WHITE PAPER

(Un)Grounded: Grounded and floating measurements and their application in electrochemical research

In this White Paper, details of the electronic (PGSTAT) and electrochemical cell grounding are presented together with the necessity of using a floating PGSTAT for different application and experimental examples.

Due to the wide variation of experimental requirements and kinds of electrochemical cells, the use of an electrochemical instrument with a selectable floating feature (such as VIONIC) which brings additional versatility to the user is recommended.

Metrohm Autolab

DEFINITIONS: GROUNDED AND FLOATING

Depending on the ground state of the analog electronics of an electrochemical instrument, the potentiostat/galvanostat (PGSTAT) can operate either «grounded» or «floating» allowing the researcher to create a variety of conditions for experimentation.

A grounded instrument has the analog (or signal) electronics connected to the EARTH ground. A floating instrument has the analog electronics disconnected from the EARTH ground (i.e. floating). These definitions will be explained in greater detail later in this white paper.

Ground is defined a place with a stable potential value, regardless of the amount of charge exchanged. It is also called the «ground point». The potential of the ground is said to be **0 V**.

Ground can be the planet Earth itself, as is the case for the electrical grid of buildings. A direct electrical connection with the Earth is made via one or more metal poles inserted into the ground while also connected to the electrical grid of the building. This ensures that the entire building is grounded.

When the electronics are considered floating, they have no direct electrical connection to the Earth. In this case, a piece of metal large enough not to be polarized is used as the ground point even though its potential value will float with respect to the ground, since there is no electrical connection between the piece of metal and the Earth.

NON–FLOATING AND FLOATING ON THE INSTRUMENT

In order to define how grounded and floating modes are implemented in a PGSTAT instrument, it is necessary to present a short overview of how the electronics of a PGSTAT work.

The electronics of any PGSTAT are divided in two areas with two different roles: the *power electronics* and the *analog (or signal) electronics*. They are connected to each other through the transformer (**Figure 1**).

The power electronics manage the power from the electrical grid, while the analog electronics manage the signals coming from the electrochemical cell or from the device under test (DUT).

The power electronics are directly connected to the mains socket, with three terminations. Two of these carry the current and the voltage. The value of the voltage (230 V, 50 Hz or 110 V, 60 Hz) is the potential difference between the live wire and the neutral wire. The third termination is the ground wire, which connects the metal chassis of the instrument to the ground point of the electrical grid via the Earth connection. For safety reasons, this direct connection to the ground is always present and cannot be removed.

The transformer is positioned between the power and the analog electronics and it changes (transforms) the current and voltage into values used by the analog electronics.

The analog (signal) electronics are connected to the electrochemical cell. The analog (signal) electronics

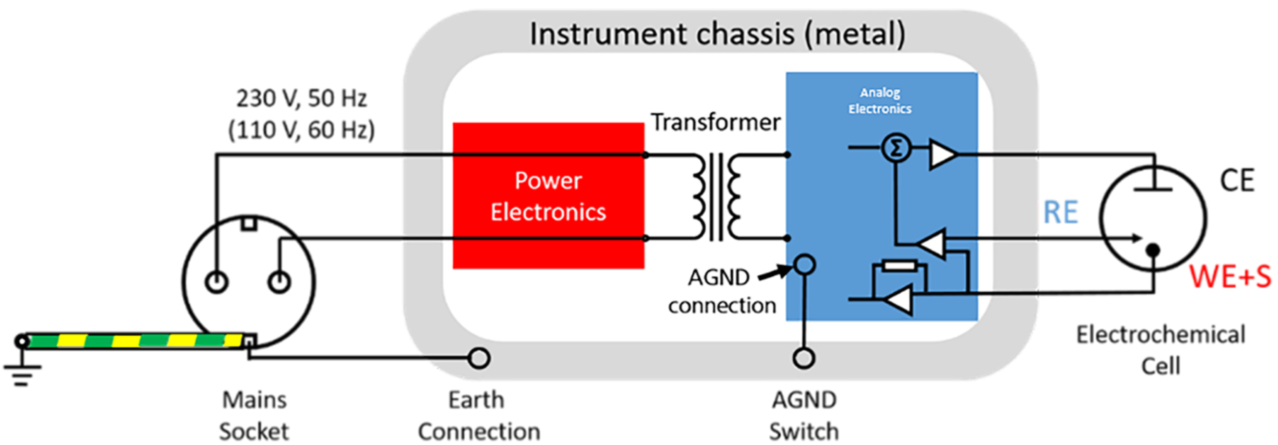

Figure 1. The schematics of a PGSTAT in non–floating mode. Note the EARTH connection (always connected to the metallic chassis of the instrument) and the analog ground (AGND) connection and switch.

have multiple connections available for the different potential and current values needed. Such connections come in couples to define the potential difference between the two wires included in each couple. The analog (signal) electronics have a ground point called *analog ground (AGND)*, to which all the potentials are referred. In addition, the AGND switch connects the analog (signal) electronics ground to the chassis of the instrument. This connection can be removed, leaving the potential of the analog (signal) electronics floating through values that differ from the 0 V value of the Earth ground.

Therefore, when the PGSTAT operates in non-floating mode the analog (signal) electronics ground (analog ground, AGND) is connected to the Earth (EARTH) via the chassis of the instrument.

When the instrument operates in floating mode, the AGND of the analog (signal) electronics is not connected to the chassis of the instrument, but to the Earth (EARTH) (**Figure 2**).

TYPICAL CELLS AND APPLICATIONS WHICH USE GROUNDED MODE

The grounded mode (Floating OFF) is used when none of the electrodes nor the cell vessel have a direct connection with the ground. This is the most commonly used mode for the vast majority of electrochemical experiments performed in laboratories.

In grounded mode (Floating OFF), the EARTH and AGND connections are equivalent. They can be used to connect a Faraday cage or to ground other devices used during the electrochemical experiments.

Following are some examples where the grounded mode (Floating OFF) is used.

– WET ELECTROCHEMISTRY

A typical electrochemical cell used for wet electrochemistry is comprised of different electrodes plus an electrolyte. The working electrode (WE) is the electrode where the half reaction of interest (e.g. reduction) occurs, and where the current is measured. The counter electrode (CE) is the electrode in which the other half reaction (e.g. oxidation) occurs.

The electrochemical cell setup can host two, three, or even four electrodes (**Figure 3 A–C**, respectively).

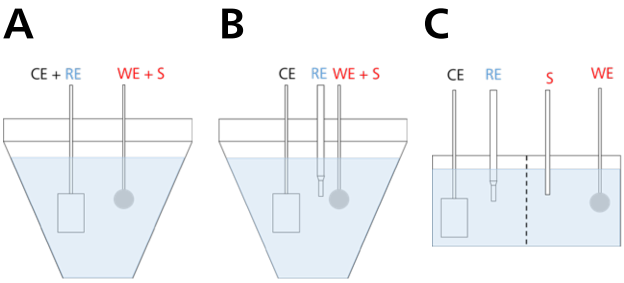

Figure 3. Schematic illustrations of electrochemical cells with two (A), three (B), or four (C) electrodes.

In all cases, none of the electrodes nor the cell itself have a direct connection to the ground. Therefore, the electrochemical cell is floating, and the PGSTAT can be used in grounded mode (Floating OFF).

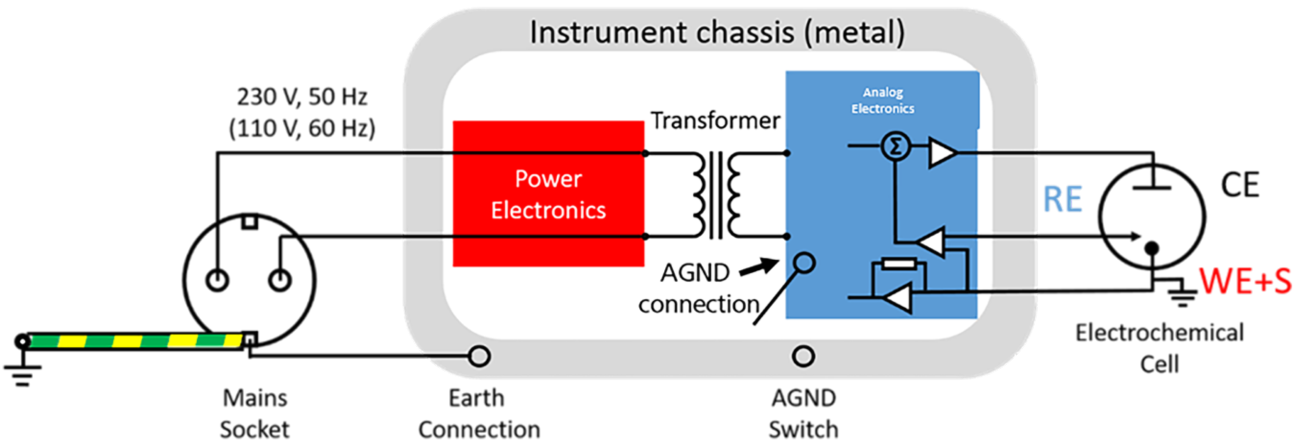

Figure 2. The schematics of a PGSTAT in floating mode. Note the analog ground (AGND) disconnected from the instrument chassis.

BATTERIES

Battery cells and battery packs usually have two connections: one for the positive electrode and the other for the negative electrode (**Figure 4**). None of the electrodes are grounded; therefore, the grounded mode (Floating OFF) is used. Some battery cells used for research can accommodate three electrodes, having a reference electrode included. In this case as well, none of the electrodes are grounded and the grounded mode (Floating OFF) is used on the PGSTAT.

Figure 4. A battery with two electrodes. The negative electrode hosts the counter and reference leads, while the positive electrode hosts the working and sense lead.

CAPACITORS AND SUPERCAPACITORS

Similar to batteries, capacitors and supercapacitors have two connections: one for the positive electrode and the other for the negative electrode (**Figure 5**). None of the electrodes are grounded, and therefore the grounded mode (Floating OFF) is used on the PGSTAT.

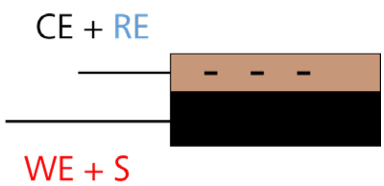

Figure 5. A capacitor (or supercapacitor) with two electrodes. The negative electrode hosts the counter and reference leads, while the positive electrode hosts the working and sense lead.

SOLAR CELLS

Solar cells have two electrodes, none of which is directly connected to the ground (**Figure 6**). Therefore, the PGSTAT should be used in grounded mode (Floating OFF).

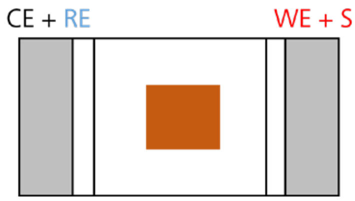

Figure 6. A solar cell with two electrodes. The negative electrode hosts the counter and reference leads, while the positive electrode hosts the working and sense lead.

FUEL CELLS

In fuel cells, two connections at the edges of the stack are present to carry the current. The potential can be sensed on a single cell, on a portion of the fuel cell, or through the entire stack (**Figure 7**). In all cases, none of the terminations are directly connected to the ground. Therefore, for these applications the PGSTAT should be set in grounded mode (Floating OFF) as well.

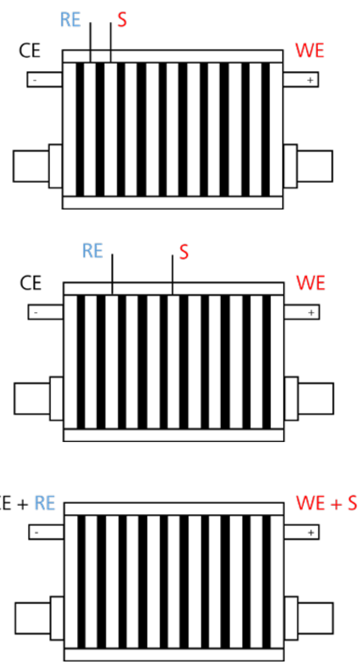

Figure 7. Top: fuel cell with the potential of a single cell sensed. Center: fuel cell with the potential of a portion of the fuel cell sensed. Bottom: fuel cell with the potential of the entire stack sensed.

CORROSION TESTS IN LABORATORIES

In the case of testing the corrosion of a sample, the inhibition properties of a corrosion inhibitor, or the properties of coatings and additives, such laboratory experiments involve a cell in which the sample undergoing corrosion tests is the working electrode. In most of the cases, the sample is not grounded, just like the other electrodes and the cell itself. Therefore, the PGSTAT should be used in grounded mode

TYPICAL CELLS AND APPLICATIONS WHICH USE FLOATING ON

There are three main cases when the PGSTAT must be used in floating mode:

A. When the working electrode is directly connected to the Earth ground (grounded WE)
B. When the counter electrode is directly connected to the Earth ground (grounded CE)
C. When the entire cell is directly connected to the Earth ground (grounded Cell)

For any of the above-mentioned cases, the correct measurement of the current is only possible if the PGSTAT is used with Floating ON.

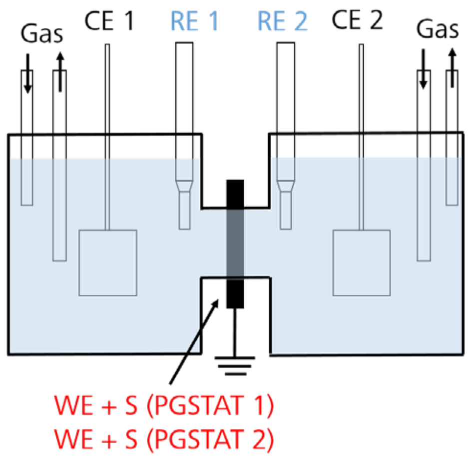

Figure 8. The schematics of a Devanathan-Stachurski cell, showing the grounded working electrode is shared between two compartments, each one with its own counter and reference electrodes. Two independent PGSTATs are connected to the same WE.

– A. GROUNDED WE

Corrosion tests in open air

Corrosion studies on buildings, bridges, and other civil engineering structures require a floating PGSTAT since the samples that are used as working electrodes of the cell are directly connected to the Earth.

Hydrogen permeation

Some corrosion processes deliver hydrogen as a byproduct which permeates through the metallic structure. In order to study hydrogen permeation, the sample that is used as working electrode (shared by two different compartments of a Devanathan-Stachurski cell) should be grounded as two independent electrochemical instruments are connected to it (**Figure 8**).

In-situ electronic microscopy

Other examples of grounded working electrodes are found in the cells designed for in-situ electrochemistry with scanning electron and scanning tunnel microscopy. Here, the electron beam used for imaging can interfere with the current developed during the electrochemical experiment. A successful way to obtain good images and reliable electrochemical data is to ground the WE with the PGSTAT EARTH connector attached to the microscope chassis, which is grounded.

– B. GROUNDED CE

Bioreactors

For example, an electrochemical cell setup with a grounded counter electrode is used in a bioreactor, in which two independent PGSTATs (connected to two working electrodes and two reference electrodes, respectively) were first employed. In order to avoid that the potential of one of the working electrodes is affected by the potential of the other working electrode, two counter electrodes were connected together and grounded (**Figure 9**) [1].

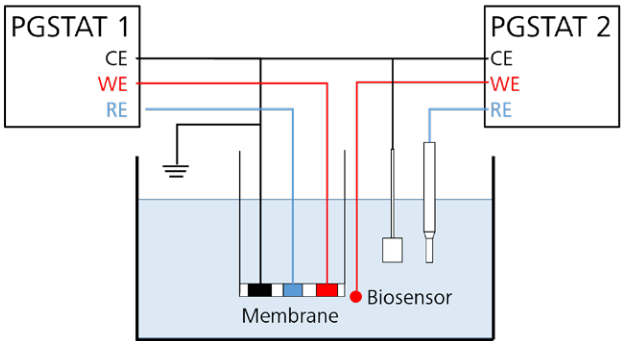

Figure 9. The electrochemical cell hosting a membrane and a biosensor. The experiment was performed with two counter electrodes connected together and grounded.

Autoclave

In some experiments, an autoclave is used for high temperature and high pressure measurements. For safety reasons, the autoclave is grounded. However, in some cases, the entire autoclave is used as counter electrode for the electrochemical cell (**Figure 10**).

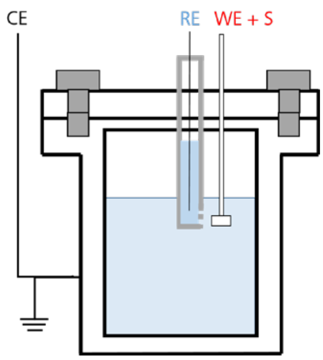

Figure 10. The schematics of an autoclave used as counter electrode.

– C. GROUNDED CELL

Autoclave

A typical example of an electrochemical experiment using a grounded cell is when electrochemistry is performed inside an autoclave, and the metallic cell body used for the experiment is in direct contact with the autoclave structure (which is grounded) [2]. For example, by using an autoclave, it is possible to perform corrosion experiments at high temperatures and pressures—conditions often found in power plants. When the metallic cell vessel is grounded, part of the current that is exchanged between the counter and the working electrodes flows to the ground through the grounded cell body. To avoid this, a Floating PGSTAT is needed for the measurement (**Figure 11**).

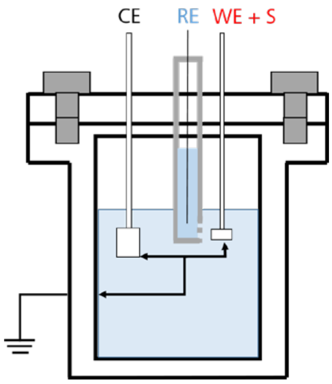

Figure 11. The current exchanged between the counter and working electrode can flow to the ground through the chassis of a grounded autoclave.

Tribocorrosion

In tribocorrosion measurements, the working electrode is in contact with the tribology device. For this type of experiments, either the tribology load (head) or the electrochemical cell could be grounded through the tribology device. For any of these cases, a Floating ON PGSTAT is needed and the exact grounding point in the cell must be identified (**Figure 12**).

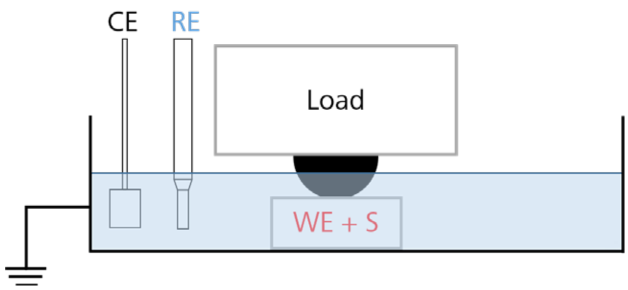

Figure 12. The schematics of a setup for tribocorrosion experiments. For this example, the working electrode is positioned on the grounded chassis of the setup.

EXPERIMENTS IN GROUNDED MODE, WE GROUNDED, AND CE GROUNDED

This section shows examples of experimental results of a cell with the instrument grounded, together with different floating options.

In all cases, a Metrohm Autolab Flat Platform Cell was used. As a working electrode (WE), an uncoated steel sample was investigated. The stainless steel counter electrode (CE) of the Metrohm Autolab Flat Platform Cell and a Metrohm Ag/AgCl 3 M KCl reference electrode completed the cell. An aqueous solution of 3% in weight of NaCl was used as electrolyte.

The procedure used was a linear polarization from -50 mV vs. OCP to +50 mV vs. OCP, with a scan rate of 1 mV/s and a step height of 500 µV. The sample was masked with a tape that exposed a surface of approximately 7 cm^2.

In **Figure 13**, the i vs E (i.e. measured current vs applied potential) plots are presented for each of the above-mentioned cases.

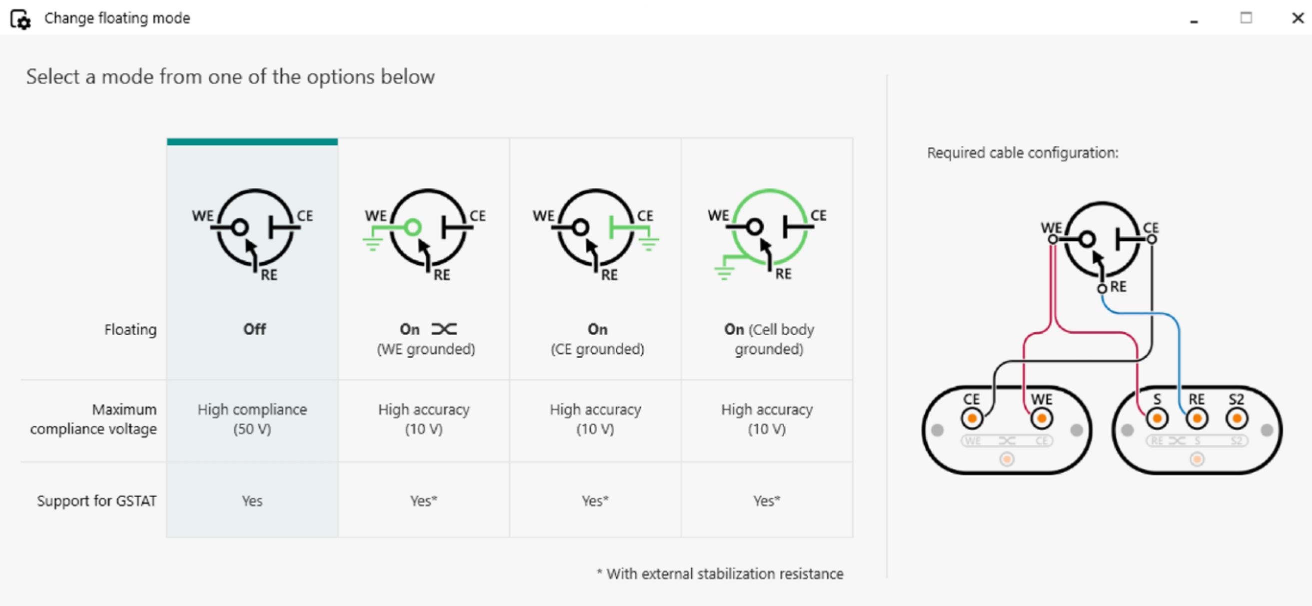

Figure 13. Connection guide in the INTELLO work system editor.

Figure 14 shows the resulting voltammogram of the experiment with VIONIC used with Floating OFF is shown.

Figure 15 shows the resulting voltammogram of the experiment with the working electrode (WE) grounded[1].

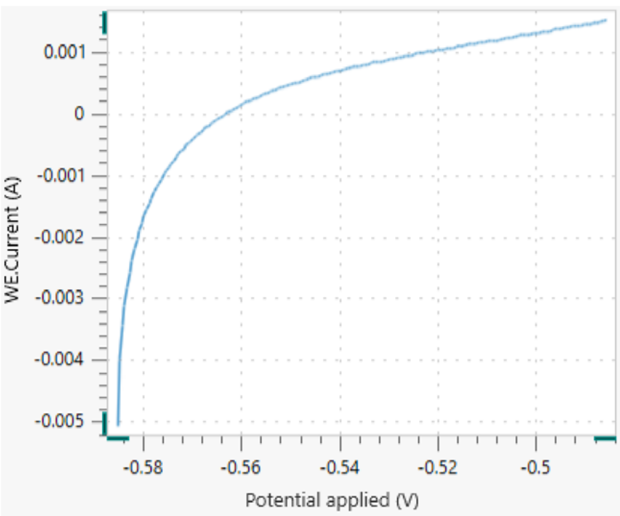

Figure 14. The i vs. E curve with floating mode OFF.

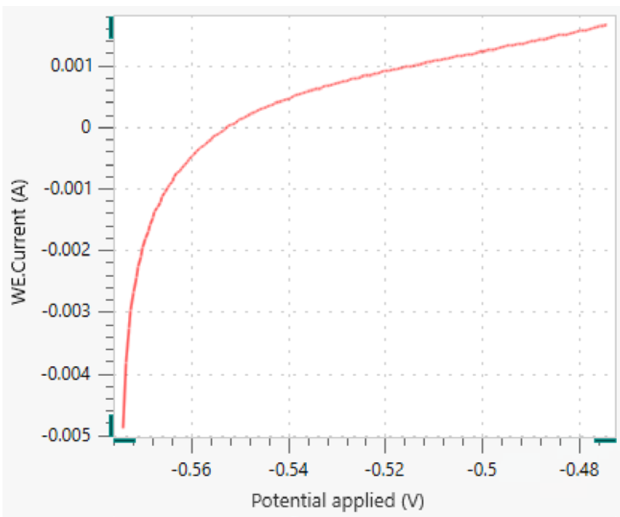

Figure 15. The i vs. E curve with cross-floating mode ON, WE grounded.

[1] In order to perform the experiment, the working electrode (WE) was connected to the EARTH ground of the Pure Signal Bridge.

Finally, **Figure 16** shows the resulting voltammogram of the experiment with the counter electrode (CE) grounded[2].

The curves are similar in all of the cases with negligible noise.

In **Figures 17 to 19**, connection guides are presented for the various floating modes described in the previous voltammograms.

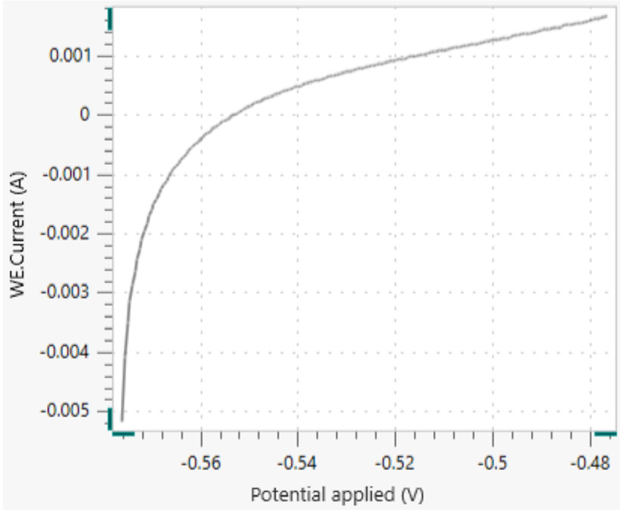

Figure 16. The i vs. E curve with floating mode ON, CE grounded.

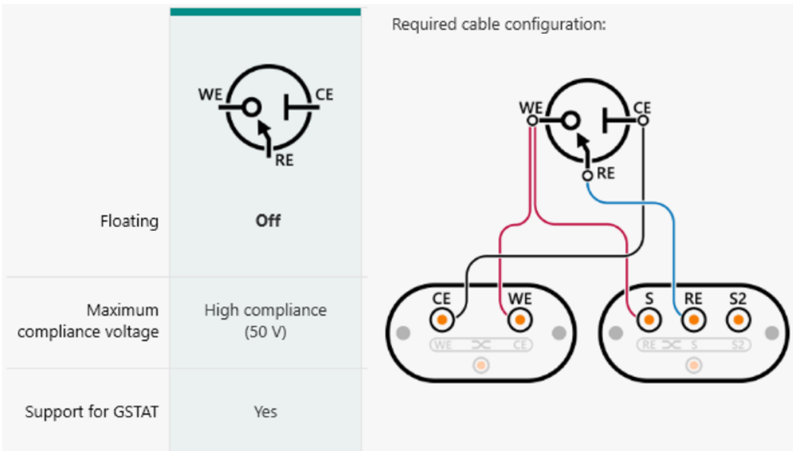

Figure 17. Connection guide for the floating mode OFF configuration.

[2] In order to perform the experiment, the counter electrode (CE) was connected to the EARTH ground of the Pure Signal Bridge.

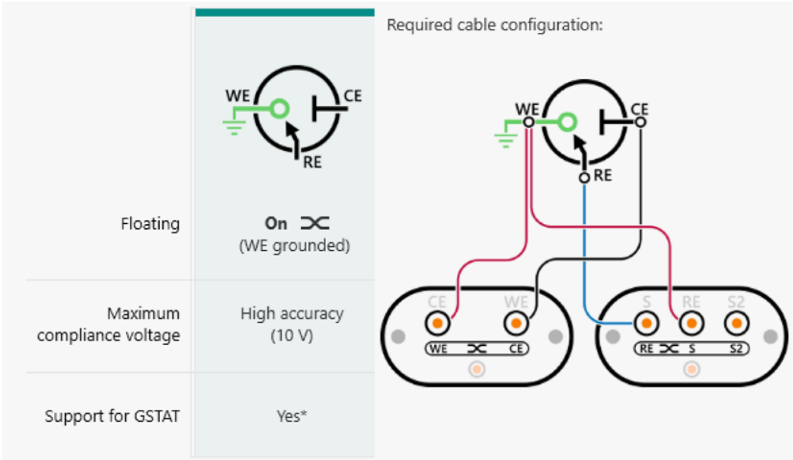

Figure 18. Connection guide for floating mode ON – WE grounded. *Please note the cross-floating mode in the wiring schematics.*

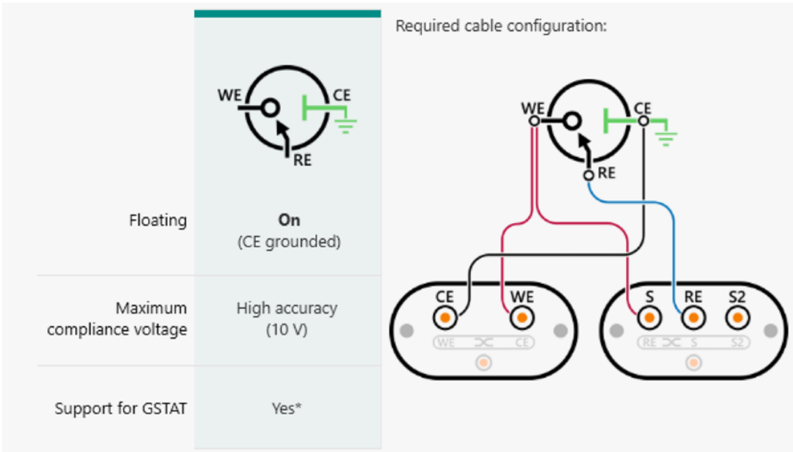

Figure 19. Connection guide for the floating mode ON – CE grounded.

CONNECTIONS TO THE I/O BOARD

When external devices are connected to a PGSTAT which is used in floating mode, special attention is needed to avoid unwanted ground connections of the floating electronics of the PGSTAT through the grounded external devices (such as oscilloscopes).

In the case of VIONIC, the analog (signal) electronics are galvanically isolated from the rest of the electronics. As a consequence, it is possible to connect an external device (such as an oscilloscope) to the I/O board of VIONIC without affecting the electrochemical measurement even when VIONIC operates in Floating ON mode.

USE OF A FARADAY CAGE, GLOVE BOX, AND METAL PARTS IN THE ELECTROCHEMICAL SETUP

For experiments that require either Floating ON or grounded (Floating OFF) configuration with a work system (experimental setup) which includes external devices, it is important to use the EARTH connection of the PGSTAT as single ground point.

In order to completely shield the cell or DUT, it is advisable to use a Faraday cage, a metal box connected to the EARTH ground of the instrument either in non-floating or floating mode (**Figure 20**).

The electrochemical cell or DUT is placed inside of the Faraday cage that must be connected to the EARTH connection of the PGSTAT. In this way, the electrochemical cell will be shielded from the external electromagnetic noise.

Figure 20. The Metrohm Autolab Faraday cage.

Finally, when a glove box is used, an isolated feed through connector (**Figure 21**) must be used on the glove box. Therefore, the use of the Floating ON or grounded mode (Floating OFF) is not influenced by the glove box but rather by the particularity of the electrochemical cell that is inside the glove box.

Figure 21. Isolated BNC Adaptive Cable Set

CONCLUSION

Selectable floating offers electrochemical researchers the flexibility to choose the ground state of the cell setup, offering even greater experimental possibilities. The electrochemical experiment can be configured to the exact specifications needed and is not limited by the electronics of the PGSTAT.

References

[1] Yarnitzky, C.N. Part I. Design and construction of a potentiostat for a chemical metal-walled reactor. *J. Electroanal. Chem.* **2000**, *491*, 160–165. **DOI:10.1016/S0022-0728(00)00150-9**

[2] Holm, T.; Dahlstrøm, P.K.; Sunde, S; et al. Method for Studying High Temperature Aqueous Electrochemical Systems: A Self Pressurized Autoclave. *ECS Trans.* **2016**, *75* (14), 1055–1061. **DOI:10.1016/j.electacta.2016.11.130**

Contact

Metrohm Autolab

autolab@metrohm.com

www.metrohm.com/electrochemistry