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Application Note

1 Introduction

There are a couple of ways of performing multiple measurements in parallel. Our products include multiplexers (MUX8-R2), bipotentiostats (PalmSens4 with BiPot) and multi-channel potentiostats (MultiPalmSens4). All these instruments increase your efficiency, but the optimal instrument for one experiment might not be a suitable option for another experiment.
It is handy if one potentiostat can be used for multiple applications in different setups. We have increased the MultiPalmSens4's versatility by implementing the possibility to use multiple working electrodes in the same cell sharing a counter and a reference electrode, while all working electrodes perform the same method at the same time.
This makes the MultiPalmSens4 a multi-channel potentiostat and a polypotentiostat.

2 Regular ways of operating

The MultiPalmSens4 and the MultiEmStat3(+) 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 MultiEmStat3(+) 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 MultiEmStat3(+) 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 Advantage of the Synched Mode

By enabling the synchronization of the channels in the MultiPalmSens4 and adjusting the setup of your cables, you can use the MultiPalmSens4 as a polypotentiostat. This means you can use multiple working electrodes, one counter and one reference electrode in the same cell at the same time. Your working electrodes all perform the same method. This setup is suitable for the following techniques:

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

PalmSens
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4 How to setup the MultiPalmSens4 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 1 and Figure 2).

Switch the MultiPalmSens4 on, start MultiTrace, wait until your MultiPalmSens4 is detected and choose the *Simultaneous mode*. Choose the channels that you have prepared as active (green highlight). Channel 1 has to be active. And 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.

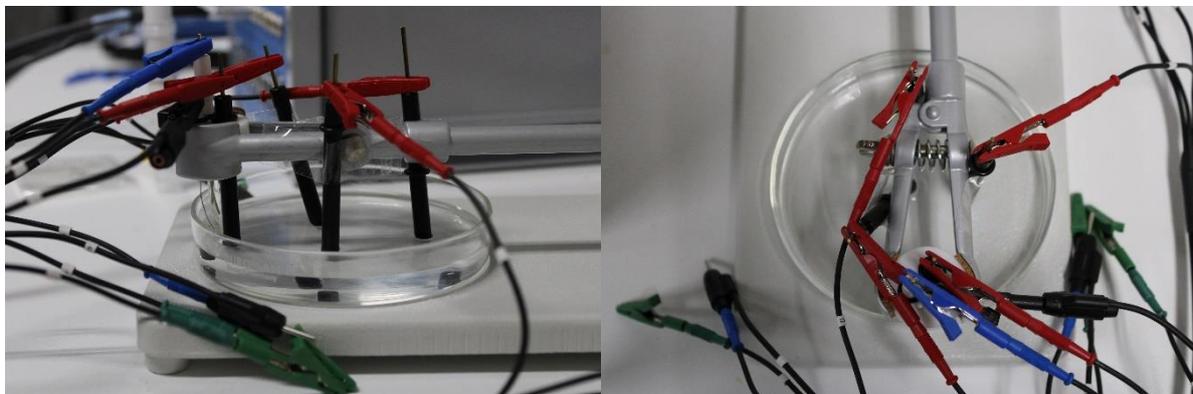Start the experiment, all active channels will perform the same experiment in the same cell.

Figure 2 A setup with 4 working electrodes, 1 reference electrode and 1 counter electrode (left side view, right top view)
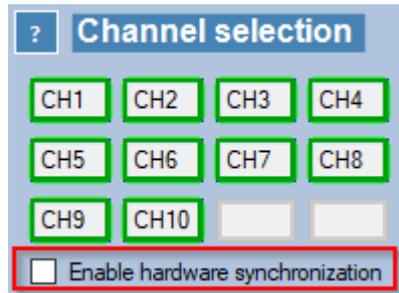
Figure 3 Checkbox to enable the synchronization

4.1   What if the MultiPalmSens4 has Galvanic Isolation

A MultiPalmSens4 with galvanic isolation cannot be used as polypotentiostat without one extra step. All the boards 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 housing can also be added to the other ground connection, which will make 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.

4.2   Multiple Cells with Multiple Working Electrodes

It is also possible not to use all the channels in one cell with the setup described above, but it is possible to have multiple cells with multiple working electrodes. 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 channel 2 to 5 as extra working electrodes. Channel 6 would again use all 3 electrodes (WE, CE and RE) in a physically separated cell and use channel 7 to 10 as four extra working electrodes. This way two cells with each five working electrodes are setup.
The channel with the three electrodes in the cell and the additional working electrodes must 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.

5   Principle

A polypotentiostat and a multi-channel device are two different devices that operate in a different way, but you can, with the setup described in chapter 4, use a multi-channel as polypotentiostat. The reason this works is quite counterintuitive for most electrochemists.
The working electrode is at ground potential for electronics engineers, 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.

Due to the fact that 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 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.

5.1   Limitations

The above described principle of the measurement show 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. 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.

6   Operating the MultiEmStat3 or MultiEmStat3+ as Polypotentiostat

The MultiEmStat3 or MultiEmStat3+ can be operated in the same way as described in chapter 4, but there are further limitations.

The MultiEmStat3 or MultiEmStat3+ do not have the synchronization the MultiPalmSens4 has. 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 4, 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, 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 a 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 a MultiPalmSens4 is required.