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Application Note

1 Introduction

There are a couple of 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 article allows you to use the MultiPalmSens4 and MultiEmStat as both, multi-channel potentiostats and polypotentiostats.

2 Regular ways of operating a multi-channel potentiostat

The MultiPalmSens4 and the MultiEmStat4 are both a collection of independent potentiostats in one chassis. Each independent potentiostat is sharing the same ground. This means you can use the different channels of a MultiPalmSens4 or MultiEmStat4 in different electrochemical cells, which are independent of each other. The channels can perform different or the same methods at different times or at the same time.
In a MultiPalmSens4 or MultiEmStat4 with galvanic isolation, the channels do not share the same ground. The boards are all floating. Due to this, the different channels can be used in the same electrochemical cell, but each channel needs its own working, counter, and reference electrode. This is explained in our document Galvanic Isolation in Applications.

3 Same technique at the same time

The first setup discussed here allows performing the same technique at the same time with multiple working electrodes in the same cell. This setup is suitable for multi-channel devices without galvanic isolation, which includes the MultiPalmSens4, MultiEmStat3(+) and MultiEmStat4. However, the MultiPalmSens4 and MultiEmStat4 offer the option to synchronize the channels, which expands its list of techniques that are available in this configuration compared to the MultiEmStat3(+).
If you want to perform the same technique at the same time with a multi-channel device that has galvanic isolation, you can find a solution for that in chapter 3.3.

3.1 Available techniques

The setup described in the following chapter allows a limited number of techniques to be used at the same time by multiple working electrodes. By enabling the MultiPalmSens4's or MultiEmStat4's synchronization of the channels significantly more techniques become available with these instruments than the MultiEmStat3(+). All the available techniques are listed in Table 1.

Table 1 Available techniques for measurement setup without galvanic isolation

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

For all the techniques listed above the MultiPalmSens4 and MultiEmStat4 can be used as a polypotentiostat with one reference, one counter, and multiple working electrodes. All the electrodes can only perform the same method with the same parameters.

3.2 How to setup multi-channel potentiostat without galvanic isolation as a polypotentiostat

Connect the reference electrode plug (blue) and counter electrode plug (black) of channel 1 to the reference and counter electrode in your cell.
Connect the reference electrode plug (blue) of channel 2 to the counter electrode plug (black) of channel 2. Connect the reference electrode plug (blue) of channel 3 to the counter electrode plug (black) of channel 3. Go on like this until all channels, which you want to use during this measurement, have their reference electrode plug connected to their counter electrode plug (see Figure 1).

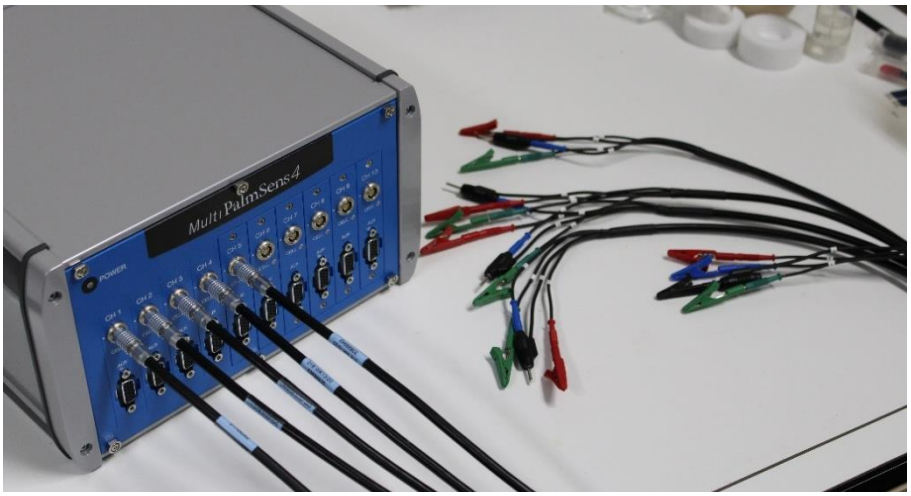

Figure 1 MultiPalmSens4 with reference and counter electrode leads for each channel connected to each other except for channel 1

Connect the working electrode plugs (red) to your working electrodes in the cell. This means the working electrode plug of channel 1 to the working electrode you want to be channel 1. The working electrode plug of channel 2 to the working electrode you want to be channel 2 and so on (see Figure 2).
Switch the multi-channel potentiostat on, start MultiTrace, wait until your potentiostat is detected, and choose the *Simultaneous mode*. Choose the channels that you have prepared as active (green highlight). Channel 1 must be active. If you are using a MultiPalmSens4 or MultiEmstat4, check the box *Enable hardware synchronization* (see Figure 3) under the channel selection. Select the method you want to perform and adjust the parameters or load a method file, just like you would for any other experiment.
Start the experiment, all active channels will perform the same experiment in the same cell.

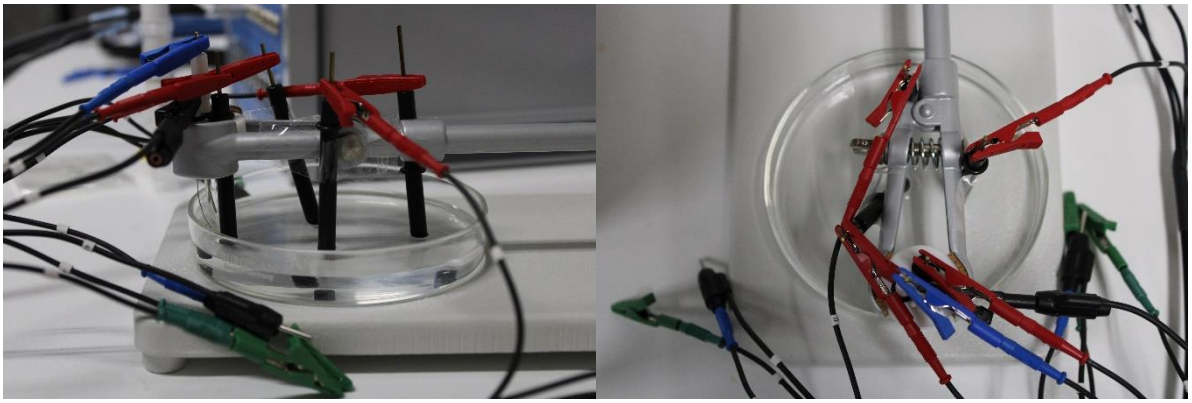

Figure 2 A setup with 4 working electrodes, 1 reference electrode, and 1 counter electrode (left side view, right top view)

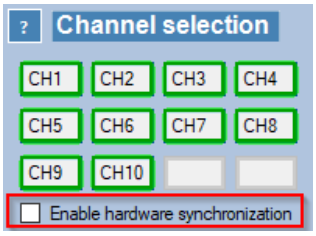

Figure 3 Checkbox to enable the synchronization

3.3 What if the multi-channel has galvanic isolation?

There are two options if your multi-channel potentiostat has galvanic isolation. You can use the setup described in chapter 4.2 or you can use the setup described in chapter 3.2 with one additional step (described below).
All the boards in chapter 3.2's setup need to share the same ground. An easy way to achieve this is to connect all the green plugs or clips of all the channels to your Faraday cage. We recommend placing all connections close to the same spot to avoid ground loops. The ground connection of the MultiPalmSens4's and MultiEmStat4's housing can also be added to the other ground connections, which will turn the housing into a Faraday cage for the boards inside.
If you are not using a Faraday cage, use another conducting object to connect all the grounds to each other.

3.4 Multiple Cells with Multiple Working Electrodes

It is possible to distribute the channels in multiple cells with the setup described above. Each cell needs one channel which has all three electrodes (working, counter, and reference electrode) connected. This channel will determine the potential of the other working electrodes present in this cell. As described above all the channels that will provide an additional working electrode for a cell need the reference and counter electrode connected to each other. Just as a reminder: the reference electrode of one channel is connected to the counter electrode of the same channel. Do not mix the reference and counter electrodes from different channels.
Then you just connect the prepared channels as extra working electrodes.
For example, you could connect channel 1 with all 3 electrodes (WE, CE, and RE) in a cell and connect channels 2 to 4 as extra working electrodes. Channel 5 would again use all 3 electrodes (WE, CE, and RE) in a physically separated cell and use channels 6 to 8 as four extra working electrodes. This way two cells with each four working electrodes are set up (see Figure 4).
All channels start their measurements exactly at the same time. This is only possible if the main channel is channel 1 and you need to use the Simultaneous Mode of MultiTrace, as a result, all your cells perform the same technique at the same time.

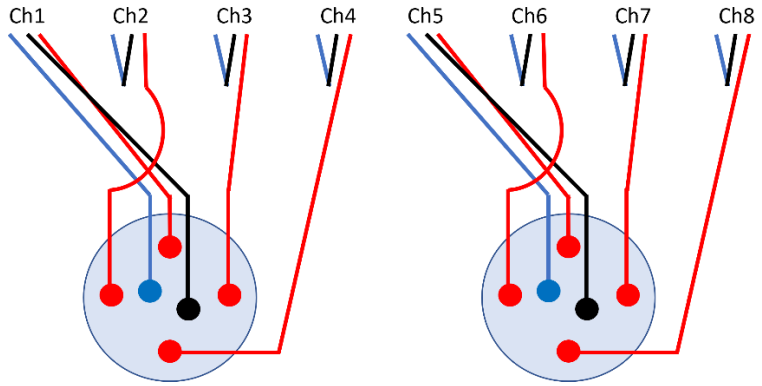

Figure 4 Connection scheme for 2 cells each with 4 WEs (no galvanic isolation present)

3.5 Principle of the above-described setup

A polypotentiostat and a multi-channel device are two different devices that operate differently, but you can, with the setup described in chapter 3.2, use a multi-channel as polypotentiostat. The reason this works is quite counterintuitive for most electrochemists.
The working electrode is at ground potential for the instrument, or more precisely virtual ground potential, which is close to ground potential but not exactly the same. The potential difference in your cell is actually achieved by controlling the potential of the reference and counter electrode.

This is exploited in this setup. All the working electrodes have the same potential. The potential of the reference electrode is set compared to working electrode 1. This means all working electrodes have this potential difference compared to the reference electrode.
Thus, the working electrodes of the additional channels perform the same technique with the same parameters as the working electrode of channel 1.
Because the working electrodes just passively follow working electrode 1, the timing for recording values at each channel must precisely match the working electrode of channel 1. The synchronization in the MultiPalmSens4 and MultiEmStat4 will make sure all channels, that receive a command to run a measurement at the same time, will start exactly at the same time.
The sum of the currents, which flows through all the working electrodes, must flow through the one counter electrode.

3.6 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 MultiPalmSens4, MultiEmStat4, or MultiEmStat3(+). For example, the maximum current for a 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 have the synchronization option like the MultiPalmSens4 and MultiEmStat4. 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 a small time delay between the channels.
If you use the method described in chapter 3.2, the applied potential and the timing for recording might not match perfectly. This is no problem for techniques with constant potential like chronoamperometry. Potential sweeps during linear sweep voltammetry (LSV) and cyclic voltammetry (CV) will be no issue as well, but there will be a small shift in the potential depending on the scan rate.
This delay is around 100 ms (depending on your computer's performance) and is especially critical for pulsed techniques. Square wave voltammetry (SWV), differential pulse voltammetry (DPV), normal pulse voltammetry (NPV), etc. rely on very precise timing. The time delay leads to a timing issue during recording the values, which will result in plots with curves that are complete artifacts.
If you want to use pulsed techniques with multiple working electrodes in the same cell a MultiPalmSens4 or MultiEmStat4 is required. Or you could use a multi-channel with galvanic isolation (see next chapter).

4 Different techniques at the same time

The second setup that allows you to use a multi-channel potentiostat as a polypotentiostat enables you 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, too. However, the channel synchronization of the MultiPalmSens4 is not available, but that should be no issue.
Galvanic isolation is a requirement. All multi-channel potentiostats that have galvanic isolation are suitable for this setup.
Galvanic isolation is an optional feature when you order a MultiPalmSens4, MultiEmStat4, or MultiEmStat3(+). Check if the serial number of the device ends on GI (MultiEmStat3(+)) or if galvanic isolation is set to *Yes* on your yellow configuration card (MultiPalmSens4).

4.1 Available techniques

All techniques supported by your potentiostat are available in this setup.

4.2 How to setup multi-channel potentiostat with galvanic isolation as a polypotentiostat

Connect the reference electrode plug (blue) of all channels you intend to use to the reference electrode in your cell. Connect the counter electrode plug (black) of all channels you intend to use to the counter electrode in your cell. This means there will be many connections to these two electrodes.
Each working electrode is connected to the working electrode plug (red) of a different channel. This means the working electrode plug of channel 1 to the working electrode you want to be channel 1. The working electrode plug of channel 2 to the working electrode you want to be channel 2 and so on.

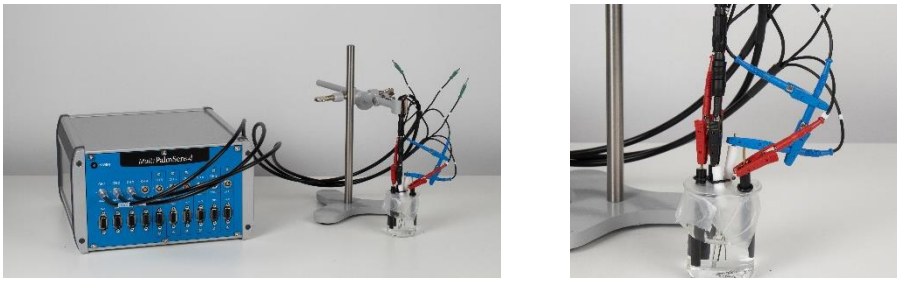

Figure 5 MultiPalmSens4 with galvanic isolation set up for 3 working electrodes in the same cell

Switch the multi-channel potentiostat on, start MultiTrace, wait until your potentiostat is detected, and choose the *Individual mode*.
In the following window, you can choose for each channel the method or script you want to use as usual. You can then start all channels at the same time or at different times.

4.3 Multiple Cells with Multiple Working Electrodes

It is also possible not to use all the channels in one cell with the setup described above. You can use multiple cells with multiple working electrodes. As described above, connect the reference and counter electrode connections to the reference electrode and counter electrode in the same cell where you want to use the working electrode.
For example, you could connect channels 1 to 5 each with all 3 electrodes (WE, CE, and RE) in one cell and channel 6 to 10 in a physically separated cell This way two cells with each five working electrodes are set up. Just connect the reference electrode plugs (blue) from channel 1 to 5 to the reference electrode in the first cell and the counter electrode plugs (black) to the counter electrode. Every working electrode gets its own connection. Do the same for channels 6 to 10 in the other cell (see Figure 6).

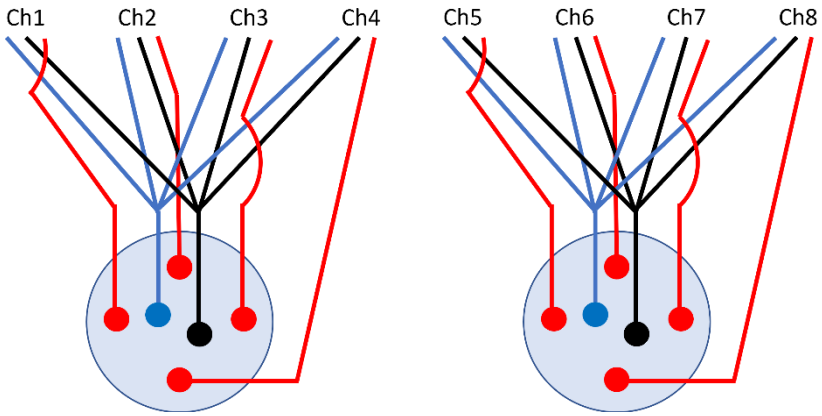

Figure 6 Connection scheme for 2 cells each with 4 WEs (galvanic isolation present)

4.4 Principle of the above-described setup

A polypotentiostat and a multi-channel device are two different devices that operate differently, but you can, with the setup described in chapter 4.2, use a multi-channel with galvanic isolation as polypotentiostat. The galvanic isolation removes the ground connection that every channel is using, this means the channels are all independent and floating. Potentials can only be measured or applied as differences. 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.

4.5 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 required current, that current needs to flow at the counter electrodes interface. For example, 10 mA are flowing through channel 1, and 10 mA flow through channel 2. That means 20 mA flow through the counter electrodes liquid-solid interface. For that reason, a large surface area of the counter electrode is recommended.
In this setup, the synchronization of the MultiPalmSens4 and MultiEmStat4 cannot be used. This is not very important for most experiments, because every channel has its own timing and works just like it would as a single channel, but it means each channel starts when it is ready and does not wait for the other channels. This results in a small time delay between the channels. If your experiment does not require a very precise simultaneous start for all working electrodes, this setup should be perfect.
Compared to a single-channel measurement some extra noise can be observed in parallel measurements, especially Electrochemical Impedance Spectroscopy (EIS) induces noise to other channels. Test measurements have shown up to now only a low increase in noise visible during chronoamperometry (see Figure 7 left). Some extra stray capacitance at high frequencies could be observed in EIS (see Figure 7 right). This capacitance could be caused by the presence of more cables and clips present, which form capacitors at high frequencies.

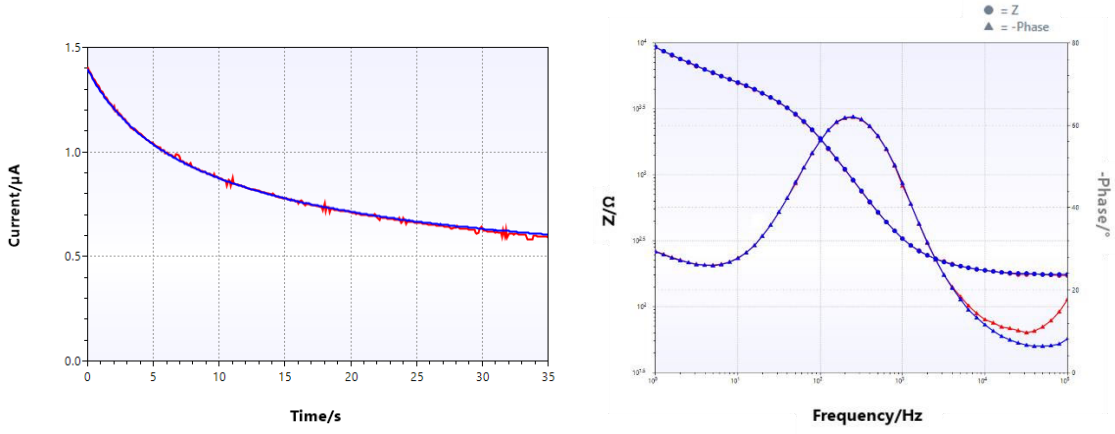

Figure 7 Chronoamperometry (left) and EIS (right) measured consecutive (blue) and parallel (red)