Multiple Working Electrodes in the Same Cell

Make your multi-channel potentiostat work as a polypotentiostat

PalmSens

Application Note PSAN0408

www.palmsens.com

Contents

1 Introduction

There are different ways to perform multiple measurements in parallel. Our products include multiplexers (MUX8-R2), bipotentiostats (PalmSens4 with BiPot), and multi-channel potentiostats (MultiPalmSens4, MultiEmStat4). All these instruments increase your efficiency, but the optimal instrument for one experiment might not be a suitable option for another experiment.
A general introduction to the different devices for parallel measurements is already available in our knowledge base. In this application note, the focus is on multi-channel devices being used for measurements with multiple working electrodes in one cell.

This application note explains how to use a PalmSens multi-channel potentiostat and as polypotentiostat

2 How Galvanic Isolation affects a multi-channel potentiostat

A multi-channel potentiostat is a collection of independent potentiostats in one chassis. We offer these systems with or without Galvanic Isolation (GI).
For most PalmSens multi-potentiostats, including MultiPalmSens4 and MultiEmStat4, the WE (Working Electrode lead) and the GND (ground lead) are internally linked, meaning they share the same potential. This characteristic has implications, depending on whether the system has GI or not.

- Non-GI systems: Each independent potentiostat shares the same ground. This means the potentials of the WEs are forced to the same level. In principle, this has no effect when working with separate samples, since the potentials between individual samples do not matter. However, because all WEs are at the same potential, shielding is easier. You can place all samples inside the same Faraday cage, connect the cage to a single GND, and all samples will be shielded.
- GI systems: The channels do not share the same ground. Therefore, the ground potentials of the channels float relative to each other. As a result, the WE potentials can also float relative to one another. This allows CE and RE leads from different channels to be combined on the same electrodes. The WE potentials can then be controlled independently.

Therefore, the GI capability is highly recommended if you need to connect two or more channels to electrodes in the same electrochemical cell (cell array). If you have a non-GI system, refer to the alternative option described in Chapter 4, limited to some techniques and Simultaneous mode.
If you have a GI system, make sure that the GND leads (green) remain disconnected from each other to maintain the GI capability. It is recommended to protect unused leads with the provided croc clips to prevent accidental contact.
Merging the GNDs will cancel the GI capability between those channels. If you intentionally merge the ground leads to convert the system to non-GI, use a star-point connection to ensure proper ground merging.

The Galvanic Isolation is an optional feature when you order a multi-channel potentiostat from PalmSens

Note that the Galvanic Isolation is an optional feature when ordering a multi-channel potentiostat from PalmSens. To check whether your device has GI:

- Since 2026 multi-channel devices end their serial umber with “G1” if GI is present and “G0” if not.
- For the MultiPalmSens4, check if Galvanic Isolation is set to “Yes” on the configuration card
- You can always verify on your invoice whether the GI option was ordered

If you have any doubts, contact info@palmsens.com, provide the serial number of your device, and ask whether your device has GI.
Refer to Galvanic Isolation in Applications for more information about GI.

3 Polypotentiostat setup for systems with Galvanic Isolation

This setup allows you to use a multi-channel potentiostat as a polypotentiostat. It is possible to use different techniques at the different working electrodes at the same or even at different times. You can use this setup to perform the same technique at all channels as well. Galvanic isolation is a requirement. With Galvanic Isolation the channels don't share a fixed reference point. As a result, the potentiostats of the different channels can share the same reference and counter electrodes. They will just apply the required potential difference between the working and reference electrode without interference from the other channels. If the working electrodes were fixed on a common potential, the reference and counter electrode couldn't be adjusted by all channels to different potential differences.
For Galvanically Isolated systems hardware synchronization is not required, as each channel can control its potential independently and switch freely between measurement states. However, if synchronization is needed for a specific application, enabling hardware synchronization should not affect the measurement results.

3.1 Available techniques

All techniques supported by your potentiostat model are available in this setup.
You can use it in both Individual and Simultaneous mode, whether you want to run different techniques on each channel or the same technique across multiple channels, respectively.

3.2 Experimental setup

Connect the Reference Electrode (RE) plug (blue) of all channels you intend to use to the reference electrode in your cell array.
Connect the Counter Electrode (CE) plug (black) of all channels you intend to use to the counter electrode in your cell array. This means there will be multiple connections to these two electrodes.
Connect each working electrode to the WE lead (red) of a different channel. For example, connect the WE plug of channel 1 to the working electrode assigned to channel 1. Then connect the WE plug of channel 2 to the working electrode assigned to channel 2, and so on.
If your device features a Sense lead (i.e. MultiEmStat4 HR and Nexus), connect it along with the WE.
This setup can also be applied to more than one cell array. See the scheme in Figure 1.

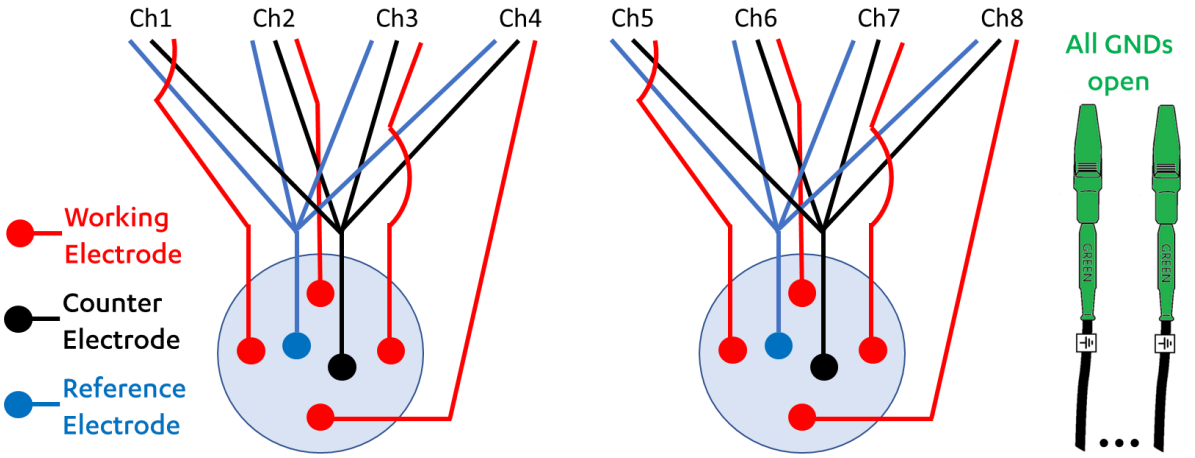

Figure 1 Connection scheme for 2 cell arrays each with 4 WEs (galvanic isolation required). All ground leads must be disconnected to ensure the GI capability.

PalmSens cell cables come with stackable CE leads. This makes it easy to merge multiple CE leads. However, the RE leads are not stackable, so they must be merged in a different way. See Figure 2 for an example.

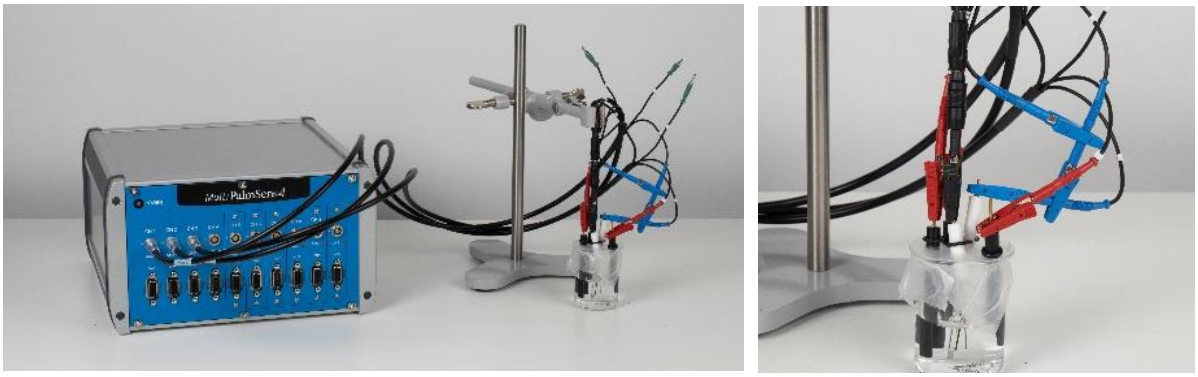

Figure 2 MultiPalmSens4 set up for 3 working electrodes in the same cell (galvanic isolation required)

Turn on your multi-channel potentiostat, start MultiTrace, wait until your potentiostat is detected, and choose the Simultaneous or Individual mode as usual. If you have any doubts about MultiTrace software, refer to its manual (hit F1 on the software window).

3.3 Limitations

The above-described principle of the measurement means that the current through the counter electrode is the sum of all working electrode currents. While each potentiostat channel can drive its current, that current needs to flow at the counter electrode interface. For example, 10 mA flows through channel 1, and 10 mA flows through channel 2. That means 20 mA flow through the counter electrode interface. For that reason, we recommend using a counter electrode with a large electrochemical surface area.
Compared to single-channel measurements, slightly higher noise can be observed during parallel measurements, especially for EIS. One channel can induce noise in other channels. Test measurements have so far shown only a small increase in noise during chronoamperometry (see Figure 3 left). In EIS, some additional stray capacitance can be observed at high frequencies (see Figure 3 right). This capacitance is likely caused by the presence of additional cables and clips, which increase capacitance at high frequencies.

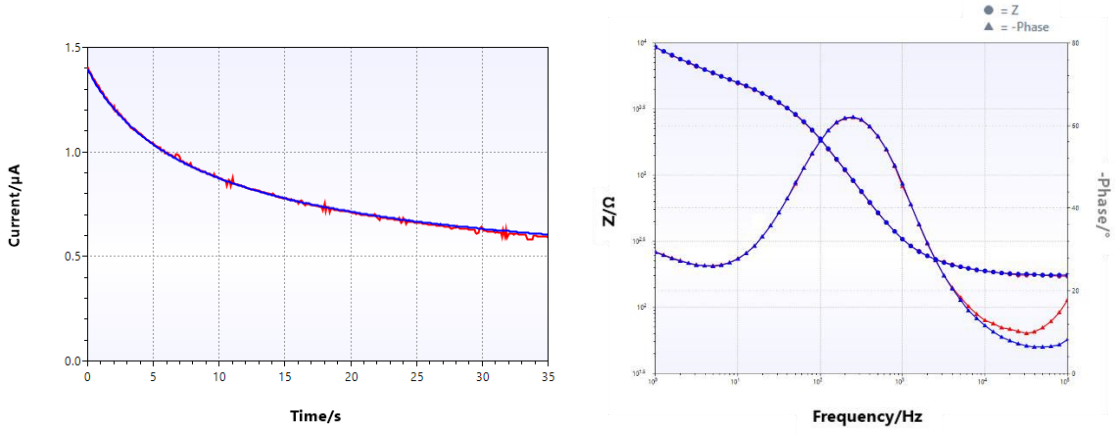

Figure 3 Chronoamperometry (left) and EIS (right) measured consecutive (blue) and parallel (red)

4 Polypotentiostat setup for systems without Galvanic Isolation

This setup allows you to run only the same technique at the same time with multiple working electrodes in the same cell. Use the Simultaneous Mode in MultiTrace.

The MultiPalmSens4, MultiEmStat4, and Nexus offer the option to synchronize the channels. This expands the list of techniques available in this configuration compared to the MultiEmStat3(+).

The use of non-GI systems with multiple working electrodes in the same cell is limited to the same technique at the same time (simultaneous mode)

4.1 Available techniques

The setup described in this chapter allows only a limited number of techniques to be used simultaneously with multiple working electrodes. The hardware synchronization feature enables many more techniques in this configuration. All available techniques are listed in Table 1.

Table 1 Available techniques for multiple electrodes in the same cell for systems without galvanic isolation

Technique	MultiPalmSens4, MultiEmStat4 and Nexus (hardware synchronized)	MultiEmStat3(+)
Linear Sweep Voltammetry	✓	✓
Differential Pulse Voltammetry	✓	
Square Wave Voltammetry	✓	
Normal Pulse Voltammetry	✓	
AC Voltammetry	✓	
Cyclic Voltammetry	✓	✓
Chronopotentiometric Stripping		
Chronoamperometry	✓	✓
Pulsed Amperometric Detection	✓	
Chronopotentiometry		
Multiple Pulsed Amperometric Detection	✓	
Linear sweep potentiometry		

4.2 Experimental setup

Connect the Reference Electrode (RE) plug (blue) and the Counter Electrode (CE) plug (black) of channel 1 to the reference and counter electrode in your cell.
For channel 2, connect the Reference Electrode (RE) plug (blue) to the Counter Electrode (CE) plug (black) of the same channel.
For channel 3, connect the RE plug (blue) to the CE plug (black) of that channel. Continue in this way until all channels you want to use in this measurement have their RE plug connected to their own CE plug (see Figure 4).
If your device features a Sense lead (i.e. MultiEmStat4 HR and Nexus), connect it along with the WE.

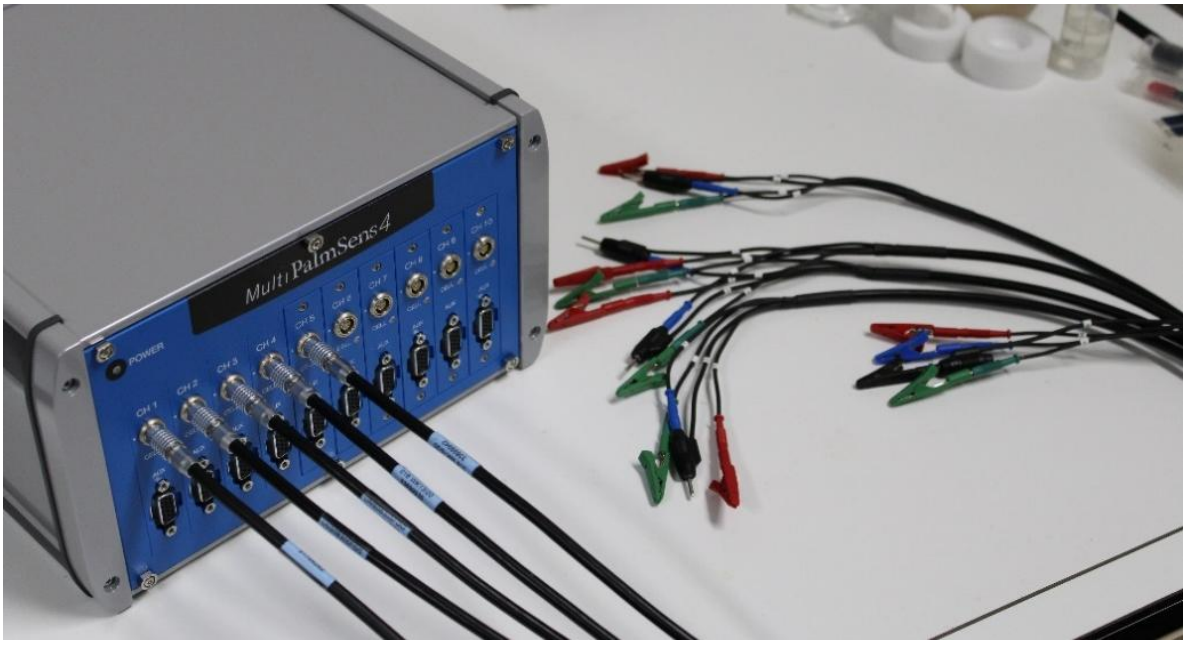

Figure 4 MultiPalmSens4 with reference and counter electrode leads for each channel connected to each other except for channel 1

Next, connect the working electrode plugs (red) to the working electrodes in your cell. For example, connect the working electrode plug of channel 1 to the working electrode assigned to channel 1, the working electrode plug of channel 2 to the working electrode assigned to channel 2, and so on. This setup can also be applied to more than one cell array. See the scheme in Figure 5. Figure 6 shows an example of how electrochemical cells are connected.

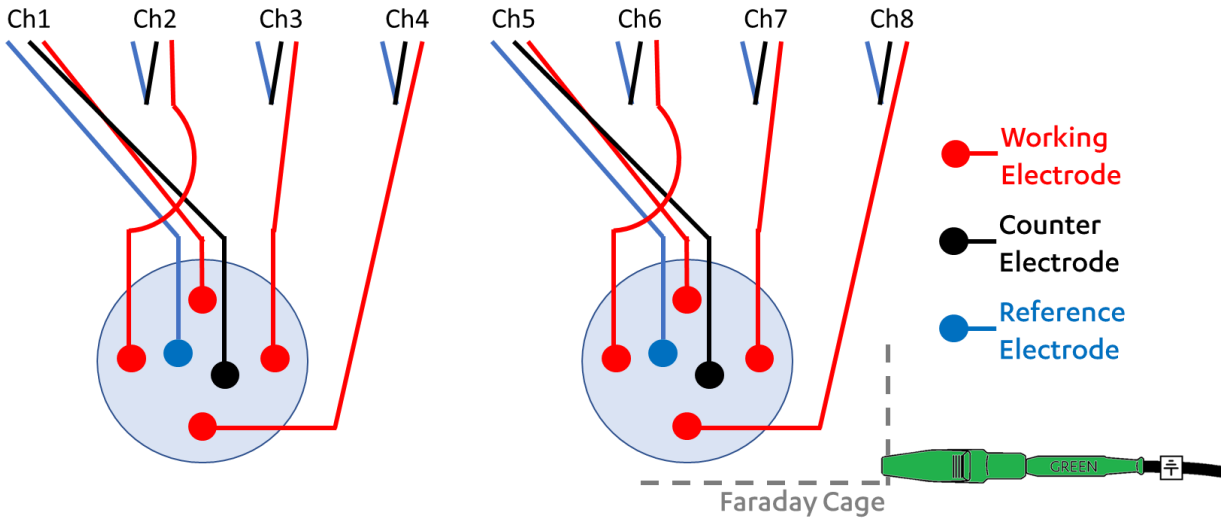

Figure 5 Connection scheme for 2 cells each with 4 WEs (no galvanic isolation present). You can connect just one ground lead to a Faraday cage if applicable. The rest of the ground leads can remain disconnected.

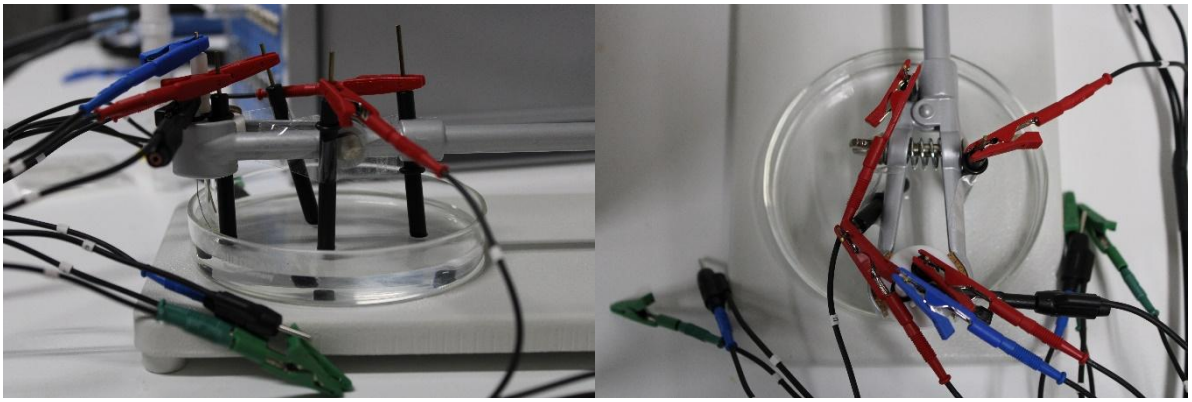

Figure 6 A setup with 4 working electrodes, 1 reference electrode, and 1 counter electrode (left side view, right top view)

Switch on the multi-channel potentiostat and start MultiTrace. Wait until the potentiostat is detected, then select Simultaneous mode. Activate the channels you have prepared (green highlight). Channel 1 must be active.
If you are using MultiPalmSens4, MultiEmStat4 or Nexus, check the box Enable hardware synchronization (see Figure 7) in the channel selection window.

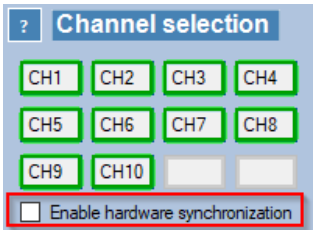

Figure 7 Checkbox to enable the synchronization

Select the method you want to perform and adjust the parameters or load a method file as you would for any other experiment. Start the experiment as usual. If you have any doubts about MultiTrace software, refer to its manual (hit F1 on the software window).

4.3 Principle of the above-described setup

A polypotentiostat and a multi-channel device are two different instruments that operate differently. However, with the setup described in this application note, a multi-channel device can be used as a polypotentiostat. The reason this works is often counterintuitive for electrochemists.
For the instrument, the working electrode is at ground potential, or more precisely at virtual ground potential. This is close to ground potential, but not exactly the same. The potential difference in the cell is achieved by controlling the potential of the reference and counter electrode.
The described setup makes use of this principle. All working electrodes share the same potential. The potential of the common reference electrode is set relative to working electrode 1. As a result, all working electrodes have the same potential difference relative to the reference electrode.
Therefore, the working electrodes of the additional channels can only perform the same technique with the same parameters as the working electrode of channel 1.
Since the additional working electrodes passively follow working electrode 1, the timing of data acquisition on each channel must exactly match that of channel 1. The synchronization feature in the MultiPalmSens4, MultiEmStat4 and Nexus ensures that all channels receiving the command to measure, measure each measurement point at exactly the same time.
The total current flowing through all working electrodes must pass through the single counter electrode.

4.4 Limitations

The above-described principle of the measurement means that the current through the counter electrode is the sum of all working electrode currents. The counter electrode is part of a single channel of a multi-potentiostat. For example, the maximum current for each MultiPalmSens4 channel is 30 mA. As a result, the sum of currents at the working electrodes must not exceed 30 mA.

Another limitation is that the additional working electrodes can only passively follow the working electrode 1. They cannot have an independent potential.

The MultiEmStat3 or MultiEmStat3+ do not feature hardware synchronization. This means when the software sends out the command to run a measurement each channel will prepare for the measurement and start it. This results in some time delay between the channels.

If you use the method described in chapter 4.2, the applied potential and the timing for recording might not match perfectly. This is not a problem for techniques with constant potential like chronoamperometry. Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) usually work well, but there will be a small shift in the potential especially for slow scan rate and/or large number of cycles.

The delay between channels is typically about 100 ms (depending on your computer's performance) and this is especially critical for pulsed techniques (Square Wave Voltammetry (SWV), Differential Pulse Voltammetry (DPV), Normal Pulse Voltammetry (NPV)). These techniques depend on very precise timing. The time delay leads to a timing issue while recording the values, which will result in plots with curves that are complete artifacts.

If you need to use pulsed techniques with multiple working electrodes in the same cell, hardware synchronization is required. Alternatively, you can use a multi-channel with galvanic isolation (see chapter 3).