of the potentiostat. Every time a switch is flicked a small charge is injected into the circuit. This is due to the moment when the switch isn't part of any circuit and thus isn't controlled by any feedback loop. At the moment the switch is closed the excess charge is injected into the measurement circuit. The charge injection is usually rather low (20 pC). However, if small electrodes or very sensitive electrodes are used, the charge injection could be sufficient to significantly change the potential of the electrode. In consecutive mode, there is only one switching event and afterwards the electrode has the whole measurement duration to re-establish its OCP. If the Alternate Mode is used, however, there are many switching events and very small time intervals for the measurement. As a result, the electrode gets a lot of charge injections and little time to stabilize its OCP. This often leads to artifact OCP measurements.

3.1.2 How to minimize the charge injection issue

To reduce the impact of the charge injection issue, the MUX8-R2 has high impedance input buffers in the reference electrode lines, which enable you to measure the OCP of small or sensitive electrodes in the alternating mode of the multiplexer. To make use this advantage, a special way to setup the measurement is required and described below.

3.2 Setting up an alternating multiplexed OCP measurement with MUX8-R2

The 8 reference electrode inputs have high impedance (>1TΩ for PalmSens4 and Emstat4 series) buffers to remove leakage and charge injection effects caused by the switches of the MUX. The working electrodes are low impedance as they connect directly to the multiplexer switches and subsequently to the current follower of the potentiostat. The current follower is necessary for any method, which requires measurement of the current flowing through the working electrode. To not obstruct this current, installing a high impedance buffer at the working electrode lines is not possible. Due to the current follower, the working electrode is not grounded, but is a virtual ground, with a potential close ground. The current follower has some inherent noise and leakage, which for most measurements is negligible, but not for sensitive OCP measurements.

For OCP experiments, the current is not measured so the current follower is unnecessary. This means that the WE leads are not required and can be disconnected. Instead of the WE leads, the ground lead, which is less noisy than the WE inputs, can be used. The ground cannot be multiplexed, so the shared reference electrode, which doesn't need to be multiplexed, can be connected to the ground lead.

As mentioned in the introduction of chapter 3, the reference electrode leads have high impedance inputs which deserve as buffers for the charge injections and the reference electrode leads can be multiplexed, so these can be used instead of the WE leads to connect the working electrodes (see **Error! Reference source not found.**).

No potential is applied and no current flows by the potentiostat, so the counter electrode is not needed. We recommend leaving it disconnected.

This setup has the lowest noise possible for OCP measurements, because it has a simpler connection with less circuitry and the high impedance input buffers are included on each electrode. As a side effect, the polarity of the measured OCP is inverted, because the ground is now the reference electrode and the working electrode connected to the reference electrode leads.

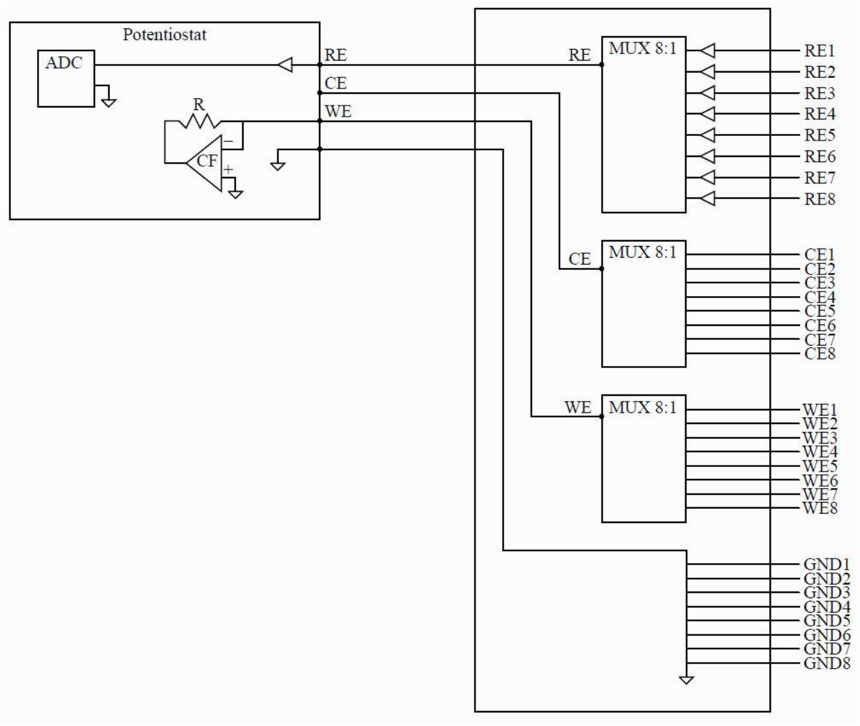


Figure 2 Schematic representation of the PalmSens4 and MUX8-R2

3.2.1 Step by Step Connection

1. Place your reference electrode and the working electrodes in your cell.
2. Connect a ground lead (green plug) to the reference electrode.
3. Connect the reference electrode lead of channel 1 (blue plug) to your working electrode 1. Connect the reference electrode lead of channel 2 (blue plug) to your working electrode 2 and so on (see Figure 4).
4. Leave the working electrode leads (red plugs) and the counter electrode leads (black plugs) open.
5. If you are using a Faraday cage, connect another ground lead to it. As all the ground leads are connected to the instrument ground, the channel number of the lead is irrelevant.

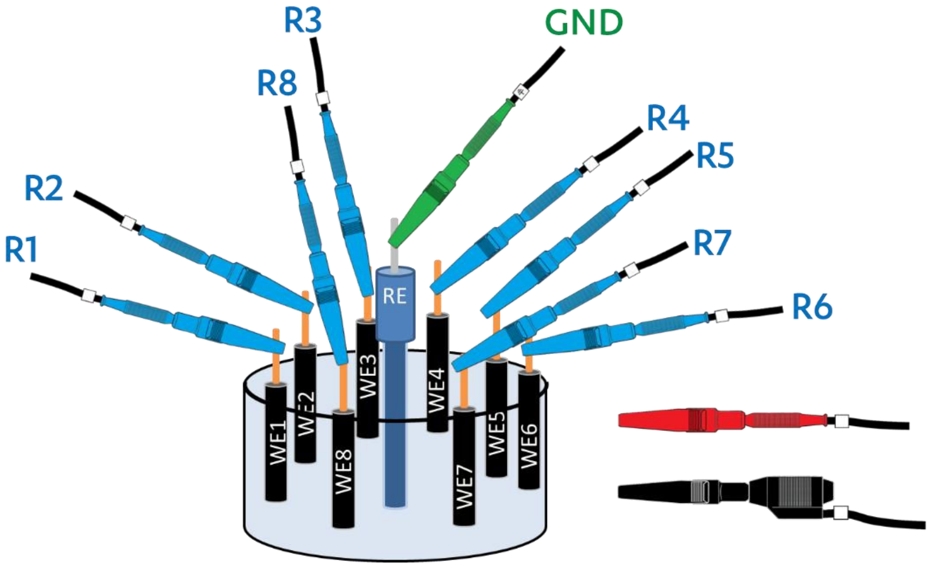


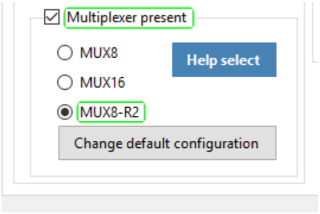
Figure 3 Scheme of the setup for the OCP measurement

3.3 Performing an alternating multiplexed OCP measurement with MUX8-R2

For performing the measurement you can run a regular multiplexed OCP measurement. The mode is *Alternating*. You should **not** check the Option to *Use the common RE and CE of channel 1*. The reference electrode leads are connected to the electrodes with the individual OCPs, so the reference electrodes shouldn't be connected to each other. If you choose the option to *Use the common RE and CE of channel 1,* all the reference electrode leads are connected to each other. If you use an EmStat3+ Blue, you need also to check the option *Connect WE to Sense*.
As the working electrode leads are not important for this measurement and the ground is used as reference potential, the unselected working electrode leads should stay floating and not be connected to the ground.

3.3.1 Step by Step Measurement

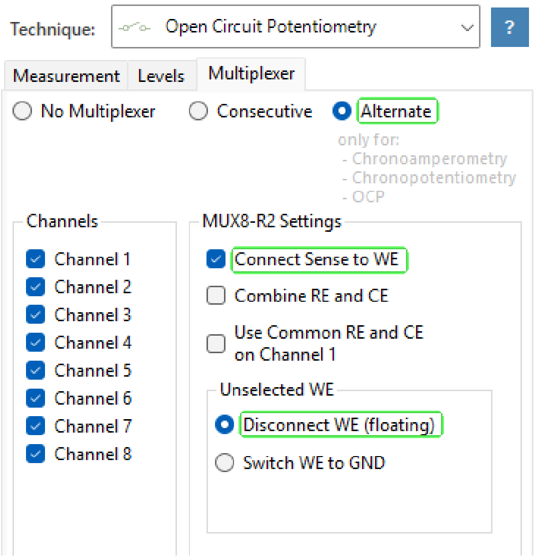
1. Setup your measurement according to chapter 3.2.1.
2. Start *PSTrace* and open the *General Settings…* menu.
3. Check Multiplexer present and choose the MUX8-R2 (see Figure 4).



☑ Multiplexer present
○ MUX8
○ MUX16
● MUX8-R2

Figure 4 Multiplexer presence in General Settings

4. Click on Change default configuration and make sure the boxes, *Combine RE and CE*, *Use common RE and CE on channel1* are **not** checked. The option *Disconnect WE (floating)* for *unselected WEs* should be chosen. If your system features Sense leads, check the option *Connect Sense to WE* (see Figure 5).



Technique: Open Circuit Potentiometry

○ No Multiplexer ○ Consecutive ● Alternate

only for:
- Chronoamperometry
- Chronopotentiometry
- OCP

Channels

☑ Channel 1
☑ Channel 2
☑ Channel 3
☑ Channel 4
☑ Channel 5
☑ Channel 6
☑ Channel 7
☑ Channel 8

MUX8-R2 Settings

☑ Connect Sense to WE
☐ Combine RE and CE
☐ Use Common RE and CE on Channel 1

Unselected WE

● Disconnect WE (floating)
○ Switch WE to GND

Figure 5 Alternate Mode settings

5. Click on *Save & Close* and then *OK* in the Settings window.
6. Choose *Open Circuit Potentiometry* from the Techniques List and activate all current ranges.
7. Set the measurement time (*t run*) and the interval time (*t interval*) according to your experiment. Also change other settings like recording additional data, pretreatment, etc., if needed.
8. Run the measurement.
9. **Pay attention**: The polarization of the measured potential is inversed, that means positive potentials will be negative and the other way around, due to the fact that the working electrode is connected to the RE lead.

4 Results Comparison

Here is an example of measurements performed with a MUX8-R2 in the regular setup (WE leads connected to working electrodes, RE leads connected to RE) and the same measurement performed with the above described setup.

In a 0.1 M KCl solution an Ag/AgCl reference electrode, a platinum wire, a copper wire, a solder tin wire and a straightened paper clip were immersed. These where first connected in a classic way, i.e. the Ag/AgCl electrode was connected to the RE1 and the platinum, copper, paper clip and solder tin were connected to WE1, WE2, WE3 and WE4. The option *Use common RE and CE on channel 1* was checked. The unselected WEs were floating. After a stable potential for each of the channels was reached a measurement in the *Consecutive* mode was performed. Afterwards a measurement in the *Alternating* mode was performed.

The results show clearly the impact of the charge injection (see Figure 6).

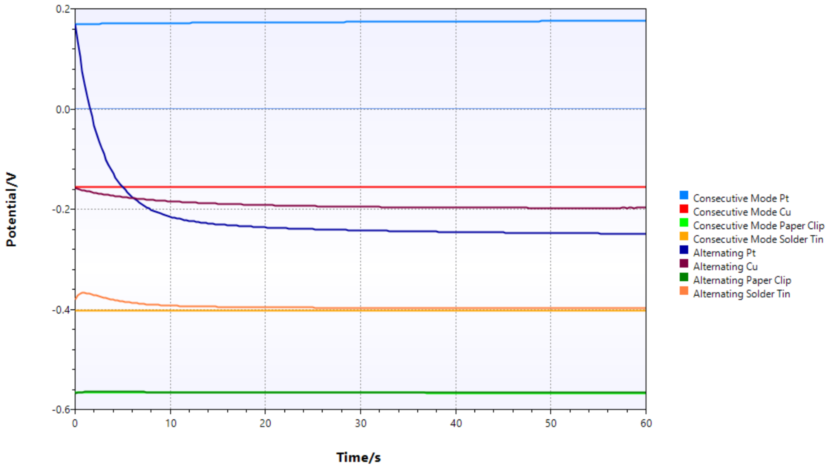


Figure 6 OCP measurements in a classic setup (RE blue plug, WE red plug); samples: platinum wire, copper wire, straightened paper clip and solder tin in 0.1 M KCl solution

Keeping in mind that in the Consecutive mode a single charge injection event takes place at the beginning of the measurement and in the Alternating mode a charge injection happens before every point of the measurement, it is clear that the OCP of noble metals changes due to the charge injections, because there are almost no ions to buffer a charge injection. Other less noble materials regain their OCP more easily due to their own oxidation or reduction. It is clearly visible that even a small charge injection under certain conditions can lead to a big impact on your measurement. If the setup described in chapter 3.2 is used the results look quite different (seeFigure 7).
It is important to notice, that due to the setup the OCP's polarity is inversed. So the potential of the Cu wire is around -160 mV in the classic setup and 160 mV in the here recommended setup.
In Figure 7 you see that the measurements for the Consecutive and Alternating mode of the multiplexer coincide. This shows how the charge injections are buffered and leakage or other noise is reduced.

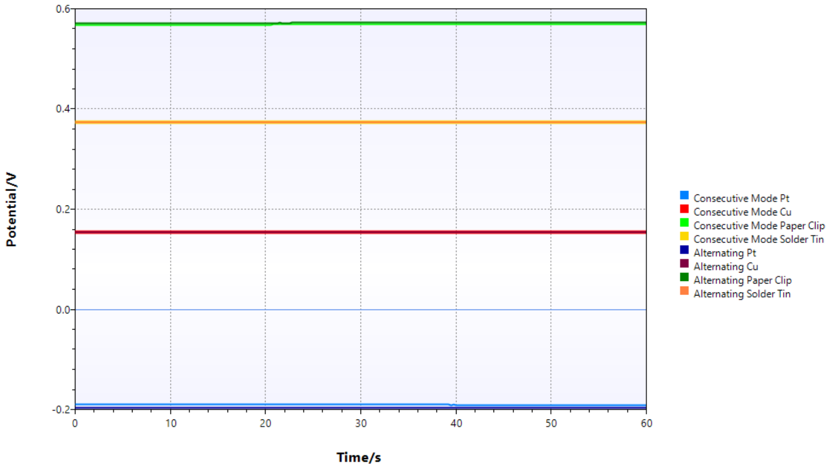


Figure 7 OCP measurements in the setup described in chapter 3.1 (RE green plug, WE blue plug); samples: platinum wire, copper wire, straightened paper clip and solder tin in 0.1 M KCl solution

5 Take Home Message

This application note explains how to do an optimal setup for Open Circuit Potentiometry using the multiplexer MUX8-R2. Furthermore, the goal of this application is to create an understanding why this setup can deliver better results than the conventional setup.