VIONIC powered by INTELLO

User Manual

1.7 / 2025

Metrohm
Autolab

Metrohm
Autolab
Woudwetering 3-5
3543 AV Utrecht
The Netherlands
+31302893154
autolab@metrohm.com
www.metrohm.com/electrochemistry

VIONIC powered by INTELLO

1.7

User Manual

1.7 /
2025

Metrohm Autolab

Metrohm Autolab
3543 AV Utrecht

Although all the information given in this documentation has been checked with great care, errors cannot be entirely excluded. Should you notice any mistakes please send us your comments using the address given above or at autolab@metrohm.com.

Table of contents

1 Conventions **1**

1.1 Scientific conventions **1**

2 Basic safety information **2**

2.1 Instrument specifications **6**

2.2 Connector type and ratings **7**

2.3 Warranty **8**

2.4 Spare parts availability **9**

2.5 Environmental protection **9**

3 EU Declaration of Conformity **11**

4 General overview and operating principle of the Autolab instrument **13**

4.1 Building blocks and operating principle of VIONIC powered by INTELLO **13**

4.2 VIONIC exterior **18**

4.2.1 Front of the instrument 18

4.2.2 Back panel 20

4.2.3 Cell cables 21

4.2.4 Adaptive cables 24

4.3 Dynamic Interface **29**

4.3.1 VIONIC and experiment state indication 32

4.3.2 Alphanumeric display 36

4.4 Bandwidth: General definition **37**

4.4.1 Bandwidth of VIONIC 38

4.4.2 Input impedance and stability 44

4.5 Resolution specifications **45**

4.5.1 Potential resolution (WE.Potential) 46

4.5.2 Current resolution (WE.Current) 48

4.5.3 Second Sense (S2) potential resolution (S2.Potential) 50

4.5.4 Applied AC signal resolution 52

4.5.5 Overview of the resolution specifications 53

4.6 Power plot **54**

4.6.1 Distributed power 55

4.6.2 Passive electrochemical cells. 55

4.6.3 Active electrochemical cells 58

4.7 Electrochemical Impedance Spectroscopy (EIS) **60**

4.7.1 EIS Contour plot 60

4.7.2 EIS Contour plot for VIONIC powered by INTELLO 62

4.7.3 EIS on S2 Contour plot for VIONIC powered by INTELLO 64
4.7.4 EIS measurements at High Frequencies 66
4.7.5 Practical tips for stable and accurate EIS measurements 68

4.8 Second Sense (S2) 69
4.8.1 Second Sense (S2) connected to the Counter electrode (CE) ... 72
4.8.2 Second Sense (S2) as stand alone probe in the cell 73
4.8.3 Second Sense (S2) and the cell parameters 75
4.8.4 Ohm's Law and the cell parameters for DC measurements 76
4.8.5 Second Sense and Electrochemical impedance (EIS) measurements 77

4.9 VIONIC detailed specifications 78
4.9.1 Scope of delivery 83

5 VIONIC in an extended Work system 85

5.1 Work system for hydrodynamic measurements 86
5.1.1 Creating the work system with the Autolab Rotating Electrode in INTELLO 87

5.2 Work system including a K-type Thermocouple (TC) for temperature monitoring 90
5.2.1 Creating the work system with a K-type Thermocouple 90

5.3 Work system for external monitoring of the measured electrochemical signals (E Monitor and I Monitor) 93
5.3.1 Creating the Work system for external monitoring of the electrochemical signals (E Monitor and I Monitor) 94

5.4 Cell Protection 96

6 Experimental setup considerations 99

6.1 Cell connections 99
6.1.1 Cell connections: 4-connectors mode (No S2) 100
6.1.2 Cell connections: 5-connectors mode (with S2) 104

6.2 Grounded and non-grounded electrochemical cells 107
6.2.1 Non-grounded electrochemical cells 108
6.2.2 Grounded electrochemical cells 109
6.2.3 Galvanostatic measurements on grounded cells 114

6.3 Passive vs Active electrochemical cells. 117
6.3.1 Passive electrochemical cells. 117
6.3.2 Active electrochemical cells 120

6.4 Faraday cage connection 122

6.5 Maximum input voltage 124

6.6 Environmental operating conditions 125
6.6.1 Instrument temperature overload 125

7 INTELLO installation 127

7.1 Computer and network requirements 127

7.2 Metrohm Autolab INTELLO Software License Agreement 128

8 Release notes 136

8.1 Version 1.0 release 137
8.2 Version 1.1 release 137
8.3 Version 1.2 release 138
8.4 Version 1.2.1 release 139
8.5 Version 1.3 release 139
8.6 Version 1.3.3 release 140
8.7 Version 1.3.4 release 141
8.8 Version 1.4 release 141
8.9 Version 1.5 release 142
8.10 Version 1.6 release 144
8.11 Version 1.7 release 147
8.12 Version 1.7.1 release 148

9 Procedures 149

9.1 Procedure view 149
9.2 Main Parameters 150
9.3 Cell properties 151
9.4 Procedure settings 151
9.5 Normalized signals 153

10 Data explorer and Procedure library 156

10.1 Data explorer 156
10.2 Procedure library 157

11 INTELLO Runs 159

12 Command tiles 162

12.1 Chrono methods command tile 162
12.2 CV linear scan command tile 163
12.3 CV staircase command tile 164
12.4 Square wave voltammetry (SWV) 166
12.5 Differential pulse voltammetry (DPV) 167
12.6 Export 168

12.7 Electrochemical Impedance commands **170**
12.7.1 EIS frequency scan command tile 170
12.7.2 EIS single frequency command tile 174

12.8 Group command tile **176**

12.9 LSV linear scan command tile **177**

12.10 LSV staircase command tile **178**

12.11 Repeat command tile **179**

12.12 Battery Cycling **180**
12.12.1 Cycle 180
12.12.2 Constant-Current (CC) Charge or Discharge 182
12.12.3 Constant-Voltage Charge or Discharge 183
12.12.4 Rest command 184
12.12.5 Battery Analysis 185

12.13 External devices **188**
12.13.1 DIO control 188
12.13.2 External devices 194

12.14 Data analysis **195**
12.14.1 Corrosion rate analysis 196
12.14.2 EIS data analysis 202

12.15 Wait command tile **210**

12.16 Measurement - general **211**
12.16.1 Apply settings command tile 211
12.16.2 Apply command tile 213
12.16.3 Switch cell 214
12.16.4 Record signals command tile 214
12.16.5 Measure OCP command tile 215
12.16.6 iR drop measurement and compensation 216
12.16.7 Reset charge command tile 222

13 VIONIC Acceptance test 223

13.1 Test procedures in INTELLO **223**

13.2 Main steps of the Acceptance testing process **224**

13.3 Autolab Test cell **225**

13.4 How to run the Acceptance test procedures **226**
13.4.1 Test CV 227
13.4.2 Test CV Linear scan 227
13.4.3 Test current limit 228
13.4.4 Test compliance voltage 229
13.4.5 Test EIS 230
13.4.6 Test floating mode 231
13.4.7 Test EIS high frequency 233

13.5 Export and save the Acceptance test data **235**

13.6 Acceptance test evaluation **236**

Index **238**

1 Conventions

The conventions detailed in this chapter are used throughout the software, unless otherwise noted.

1.1 Scientific conventions

The following scientific conventions are used:

- All units are specified in the International System of Units (SI), unless otherwise specified. See *B. N. Taylor, A. Thomson, The International System of Units (SI), NIST Special Publication 330, 2008 Edition* for more information.
- Electrochemical values like potential and current are indicated according to the International Union of Pure and Applied Chemistry (IUPAC) convention. Positive currents and (over)potentials are associated with oxidation processes. Negative currents and (over)potentials are associated with reduction processes. See *A. D. McNaught, A. Wilkinson, IUPAC, Compendium of Chemical Terminology: IUPAC Recommendations, Blackwell Science: Oxford, England; Malden, MA, USA, 1997* for more information.

2 Basic safety information

General introduction

Always read through and follow the safety instructions provided below.

Metrohm Autolab makes every effort to keep the highest safety standards of its products and to provide the highest degree of safety to its customers.

The Metrohm Autolab products are designed, tested and built according to the safety standards which apply. The compliance to the safety standards is monitored by the quality assurance system. The manufacturing facility fully complies with the applicable safety standards.

The Metrohm Autolab instruments and accessories are intended for use in a laboratory environment for research, testing and quality control purposes. Using the Metrohm Autolab instruments and accessories require basic technical skills, basic knowledge of electrochemistry and, in some cases, basic knowledge of English.

It is the users responsibility to use the Metrohm Autolab products as intended and as described in the provided documentation and within the performance specifications of the product.

The following practices are necessary to ensure safe operation of the Metrohm Autolab instruments. Not following these instructions may result in unsafe operation. Metrohm Autolab is not liable for any damage or injury caused by not complying with the following instructions. Warranty can be voided in case of unsupported use of the instrument.

For any questions or if any guidance is needed, please contact your local Metrohm Autolab distributor (*https://www.metrohm.com/en/contact.html*) or contact Metrohm Autolab directly (*autolab@metrohm.com*).

General precautions

This section outlines general precautions for working with the Metrohm Autolab instruments.

- Always place the instrument in the position in which it was designed to be used (upright, vertical position).
- Always place the instrument so that the the main power switch and the power cord connection is reacheable by the user so that the instrument can be powered off in case of emergency.
- Do not place the instrument on an unstable surface.
- Do not expose the instrument to wet conditions.

- To prevent overheating, do not to cover any of the instrument ventilation holes (located at the back and bottom sides of the instrument) and do not to place the instrument close to a heating source.
- Do not place any objects on top of the instrument.
- Do not cover the instrument while it is in use or powered on.

VIONIC must be placed and used in an upright, vertical position. Do to place in any cirtunstances VIONIC on its side or upside down the position.

Electrical hazards

This section provides information on the safe operation of the equipment with respect to electrical hazards.

There are no user-serviceable parts inside. Servicing must only be done by qualified personnel.

Removal of the protective external panels results in exposure to potentially dangerous voltages; this must only be done by qualified personnel. The instrument must be disconnected from all power sources before removing the protective panels.

Removal of the protective panels (i.e. opening the instrument) by non-authorized personnel results in loss of instrument warranty.

- **Cords:** Operation of the Metrohm Autolab instruments is permitted only with power cords with the correct rating and type of socket. Use only approved type of power cords that conforms to local regulations. Immediately replace any faulty or frayed power cords and control cables. Replace control cables only with original spare parts. Do not use dusty and dirty power sockets. Do not place anything on top of the cords or cell cables.
- **Fuses:** For instruments which have user exchangeable fuses, replace blown fuses only with size and rating stipulated on or near the fuse panel holder and in the manual. VIONIC instrument *does not* have any user exchangeable fuses.
- **Grounding:** For safety and shielding purposes, the frame of the instrument is always connected to the protective ground. Ensure that power cords are plugged into the correct mains voltage source and always use a wall outlet with protective earth. If used, all extension cords or power strips must have ground connection. Check all connected equipment and accessories for proper grounding.
- **Liquids:** Unless specified otherwise, the Metrohm Autolab instruments are not liquid proof. Therefore, the instrument and cables must be protected against penetration of liquids. If precautions are not followed, the instrument can be damaged and personal injury can occur.

- **Condensation:** Never use the Metrohm Autolab instruments in conditions in which condensation might have occured on or in the instrument. When the instrument is moved from a cold place to a warm room, do not connect the instrument to the power until the instrument reaches the room temperature.
- **Cleaning, moving:** Do not clean or move the instrument with power cords connected.

Unpacking and carrying the instrument

This sections describes the safe method for carrying and lifting the VIONIC instrument.

The Metrohm Autolab instruments are very high precision research tools and are carefully adjusted and calibrated to the lowest tolerances. Please handle the Metrohm Autolab instruments with care.

These guidelines must be followed when unpacking and carrying the VIONIC instruments.

The weight of VIONIC is 13 kg.

- Remove VIONIC from the box by grabbing the box insert from the handles and lifting the complete content of the box including the instrument, the filling foam and the insert.
- Place the content on a stable desk or on a clean floor and remove the accessory box and the filling material one by one.
- Grab VIONIC from the designated handles located below the front and the back of the instrument. The handles are not visible and therefore, to notice the handles, hands must reach beneath the front and the back of the instrument.
- The Pure signal bridge (cell cables) of VIONIC are fixed. To avoid damaging (scratching) the side panels and the boxes on the cables, make sure that the cables are secured in your hand when moving VIONIC. Remove the protective foil around VIONIC and around the boxes on the cables only after the instrument is placed on the desk.
- Follow the installation guide to start using VIONIC.

We recommend to store the empty shipping box and the filling materials in an available storage place in case VIONIC will need to be moved or shipped to another location.

Instrument operation

This section describes the safe method for operating the Metrohm Autolab instruments.

- Before operating the Metrohm Autolab instruments, please read the additional documentation provided with the instrument.

- Familiarize yourself with the labeling on the cables and the conventions used in the software. Details are available in the extended user manual. For a safe operation of the Metrohm Autolab instruments, it is helpful but not necessary for the user to be familiar with the working principle of the instrument. For help and support, please contact your local Metrohm Autolab distributor or Metrohm Autolab directly.
- The Metrohm Autolab instruments are not meant to be used for *in-vivo* measurements. Do not connect any Metrohm Autolab instruments to the human body or animals.
- In case of fire or smoke coming out of the instrument, disconnect immediately from the power and take all the local required safety measures. Wear protective masks and suitable protective clothing to minimize the exposure to any hazardous substances which may be released.

Repair and service

This section describes the safe method for repairing and servicing the Metrohm Autolab instruments.

- There are no user serviceable parts in the Metrohm Autolab instruments. The instrument can be opened ONLY by authorized and trained personnel
- To avoid the risk of electric shock, before any service work is done, the Metrohm Autolab instrument must be disconnected from the power grid.
- Service and repair related issues such as spare parts and maintenance, please contact your local Metrohm Autolab distributor (*https://www.metrohm.com/en/contact.html*). Only original Metrohm Autolab spare parts can be used.

Contact details

For technical assistance, please locate and contact your local distributor at *https://www.metrohm.com/en/contact.html* or contact us directly:

Metrohm Autolab

Woudwetering 3-5

3543 AV, Utrecht, The Netherlands

tel: +31 30 2893154

e-mail: *autolab@metrohm.com*

www.metrohm.com/electrochemistry/

2.1 Instrument specifications

Below is the short list of specifications of VIONIC.

Table 1 The main specifications of the VIONIC instrument

Specification	Value
Operation modes	Potentiostatic, Galvanostatic
Compliance voltage	±50 V
Maximum applied and measured potential	±10 V
Maximum applied and measured current	±6 A (at ±10 V compliance) ±3 A (at ±50 V compliance)
Maximum applied power	150 W
Maximum dissipated power	50 W
EIS	Yes
Maximum EIS frequency	10 MHz
Number of cell connectors	5 (WE, CE, RE, S, S2)
Switchable floating	Yes
On-board data buffer	Yes
Connection type	Ethernet
Ground connections	Earth ground and Analog ground
Cell cables	Fixed, (1 m) with removable adaptive cables (0.5 m)
Dimensions	20 cm x 27 cm x 40 cm
Weight	13 kg
Power requirements	300 W, 100..240 V, 50/60 Hz

2.2 Connector type and ratings

The following connectors with their ratings are used in the VIONIC instrument:

Table 2 Connector types and ratings available on VIONIC instrument

Connector type	**Location on VIONIC**	**Function**	**Rating**
BNC socket	Pure signal bridge	WE, CE	±6 A, ±50 V
BNC socket	Back panel	Analog-IN Analog-OUT	±10 V input with Hi-Z ±10 V output with Hi-Z load (Z_0 = 50 Ω series resistance)
SMB socket	Pure signal bridge	RE, S, S2 Hi-Z inputs	Max. ±50 V
4 mm Banana socket	Pure signal bridge	EARTH	n.a.
2 mm Banana socket	Pure signal bridge	Analog Ground (AGND)	n.a.
4 mm Banana plug	Adaptive cables	WE, RE, CE, S, S2, EARTH, AGND	±6 A (WE, CE), ±50 V
2 mm Banana plug	Adaptive cables, optional	WE, RE, CE, S, S2, EARTH, AGND	±2.5 A (WE, CE), ±50 V
BNC plug	Adaptive cables, optional	WE, RE, CE, S, S2, EARTH, AGND	±1 A (WE, CE), ±50 V
Alligator clips	Adaptive cables, optional	WE, RE, CE, S, S2, EARTH, AGND	±2.5 A (WE, CE), ±50 V
DB15 socket	Back panel	Digital-IN Digital-OUT	5 V TTL $I_{out\ H,L}$ = 7 mA (max.)

Connector type	Location on VIONIC	Function	Rating
Miniature K-type thermo-couple socket	Back panel	Temperature measurement	n.a.
M12-5 A-coded socket	Back panel	Emergency stop	5 V, 5 mA Interlock
Ethernet (LAN): 0/100/1000BASE-T IEEE 802.3, RJ45 socket	Back panel	Instrument connection and control	n.a.
Standard HDMI type-A style socket	Back panel	Intended for future use. Not used as an HDMI interface	LVDS

2.3 Warranty

The warranty on Metrohm Autolab products is limited to defects or failures that are traceable to material, construction or manufacturing errors, which occur within 36 months from the day of delivery. In this case, the defects or failures will be rectified by Metrohm Autolab free of charge. Transport costs are to be paid by the customer, if applicable.

3 year
instrument warranty

Glass breakage in the case of electrodes, cells or other parts is not covered by the warranty. Consumables (electrodes, QCM crystals, etc.) are not covered by the warranty.

If damage of the packaging is evident on receipt of the goods or if the goods show signs of transport damage after unpacking, the carrier must be informed immediately and a written damage report is demanded. Lack of an official damage report releases Metrohm Autolab from any liability to pay compensation.

If any instruments or parts have to be returned, the original packaging should be used. This applies to all instruments, electrodes, cells and other parts. If the original packaging is not available it can be ordered at Metrohm Autolab or at your local distributor. For damage that arises as a result of non-compliance with these instructions, no warranty responsibility whatsoever will be accepted by Metrohm Autolab.

Do not modify the cell cable or the cable connectors. These cables are designed for the best possible operation. Modifications of these connections, i.e. with other connectors, will lead to the loss of any warranty.

2.4 Spare parts availability

All products designed, produced and tested by Metrohm Autolab are covered by 10 years spare part availability, from the day of delivery. Failures or defects experienced during this period will be rectified by Metrohm Autolab in such a way that the product will comply with all the original requirements and specifications. After the period of ten years, products supplied by Metrohm Autolab may no longer be serviceable. Metrohm Autolab will however attempt to repair any failure or defect beyond this time limit as long as spare parts remain available.

2.5 Environmental protection

The pictogram shown in the figure located on the product(s) and / or accompanying documents means that used electrical and electronic equipment (WEEE) should not be mixed with general household waste. For proper treatment, recovery and recycling, please take this product(s) to designated collection points where it will be accepted free of charge.

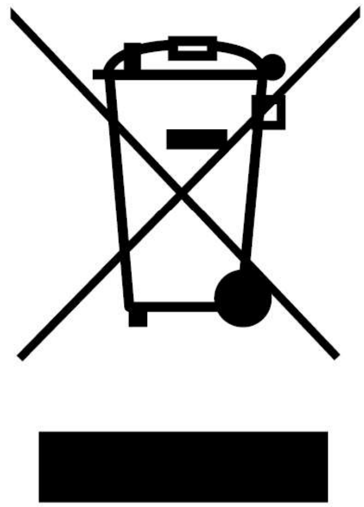


Figure 1 WEEE (Waste Electrical and Electronic Equipment) pictogram

Alternatively, in some countries, you may be able to return your products to your local retailer upon purchase of an equivalent new product. Disposing of this product correctly will help save valuable resources and prevent any potential negative effects on human health and the environment, which could otherwise arise from inappropriate waste handling.

Please contact your local authority for further details of your nearest designated collection point. Penalties may be applicable for incorrect disposal of this waste, in accordance with you national legislation.

3 EU Declaration of Conformity

This declaration attests the compliance of the instrument with the standard specifications for electrical instruments and accessories and with the standard specifications for safety and system validation of the manufacturing company.

Product validity

This declaration is valid for the following products or product versions:

VIONIC

Potentiostat/galvanostat laboratory measurement equipment used for measuring electrochemical cells.

Directives

VIONIC instrument has the CE marking and comply with the following EU directives:

- 2014/35/EU (Low Voltage Directive, LVD)
- 2014/30/EU (EMC Directive, EMC)
- 2011/65/EU (Directive for certain hazardous substances, RoHS)

Safety specifications

VIONIC instrument complies with safety specifications according to the following standards:

Design and type testing

- EN 61010-1:2016
Safety requirements for electrical equipment for measurement, control, and laboratory use.

Testing in production

Every instrument is routine-tested in the production division according to:

- EN/IEC 61010-1 Appendix F
Check of the protective conductor connection and the insulation from power circuit.

Electromagnetic compatibility (EMC)

VIONIC instrument has been built and has undergone final type testing according to the standards:

Requirements

- EN 61326-1:2013
Electrical equipment for measurement, control, and laboratory use - general EMC requirements.

Emission: Standards fulfilled

- EN 61000-3-2:2014
- EN 61000-3-3:2013
- EN 61326-1:2013

Immunity: Standards fulfilled

- EN 61326-1:2013

Manufacturer

Metrohm Autolab B.V., Woudwetering 3-5, 3543 AV Utrecht, The Netherlands

Metrohm Autolab B.V. is holder of the TŰV-certificate of the quality system ISO 9001:2015 for quality assurance in development, production, sales, and repair of measuring instruments and accessories in electrochemistry including technical support (registration number 7528).

Utrecht, September 8th, 2025

J. J. M. Coenen
Head of R&D

A. Idzerda
Head of Production

4 General overview and operating principle of the Autolab instrument

This chapter presents a general overview of the building bloks of the instrument as well as specific hardware properties which can influence the results of the electrochemical experiments.

4.1 Building blocks and operating principle of VIONIC powered by INTELLO

VIONIC powered by INTELLO is a computer controlled electrochemical instrument. VIONIC is developed with modern engineering practices, using the most sophisticated components on the market. The data communication is based on TCP/IP-Ethernet which gives a lot of unexplored possibilities. The functionality of the components is combined for use over different techniques. Components used for DC techniques, like Cyclic Voltammetry, are also used for AC techniques (such as EIS) and therefore, the use of optional additional modules for adding additional functionality or expanding the specifications is not necessary anymore.

The heart of the instrument is a dual core processor which enables flexibility for future developments and innovations in electrochemistry.

VIONIC instrument is powered by the INTELLO software which runs on a host computer.

The basic block diagram of VIONIC powered by INTELLO is represented in the figure below. In the block diagram, the analog signal path is shown in blue and the digital signal path is shown in orange. An analog-to digital (ADC) or digital-to-analog (DAC) conversion takes place every time the color of the path is changing.

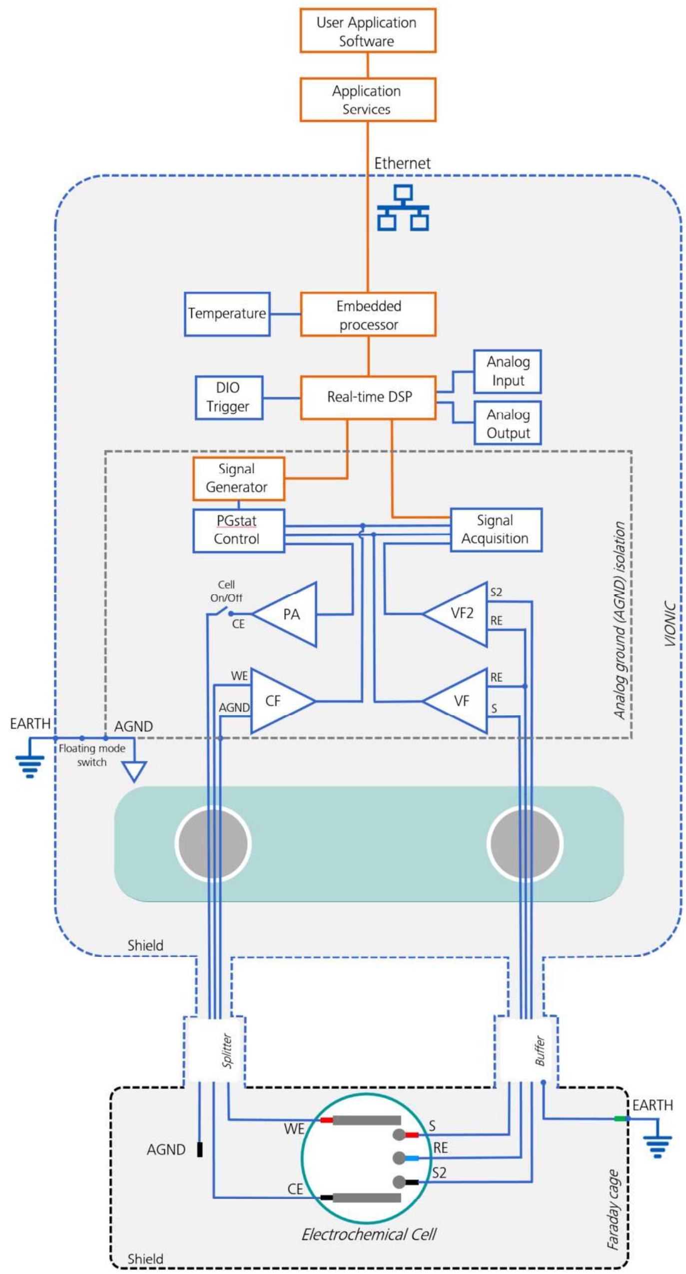


Figure 2 *Block diagram of VIONIC showing an optional Faraday cage. The analog signal path is shown in blue and the digital signal path is shown in orange.*

From top to bottom, the block diagram of VIONIC consists of:

- **The System software - INTELLO** The functionality of INTELLO is spread over the instrument and the host computer. The location for each software function was chosen based on feature and performance requirements keeping the flexibility in the software design to allow to adapt to future requirements in the ever-changing software landscape. The simplified design is comprised of the User Application Software, also known as the INTELLO User Interface, running on a host computer. The User Interface gives the user a powerful tool to create electrochemical procedures, to input experiment specific parameter settings, and to set the instrument in specific states. Standard measurement procedures as well as tailored procedures can be used to control the measurements.
- **The Application Services** is a middle-ware layer which takes care of many functions of the software including the data communication between the User Interface and lower level software located on the instrument. The customer cannot and does not have to interact or modify the Application Services.
  A single INTELLO installer and update process will install or update all software components.
- **TCP/IP-Ethernet connection interface** The communication is through TCP/IP-Ethernet which makes it possible to control and monitor the instrument from different places in a network.
- **Embedded processor and the Embeded software** The Embedded processor of VIONIC is a dual-core ARM processor and it communicates with the Application Services.
  The Embedded processor and the Embedded software take care of the control of the Real-time Digital Signal Processor (DSP). The measurements are executed with a very exact timing with an accuracy less than nanoseconds depending on the specified step duration.
  The Embedded processor and the Embedded software can also perform measurements of slowly changing signals (e.g. signals for which the accuracy of the timing is of less importance, such as temperature measurements).
  The Embedded processor and the Embedded software are also responsible for the synchronization of all the measured data.
  The Embedded processor and the Embedded software make it possible to continue a measurements when the connection to the Application Services and User Application Software is lost (e.g. when INTELLO is closed or the computer is switched off or disconnected). Disconnections can be accidental (e.g. computer crash), or deliberate (e.g. in the case of untethering, physically disconnect the computer from VIONIC). In this case, the internal memory of the instrument stores the measurement data and once the connection is restored, the data will be transferred to the database which is located on the host computer. The data from the database will be displayed in the User Interface of INTELLO.

- **Real-time digital signal processor (DSP)** The Real-time DSP, together with the Signal Generation and the Signal Acuisition block, is taking care of the exact timing of the signal generation and acquisition.
- **Signal generator** The Signal generator is used for the generation of the waveforms which are intended to be applied to the electrochemical cell.
- **PGSTAT control** The PGSTAT control block, as a whole, is responsible for the accurate control of the state of the electrochemical cell. It consists of the following parts: power amplifier (PA), Voltage Follower (VF), Current Follower (CF) and a Second Voltage Follower (VF2)
- **The Power Amplifier (PA)** is responsible for applying the signals to the Electrochemical cell. The PA is capable of applying both high and low power signals (DC and AC) in a fast way. The PA provides the output voltage on the Counter Electrode (CE) with respect to the Working Electrode (WE) required to keep the potential difference between the Reference Electrode (RE) and the Sense Electrode (S) at the user defined setpoint in potentiostatic mode, or the user required current through the Counter Electrode (CE) and the Working Electrode (WE) in galvanostatic mode.
- **The Voltage Follower (VF)** senses the voltage between the Reference Electrode (RE) and Sense Electrode (S). In Potentiostatic mode, this measured voltage is fed back to the PGSTAT control and Power Amplifier (PA) so that the voltage between RE and S is kept at the set value.
- **The Current Follower (CF)** measures the current which flows through the cell, between the Working Electrode (WE) and the Counter Electrode (CE). The current measurement sensors are sensing the current at the Working Electrode. In Galvanostatic mode this current is fed back to the PGSTAT control and Power Amplifier so that the current flowing through the cell is kept at the set value.
- **The second Voltage Follower (VF2**) measures a second voltage between the Reference Electrode (RE) and a Second Sense (S2). If S2 is connected to the CE, the voltage of the CE vs the RE can be monitored.
- **Signal acquisition block**The measured signals, voltage and current are sampled in a very accurate way by VIONIC's *True Parallel* Analog to Digital converter in the signal acquisition part. The smallest possible sampling interval is 1 µs for DC techniques like Cyclic Voltammetry and 40 ns for AC techniques (e.g. EIS). The measured signals are processed in the Real time DSP and derived signals such as the Charge (Q) are calculated and synchronized with externally measured signals. These signals are transferred to the Embedded processor and synchronized with less accurately timed signals such as the Temperature (T).

- **Cell On/Off Switch** is a software operated switch and is used to disconnect the Power Amplifier (PA) from the electrochemical cell, i.e. switch the cell off. If the cell is switched OFF, the potential measured between the WE and RE (with S connected to WE) corresponds to the Open Circuit Potential (OCP) and the current flow through the electrochemical cell will be interrupted (the current will be zero)
- **The Pure Signal Bridge** is used to connect VIONIC with the electrodes of the electrochemical cell (i.e. WE, CE, RE, S, S2). The Pure Signal Bridge is comprised of fixed cables ending with a set of connector boxes: the Splitter box and the Buffer box. The instrument specifications are guaranteed up to the connector boxes as there is no external or parasitic influence on the measuread and applied signal.
  The Adaptive Cables are the cables from the connector boxes to the electrodes. The Adaptive Cables are kept as short as possible in order to reduce signal losses through the cables. They are exchangeable and adaptive. i.e. different type of connectors are available. Any cables or adaptors which are used between the connector boxes and the electrochemical cell can affect the signal correctness. Therefore it is very important to use only original sets of adaptive cables.
  The EARTH connector is directly connected to the protective (safety) ground and it can be used to ground a Faraday cage or an external devicein order to reduce 50/60Hz noise pick-up. The entire Pure Signal Bridge allows you to create the best set-up for shielding against 50/60Hz disturbance.
  The AGND connector is directly connected to the electronic ground (analog ground) and it can be used in special cases only, such as Zero Resistance Ammeter (ZRA) or electrochemical noise (ECN) measurements executed in floating mode.
- **Selectable Floating switch** is a software operated switch and is used to switch VIONIC between non-floating and floating mode operation. When the instrument is operated in floating mode the protective EARTH will be isolated from the Analog Ground (AGND). In this case, the analog electronics is *floating* with respect to the protective EARTH.
  Non-Floating mode operation is the most common and it should be used all the time when none of the electrodes or parts of the electrochemical cell are grounded (have a direct connection to the Earth ground).
  Floating mode must be used for measurements on a grounded Working Electrode (WE), grounded Counter Electrode (CE) or in a grounded Electrochemical Cell like an autoclave or glovebox. External (normally grounded) devices can still be used when VIONIC is operated in Floating mode the external Analog input and output and DIO Trigger blocks are outside the floating ground part of the Analog electronics.

- **Temperature** measurement block has a dedicated electronic interface and used for connecting a standard thermocouple. This can be used to monitor the temperature in real time, during an experiment. The temperature signal is handled directly by the Embedded processor.
- **Analog Input/Output** is the I/O board used to monitor signals and interface exdevices. The timing of the external signals has the same accuracy as the main electrochemical signals measured from the electrochemical cell they being handled by the Real-Time DSP. The grounding of the I/O board is galvanically separated from the analog electronics of the PGstat control. This enables the use of non-floating external devices while VIONIC operates in Floating mode.
- **DIO Trigger** or the Digital I/O is part of the I/O board and is used to input and output digital signals. It is used for sending and receiving trigger (TTL).

When the instrument operates in Non-floating mode, the EARTH and AGND are internally connected to each other through the selectable floating switch.

When the instrument is operated in *Floating mode*, the analog ground (AGND) may NOT be connected to the EARTH ground (directly or through external devices).

When the instrument is operated in *Floating mode* and a thermocouple is plugged in the instrument and used for monitoring the temperature of the electrochemical cell, the outside of the thermocouple sensor which contacts the electrochemical cell must be insulated with an electric insulator.

4.2 VIONIC exterior

Below are the external parts of VIONIC which are part of the user experience during the instrument operation:

4.2.1 Front of the instrument

On the front of VIONIC the following individual parts can be identified:

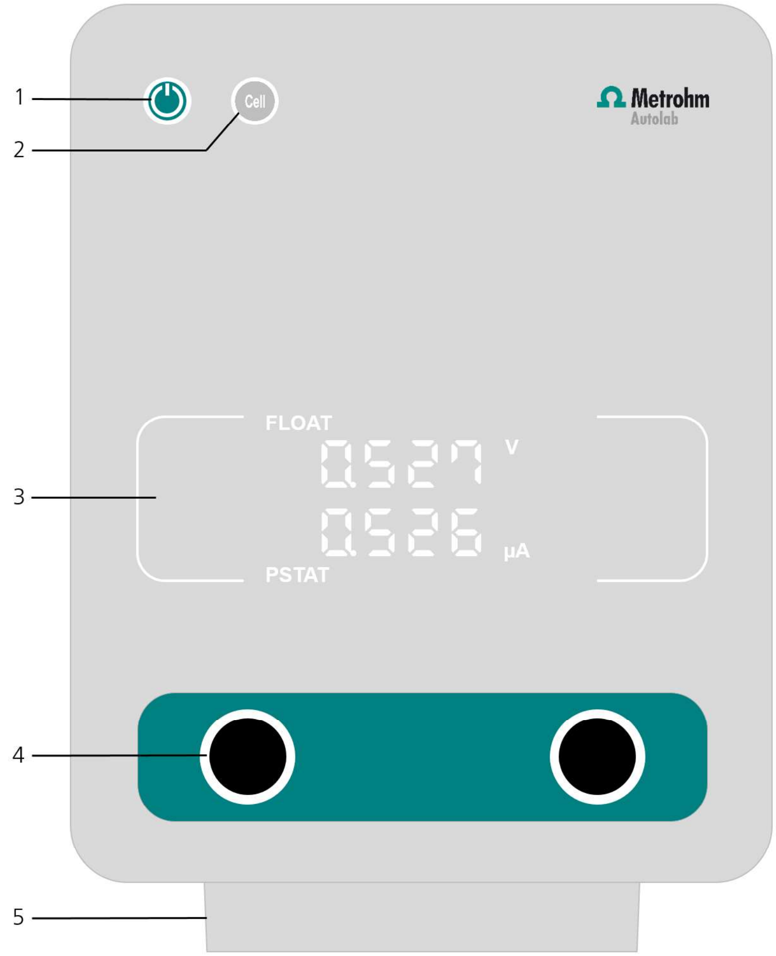


Figure 3 The front VIONIC

1	**Power button**	**2**	**Cell button**
3	**Functional and alphanumeric display**	**4**	**Cell cable block with cable light rings**
5	**Instrument foot (bottom part)**		

The **Dynamic interface** is a special and unique feature of VIONIC and it includes the Power (1) and the Manual Cell buttons (2), the Functional and alphanumeric display (3), the cell cable light rings (part of 4). The complete **Dynamic interface** is visible only when the instrument is powered on. For additional details on the Dynamic interface and stale indications, please see the dedicated paragraph.

4.2.2 Back panel

The back panel of VIONIC includes the following:

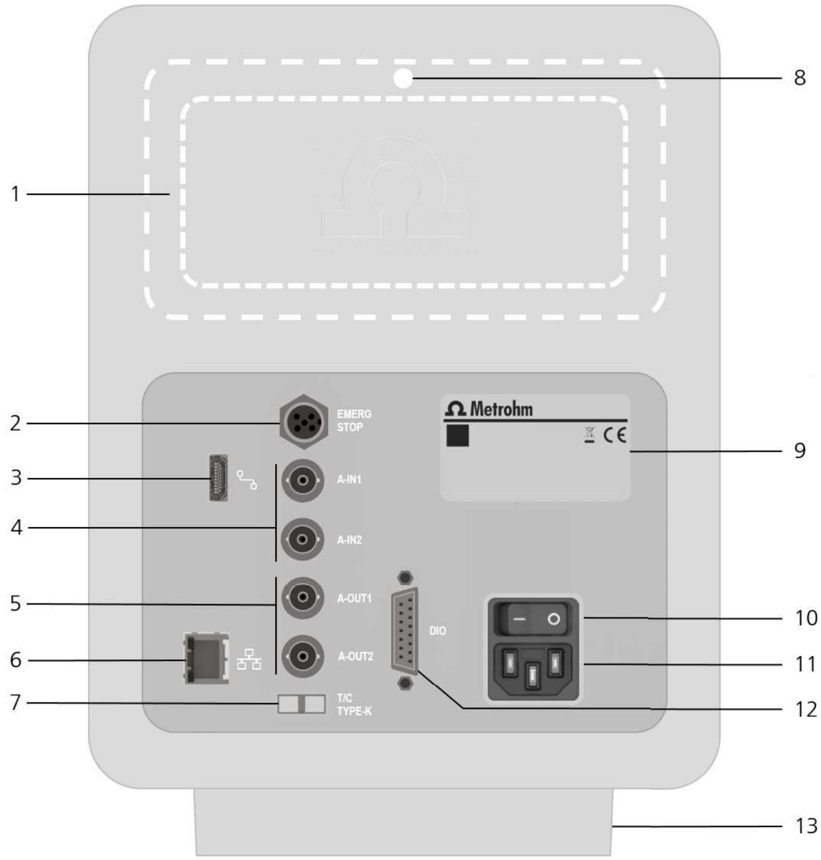


Figure 4 The back panel VIONIC

1	**Cooling fan**	**2**	**Emergengy stop button connection**
3	**Not used**	**4**	**Analog Input connectors (2x, BNC)**
5	**Analog Output connectors (2x, BNC)**	**6**	**Ethernet (LAN) connector**
7	**Thermocouple input connector (K-type)**	**8**	**Fixing screw for top and side pannels**
9	**Instrument label with serial number**	**10**	**Main power On/Off switch**
11	**Power net entry**	**12**	**Digital In/Out (DIO, Trigger) connector**
13	**Instrument foot (bottom part)**		

VIONIC can be opened only by Metrohm Autolab certified service personeel. Opening the instrument by non-certified personeel will void any instrument warranty.

4.2.3 Cell cables

VIONIC connects to the electrochemical cell through the Pure signal bridge:

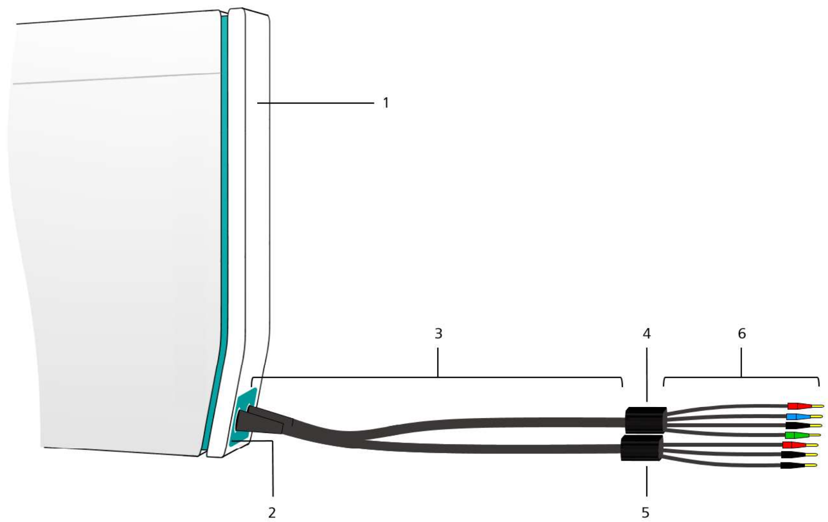


Figure 5 VIONIC Pure signal bridge with the included parts

1	**VIONIC**	**2**	**Cell cable connector bock (part of VIONIC)**
3	**Main cell cables, fixed, 1 m long**	**4**	**Buffer box, fixed to the main cable**
5	**Splitter box, fixed to the main cable**	**6**	**Removable adaptive cables, 0.5 m long**

The pure signal bridge consist of

- **Main cell cables**, 1 m long, fixed to the front of the instrument and directly connected to the main electronics of the PGSTAT through the **cell cable connector block**.
  The Reference (RE), Sense (S) and second Sense (S2) electrode leads (used for voltage measurements) are combined in one of the main cables and the Working (WE), Counter (CE) electrode (used for current measurements) together with the analog ground (AGND) leads are combined in the second main cable.
- **Buffer** and **Splitter** boxes, fixed to the main cell cables.
  The Buffer and Splitter boxes contain active electronics and will assure the accuracy and precision of the measured and applied signals to the electrochemical cell without any loss or distortion due to the cables. The buffer and the Splitter boxes are fixed to the main cables and cannot be removed.

- **Removable adaptive cables**, 0.5 m long, are used to physically connect VIONIC to the electrodes in the electrochemical cell. The adaptive cables connect to the Buffer and Splitter boxes with standard SMB and BNC connectors, respectively. The EARTH connector makes direct connection to the protective Earth ground through the enclosure of the Buffer box.

The technical specifications of VIONIC are guaranteed only when original adaptive cables are used. It is strongly recommended to avoid using any additional cables or adapters in the experimental setup.

The VIONIC instrument is delivered standard with the Pure signal bridge including one set of 4 mm banana connectors. If other type of connectors are needed, please see the optional adaptive cables available for VIONIC.

Figure 6 The Buffer (1) and Splitter (2) boxes with the connectors and labeling.

1	**Buffer box**
2	**Splitter box**

The following connectors are available from the Pure signal bridge (on the Buffer and Splitter boxes)

Table 3 Available connectors on the Pure signal bridge (Buffer and Splitter boxes)

Box	Label	Connector / socket	Description / Role
Splitter	WE	BNC	Internally connected to the current sensors in the instrument. Role in the control and measurements of voltage and current on the working electrode. Connects to the Working electrode in the electrochemical cell.

Box	Label	Connector / socket	Description / Role
Splitter	CE	BNC	Internally connected to the control amplifier in the instrument. Role in the control of the applied voltage and current to the cell. Connects to the Counter electrode in the electrochemical cell.
Buffer	RE	SMB	Internally connected to the voltage sensor. Role in the control and measurements of the voltage between the reference and sense electrodes. Connects to the Reference electrode in the electrochemical cell.
Buffer	S	SMB	Internally connected to the voltage sensor. Role in the control and measurements of the voltage between the reference and sense electrodes. Connects to the Sense electrode in the electrochemical cell..
Buffer	S2 (#)	SMB	Internally connected to the second voltage sensor. Role in the measurements of a second voltage between the reference and the second sense electrodes. Connects to the second potential sensing electrode in the electrochemical cell (e.g. Counter electrode). Only if needed. (#)
Splitter	AGND (#)	2 mm banana	Internally connected to the analog reference ground of the electronics. To be used as ground *only for ZRA measurements in floating operation mode or with the HF EIS cable set*. (#)
Buffer	EARTH (#)	4 mm banana	Connected to Earth ground of the power grid. Role in grounding connecting ancillary equipment and Faraday cages used in the experimental setup. (#)

(#) - to be used only if the application requires.

The removable Adaptive cables must be always connected according to the labeling available on the pure signal bridge. In case of Cross Floating mode operation, the labeling with the cross (X) sign must be used for connecting the Pure signal bridge to the electrochemical cell. Additional details are provided in the dedicated Floating mode operation and a connection guide is provided in the INTELLO user interface.

When the VIONIC is operated in floating mode, the EARTH ground connector continues to provide direct connection to the protective Earth ground. In this case (floating operation mode), DO NOT connect the analog ground (AGND) connector to the EARTH ground connector or to any devices which have direct connection to the protective ground.

- Do not modify the cell cables, the Buffer or Splitter boxes or the cable connectors.
- The external Buffer and Splitter boxes mounted on the cell cables are part of the complete instrument electronics and cannot be removed.
- The Pure signal bridge uses active (driven) shielding necessary for achieving the performance specifications of the instrument. They are specially designed for the best possible performance. The performance specifications of VIONIC are valid only when original cell cables are used. Modifications and repairs of the cables or connectors can be done only by Metrohm Autolab qualified personnel.
- The modification of the cables or connectors done by non-qualified personnel will lead to the loss of warranty.

4.2.4 Adaptive cables

The Adaptive cables are part of the Pure signal bridge of the VIONIC instrument making the connection between the instrument and the electrochemical cell. The Adaptive cables are 0.5 m long, removable and can be exchanged by the user. They connect to the Buffer and Splitter boxes with standard SMB and BNC connectors, respectively

The VIONIC instrument is **delivered standard** with the following:

- Adaptive cable set with 4 mm banana connectors (with isolation shield) consisting of:
  - Working electrode cable (WE), 0.5 m with red 4 mm male banana connector
  - Counter electrode cable (CE), 0.5 m with black 4 mm banana connector
  - Reference electrode cable (RE), 0.5 m with blue 4 mm banana connector
  - Sense electrode cable (S), 0.5 m with red 4 mm banana connector
  - Second Sense electrode cable (S2), 0.5 m with black 4 mm banana connector
- Earth ground cable (EARTH), 0.5 m with red 4 mm banana connectors
- High frequency cables with 4 mm banana connectors used for EIS measurements at frequencies higher than 1 MHz, consisting of:
  - Reference electrode cable (RE) for High frequency (HF) EIS measurements, 0.25 m with 4 mm banana connectors
  - Sense electrode cable (S) for High frequency (HF) EIS measurements, 0.25 m with 4 mm banana connectors
  - Ground bridge cable (EARTH/AGND) for High frequency (HF) EIS measurements, 0.25 m with 4 mm / 2 mm banana connectors

Details concerning the use of this cables are available in the chapter dedicated to the EIS accuracy and contour plot.

Figure 7 Standard Adaptive cable set, 0.5 m with 4 mm banana connectors

Figure 8 Standard EARTH cable, 0.5 m with 4 mm banana conectors.

Figure 9 High frequency (HF) cables used for EIS measurements at frequencies higher than 1 MHz, 0.25 m with 4 mm banana conectors.

Optional adaptive cables

For electrochemical cells which require different type of connections, the following type of adaptive cables are available *optionally*:

- Adaptive cable set including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with **isolated BNC cell connectors**. This cables and connectors are rated to *maximum 1 A* and they are recommended when connecting directly to feed-through components or other devices through BNC connections.

- Adaptive cable set including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m **with 2 mm banana cell connectors**. This cables are rated to *maximum 2.5 A* and they are recommended to be uesed with electrodes which have 2 mm female connector sockets.

- Adaptive cable set including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with **isolated Alligator clip cell connectors**. This cables and connectors are rated to *maximum 2.5 A* and they are recommended to be used when connecting to the electrodes by "clipping" directly to the contacts.

-
- Analog ground (AGND) cable for ZRA measurements in floating mode, 0.5 m with 4 mm / 2 mm banana connectors.

The technical specifications of VIONIC are guaranteed only when original adaptive cables are used. It is strongly recommended to avoid using any additional cables or adapters in the experimental setup.

The removable Adaptive cables must be always connected according to the labeling available on the pure signal bridge. In case of Cross Floating mode operation, the labeling with the ⤨ sign must be used for connecting the Pure signal bridge to the electrochemical cell. Additional details are provided in the dedicated Floating mode operation and a connection guide is provided in the INTELLO user interface.

- Do not modify the cell cables, the Buffer or Splitter boxes or the cable connectors.
- The external Buffer and Splitter boxes mounted on the cell cables are part of the complete instrument electronics and cannot be removed.
- The Pure signal bridge uses active (driven) shielding necessary for achieving the performance specifications of the instrument and are specially designed for the best possible performance. The performance specifications of the Autolab Instrument are valid only when original cell cables are used. Modifications and repairs of the cables or connectors can be done only by Metrohm Autolab qualified personnel.
- The modification of the cables or connectors done by non-qualified personnel will lead to the loss of warranty.

4.3 Dynamic Interface

The **Dynamic Interface** of VIONIC is the feature which allows the user to continuously follow the state of the instrument and experiment with a visual sharpness from a distance up to 6 m, in most laboratory conditions. It consists of an intuitive combination of visual indicators, colors and modulation patterns which is specific for each state the instrument is at a certain moment. The Dynamic interface gives the possibility to the user to move freely in the laboratory bringing additional efficiency and productivity.

The following **visual indicators** are part of the Dinamic interface:

- The **Power button**
- The **Cell button**
- The **Alphanumeric and functional display**
- The **Cell cable light rings**

The following **colors** are used on the instrument display:

- **White** indicating thet the instrument is ready and operates in normal conditions

- **Amber** (yellow), indicating that the instrument is booting or is in an untethered state (instrument continues to measure with the computer disconnected from VIONIC)
- **Red** indicating an instrument error state

The following **modulation patterns** are used on the instrument display:

- **Light Off** indicating that the action is paused or stopped
- **Continuous Light On** indicating a ready state
- **Flashing**, 3 Hz (fast) modulation, indicating that the user attention is needed
- **Heartbeat**, 0.5 Hz (slow) modulation, indicating that the instrument is busy

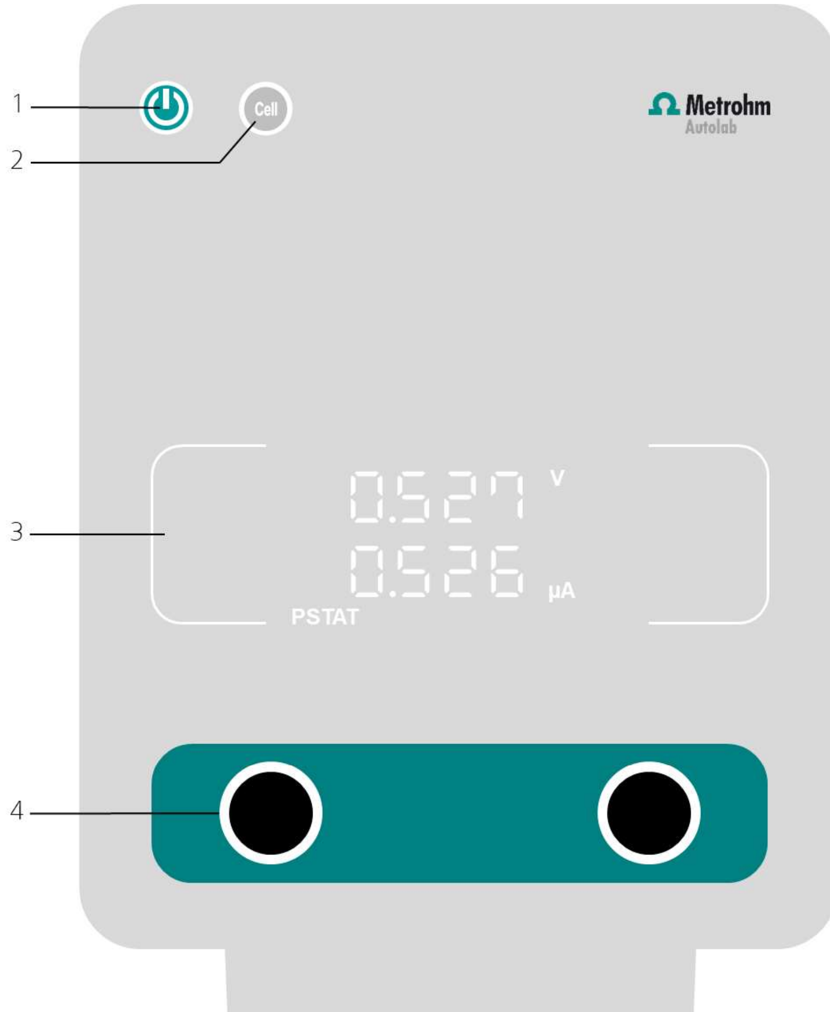


Figure 10 General overview of the instrument display.

1	**Power button** uses *white, amber and red light* with different modulation patterns indicating a specific state of the instrument.	**2**	**Cell button** uses *white light* with different modulation patterns indicating a specific state of the instrument.
3	**Functional and alphanumeric display** shows the instantaneous value of the measured/applied potential and current, the operation mode, floating mode, error state (if any), signal overloads	**4**	**Cell cable light rings** use *white light* with different modulation patterns indicating a specific state of the instrument.

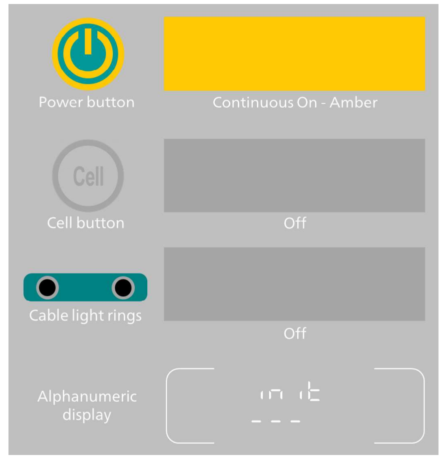
The detailed overview of each instrument state and the corresponding indication is presented in the dedicated paragraph.

4.3.1 VIONIC and experiment state indication

Below is a complete overview of the Dynamic Interface signage and the corresponding states of VIONIC and the measurement.

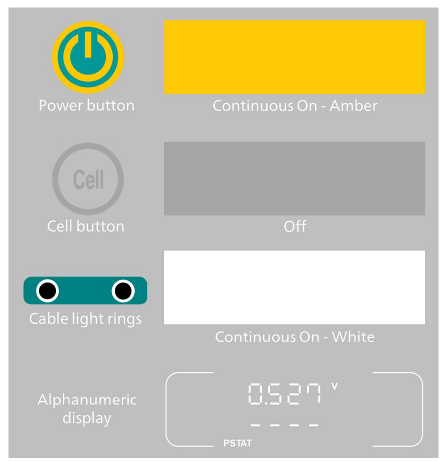
Initialization

- Vionic is booting after power on
- The state of the booting is indicated by the number of segments (between 1 and 4 segments) on the alphanumeric display



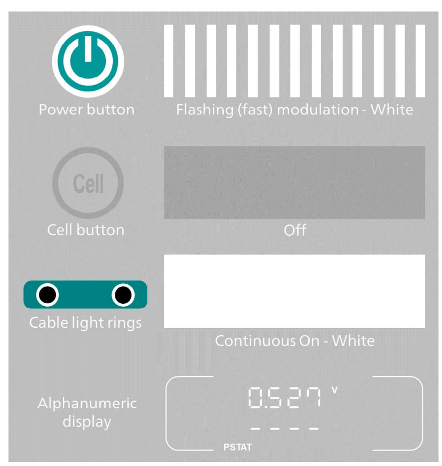
Ready for connection

- VIONIC finished booting and is waiting for connection to INTELLO
- The alphanumeric display shows the Open Circuit Potential (OCP). The cell is switched Off, no current flows through the cell (four dashes shown)



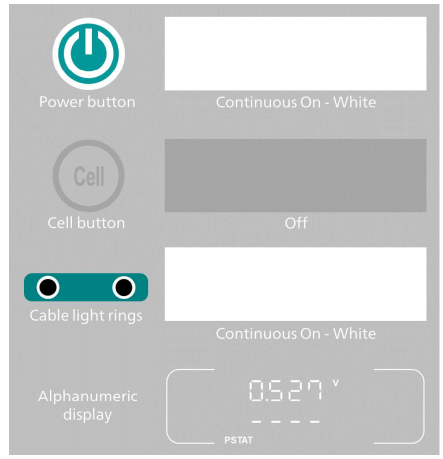
Claiming in INTELLO

- very short state which indicates the moment VIONIC is being claimed in INTELLO
- The alphanumeric display shows the Open Circuit Potential (OCP). The cell is switched Off, no current flows through the cell (four dashes shown)



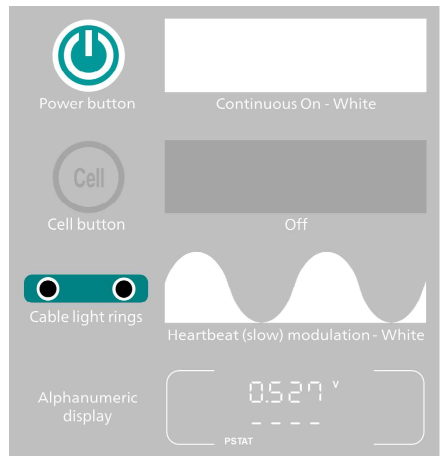
Ready to measure

- VIONIC is claimed in INTELLO and the measurement can be started anytime
- The alphanumeric display shows the Open Circuit Potential (OCP). The cell is switched Off, no current flows through the cell (four dashes shown)
- The default state after booting: PSTAT, non-floating, cell switched Off



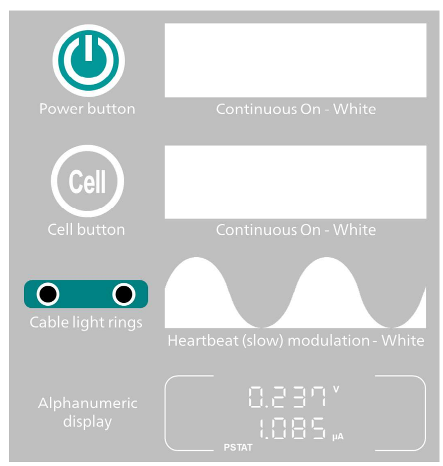
Measuring with Cell Off

- The measurement is started in INTELLO but the cell is not switched On in the procedure
- The alphanumeric display shows the Open Circuit Potential (OCP). The cell is switched Off, no current flows through the cell (four dashes shown)



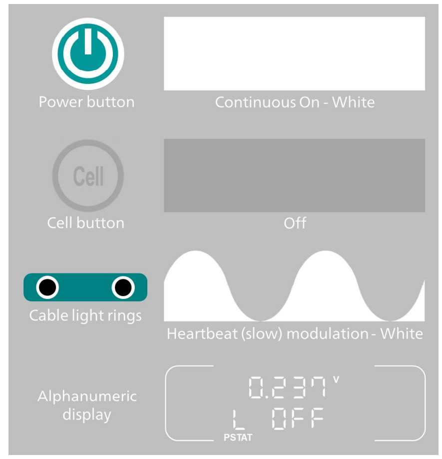
Measuring with Cell On

- The measurement is started in INTELLO and the cell is switched On in the procedure
- The alphanumeric display shows the applied/measured signals with the corresponding units or subunits



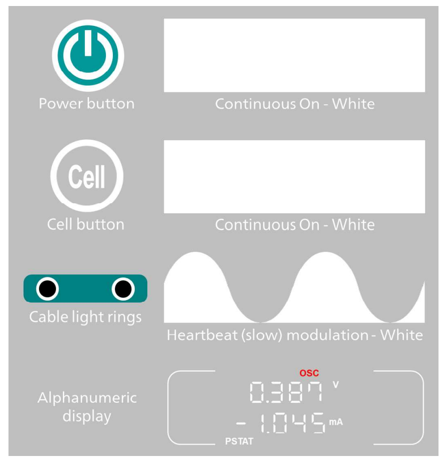
Cell Off from Cell button

- The measurement is started in INTELLO
- The user switches the cell Off from the manual Cell button on the instrument
- The alphanumeric display shows the OCP and the "CELL OFF" text is scrolling
- The cell can be switched On only from the manual cell button



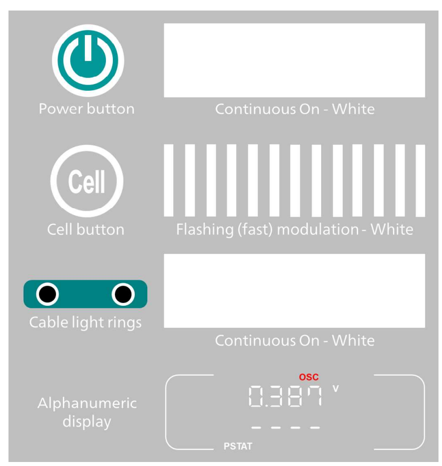
Oscillation detection

- Oscillation is detected during the measurement
- The cell stays On and the measurement continues
- The alphanumeric display shows the applied/measured signals with the corresponding units or subunits and the red "OSC" indication



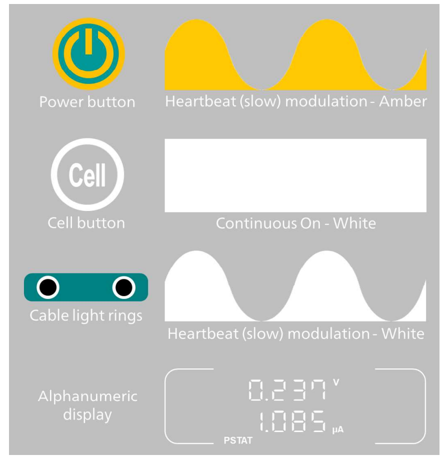
Oscillation detection and protection

- Oscillation is detected during the measurement
- The cell is switched Off and the measurement is aborted
- The End state set in the procedure in INTELLO is applied



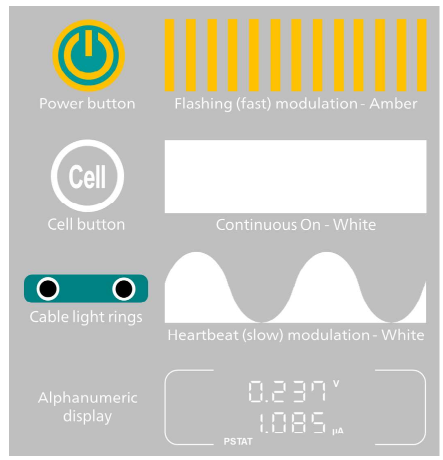
Connection lost, measuring

- Connection to computer lost due to Untethering or disconnection
- Measurement continues to run until user intervention is necessary



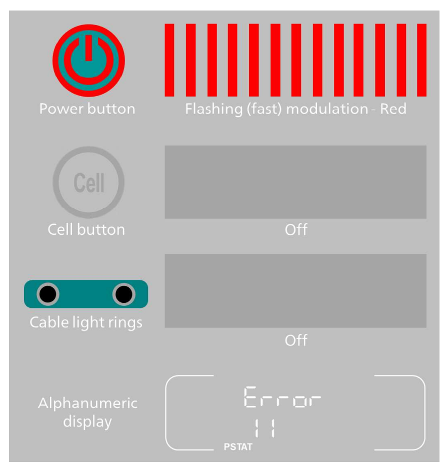
Connection lost, user intervention required

- Connection to computer lost due to Untethering or disconnection
- User intervention is needed:
  - user input required to continue
  - memory buffer limit at 80% or higher



Error mode

- the instrument is in error mode
- Error code is displayed
- Contact the local Metrohm Autolab support office



Additional details about the indicators used on the alphanumeric display can be found in the dedicated paragraph.

4.3.2 Alphanumeric display

Part of the Dynamic Interface, the VIONIC is equipped with a 7-segment alphanumeric multi functional LED display. The alphanumeric display shows in real time the applied and measured potential and current values, the mode of operation (potentiostatic or galvanostatic, floating, cross-floating or non-floating). Additionally, the alphanumeric display informs about any overloads which are detected during the measurement and when the instrument is in oscillation mode (i.e. control loop is out of control).

The following individual fields are available on the alphanumeric display:

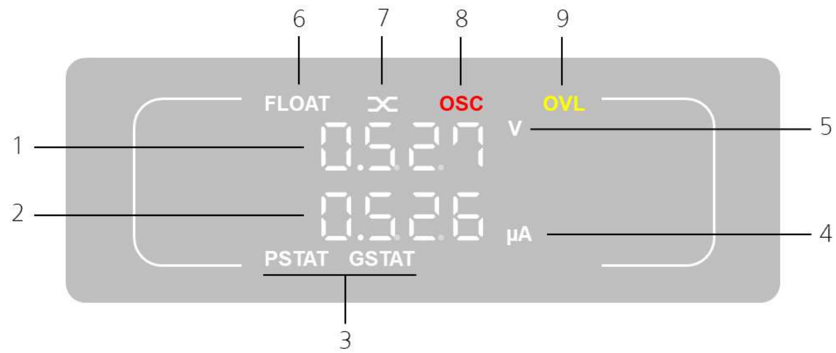


Figure 11 Detailed overview of the numeric and functional display

1 Applied / measured potential displays in real time the value of the applied or measured, in V or sub-units of V.	**2 Measured / applied current** displays in real time the value of the measured or applied current, in A or sub-units of A.
3 Instrument mode displays the mode of operation of the instrument: Potentiostatic (PSTAT) or Galvanostatic (GSTAT).	**4 Units and sub-units of current** displays the units or sub-units of Ampere of the measured or applied current signal.
5 Units and sub-units of potential displays the units or sub-units of Volt of the measured or applied potential signal.	**6 Floating mode** indicates VIONIC operates in floating mode (analog ground (AGND) disconnected from Earth ground (EARTH)). Switching between floating and non-floating is done in INTELLO.

7 Cross-Floating mode
indicates when VIONIC operates in the Cross-Floating mode (special Floating mode used for grounded Working electrodes (WE)). Switching between floating and non-floating is done in INTELLO.

8 Oscillation
indicates an oscillation state of the control loop (control loop of control). When the Oscillation protection is activated in INTELLO, the Cell is automatically switched Off.

9 Overload
the OVL indicator is activated by the overload detection circuit which is part of VIONIC. The instrument recovers from an overload state as soon as the signal is not exceeding the overload limit.

The refresh rate of the Alphanumeric display is 500 ms.

The displayed parameter values and settings are volatile properties. In order to record and save the parameters and settings, INTELLO must be used.

The measured / applied potential and current parameters are displayed with four significant digits. The units and sub-units are automatically adjusted

4.4 Bandwidth: General definition

In simple and general terms, bandwidth can be described as the parameter that defines how fast the instrument is able to react to any changes of the signal.

The bandwidth of an electronic circuit is taken as the frequency range (in Hz) for which the output amplitude of a signal can be maintained to a certain treshold value (e.g. 70%) of the level of the input (i.e. unaffected) signal. In a more practical approach, the bandwidth is the frequencies beyond which the performance of the system is degraded.

A common way of specifying the treshold value is in dB and a typical, widely used threshold value is -3 dB defined relative to the maximum (input signal) value.

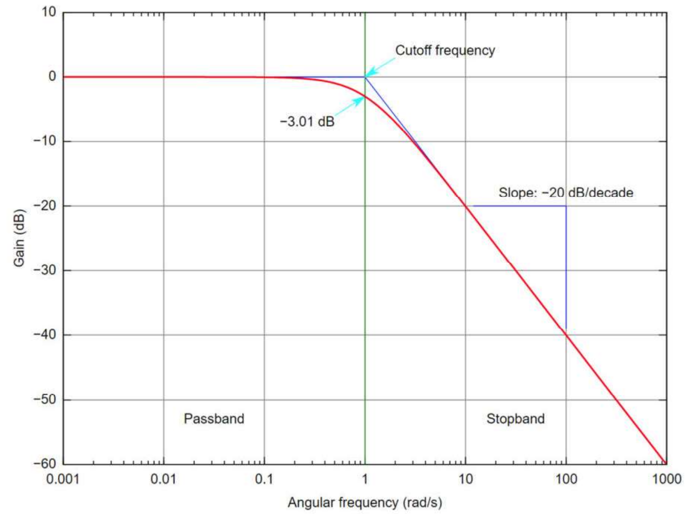


Figure 12 General example of bandwidth, treshold and decaying signal.

In the general example shown in the figure above, the signal is being unaffected until 70% (threshold) of the frequency value, after which the signal is starting to decay.

If we consider a signal decay with a slope of 20 dB per decade, to calculate the threshold in percentage (%):

$$10^{-\frac{treshold\,(dB)}{decay\,slope\,(dB/decade)}} = 10^{-\frac{3\,dB}{20\,dB/decade}} = 70\%$$

4.4.1 Bandwidth of VIONIC

In electrochemical research, the speed and stability of the measurement is very important. Therefore, bandwidth is an important specification which defines the speed and stability of any electrochemical setup. In order to collect valid experimental results, choosing the optimal measurement conditions for any type of electrochemical cell and any type of experiment is crucial.

It is important to keep in mind that the electrochemical cell is always part of the electrochemical setup and the PGstat control (feedback) loop (independently of the measurement modes used). The electrochemical cell directly influences the speed and stability of the complete electrochemical setup. Depending on the electrochemical system investigated in the cell, the stability and speed of the measurement might be limited by the cell. For example, high capacitive and high resistance cells will have a slow response time (i.e. high RC constant of the cell) while cells with high capacity and low resistance may cause stability problems and even oscillations especially when the instrument in high speed mode.

In this chapter, the following VIONIC and INTELLO specific bandwidth considerations are presented:

- Bandwidth of the coltrol loop of the potentiostat
- Bandwidth of the Galvanostatic control loop
- Bandwidth selection in case of Electrochemical Impedance (EIS) measurements

4.4.1.1 Bandwidth of the PGSTAT control

The bandwidth of the **control loop** of the PGstat (i.e. bandwidth of the instrument) indicates how fast the applied signal is controlled through the feedback loop of the power amplifier (PA).

In Potentiostatic mode, the measured voltage is fed back to the PGStat control loop and the power amplifier so that the voltage between reference electrode (RE) and the sense electrode (S) is kept constant. In Galvanostatic mode the current is fed back to the PGStat control loop and the power amplifier so that the current flowing through the cell, between the working electrode (WE) and the counter electrode (CE) is kept constant.

Higher bandwidth means that the instrument uses a faster control loop (faster feedback). As a consequence, the applied signal will reach the desired set point faster and in ideal circumstances, the output signal will be identical with the theoretical waveform. However, *depending on the properties of the electrochemical cell* connected to the instrument , the applied signal might overshoot and in extreme cases, the instrument feedback loop might get out of control making the potentiostat to oscillate.

Lower bandwidth settings increase in the overall stability of the PGstat by reducing the speed of the control loop. In this case, the consequence is that, for very high measurement speeds, the output of the applied signal might be slightly less accurate (slower slew rate). Nevertheless, for experiments which do not require a very small timebase (i.e. high speed measurements), using the instrument with a lower bandwidth setting is recommended allowing highly accurate experimental results.

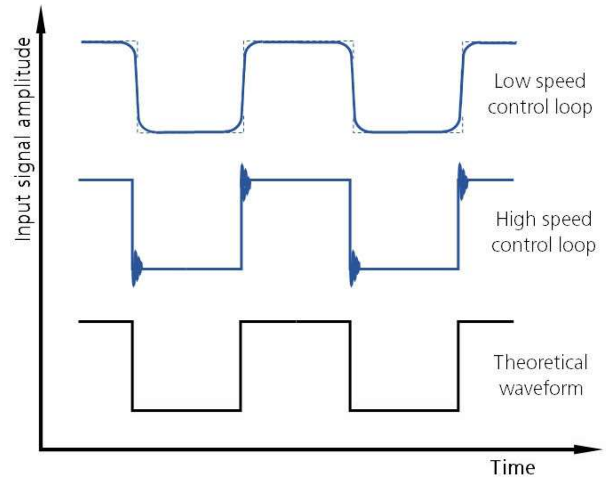


Figure 13 Graphical illustration of the resulting waveforms compared with the theoretical one when the PGSTAT control loop is set in higher and lower speed modes.

There are three control loop bandwidths available in VIONIC:

- 10 kHz - High stability - recommended when measurements use sampling intervals are higher than 100 µs
- 100 kHz - Fast - recommended when measurements use sampling intervals between 10 µs and 100 µs
- 1 MHz - Ultrafast - recommended when measurements use sampling intervals smaller than 10 µs

The bandwidth of the control loop of the VIONIC instrument can be set in INTELLO.

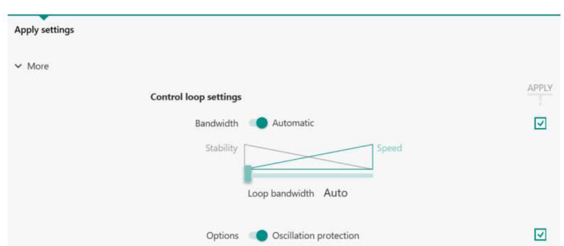


Figure 14 Bandwidth selection in the Application settings command in INTELLO

When the *Automatic* bandwidth selection is enabled, the optimal bandwidth of the control loop is selected automatically based on the measurement parameters set in the procedure.

The PGSTAT bandwidth can be also set manually, if the experiments requires. In this case, the user can decide between speed and stability of the measurement. As a general guideline, the following correlation between bandwidth of the control loop and the sampling interval (or the time base of the measurement) helps to assure the highest accuracy of the applied and measured signal (i.e. no waveform distortions relative to the used time base)

$$PGSTATBW \geq \frac{1}{Sampling\ \ Interval}$$

The bandwidth selection of control loop is part of the Apply settings command, in INTELLO. The default PGSTAT control bandwidth setting is *Automatic*. Please see additional details in the dedicated chapter presenting the details of the Apply settings commend.

Faster measurements may require a higher bandwidth setting but the risk of oscillations is also higher when compared with operation on lower bandwidth modes. This is especially the case with electrochemical cells exhibiting a high capacitance. There is a significant oscillation risk in this mode of operation and, additionally, the noise in the measured potential and current signals will be higher when compared with measurements done with lower bandwidth selected.

High speed control loop bandwidth (1 MHz) is needed only in experiments where the sampling interval is smaller than 10 µs

The higher the bandwidth, the higher the noise and probability of oscillation.

When working with a high bandwidth setting, it is necessary to pay attention to adequate shielding of the cell and electrode connectors. The use of a Faraday cage is recommended in these cases.

The use of a high impedance reference electrode (RE) (e.g. double junction reference electrode, a salt bridge with frit) in combination with a high bandwidth of the control loop might lead to an instability of the PGstat and even to oscillations. The use of the *Oscillation protection* option is recommended.

When VIONIC is operated in galvanostatic mode, the bandwidth of the control loop is influenced and limited by the bandwidth of the current sensing circuit (i.e. current range) used.

4.4.1.2 Bandwidth of the current ranges

VIONIC measures the current response of the electrochemical cell (in potentiotatic mode) and controls the value of the applied current (in galvanostatic mode) with specially designed current sensors. In order to achieve the best sensitivity and resolution for the measurement, individual current sensors are used depending on the magnitude of the measured current. When a specific *current range* is selected in the software, the correspondig *current sensing* circuit will be used for the current measurement.

The selection of the current range which is used during a measurement can be done *automatically* by VIONIC and INTELLO or it can be selected *manually* by the user.

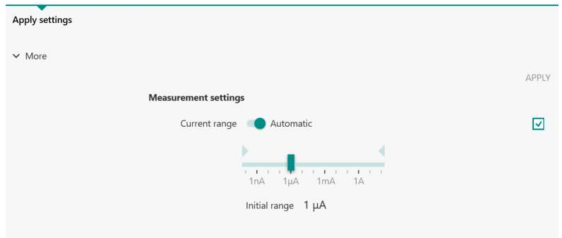


Figure 15 Automatic current range selection in the Apply settings command in INTELLO

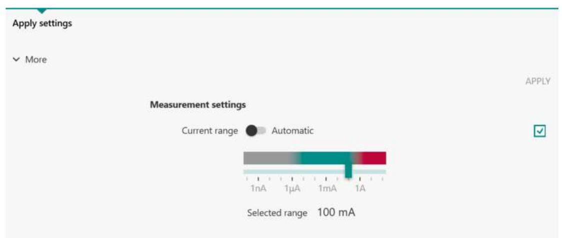


Figure 16 Manual current range selection in the Apply settings command in INTELLO

When the current range selection is set to *Automatic* in Potentiostatic mode, VIONIC and INTELLO will choose the optimum current sensing circuit for the measurement, based on the magnitude of the measured current and the sampling interval used. In case the application requires to use *Manual* current range selection, the desired current sensor can be selected in INTELLO by disabling the Automatic current ranging and selecting the current sensor which is the most appropriate for the measurement.

The use of the *automatic* current ranging is highly recommended for measurements done in potentiostatic mode.

In galvanostatic mode, the use of automatic current ranging is not possible. The manual selection of the appropriate current range is necessary before the respective current is applied to the cell.

Each current sensor circuit (which corresponds to a current range) has a specific bandwidth (response time). Therefore, for accurate results, especially important for fast, time resolved experiments, the bandwidth of the current range should not be the limiting factor for the time response (speed) of the measurement. This becomes more important when currents sensors having a lower bandwidth (low current ranges) are selected for the measurement.

The maximum bandwidth for each current sensor and the respective current range are presented in the table below.

Table 4 Maximum bandwidth of the current ranges (current sensors) use

Current range	Bandwidth
1 nA	140 Hz
10 nA	140 kHz
100 nA	1.4 kHz
1 µA	14 kHz
10 µA	140 kHz
100µA	300 kHz
1 mA	1.5 MHz
10 mA	11 MHz
100 mA	11 MHz
1 A	3 MHz
10 A	3 MHz

It is important to keep in mind that the electrochemical cell is always part of the electrochemical setup and the PGstat control (feedback) loop (independently of the measurement modes used). The electrochemical cell directly influences the speed and stability of the complete electrochemical setup. Depending on the electrochemical system investigated in the cell, the stability and speed of the measurement might be limited by the cell. For example, high capacitive and high resistance cells will have a slow response time (i.e. high RC constant of the cell) while cells with high capacity and low resistance may cause stability problems and even oscillations especially when the instrument in high speed mode.

The time constant of the cell is an exclusive property of the cell and is NOT influenced by the instrument.

4.4.1.3 Bandwidth selection in case of Electrochemical Impedance (EIS) measurements

In case of Electrochemical Impedance Spectroscopy (EIS) measurements, a frequency scan of an AC signal is applied to the electrochemical cell and the AC response is measured and analyzed. Obviously, to measure the response of the electrochemical process in the cell, both the applied and measured AC frequencies cannot be obstructed by any bandwidth limitations of the instrument.

From the VIONIC and INTELLO perspective, for EIS measurements, the bandwidth selection of the control loop is done automatically when enabled in the Apply settings command in INTELLO. In this case, always the optimal bandwitdth will be used depending on the applied EIS frequency range.

For EIS measurements at higher frequencies (i.e. above 1 MHz), a specially designed high speed path is used automatically for the AC signals.

Within the EIS frequency scan command, it is possible to optimization of the EIS measurement for speed and quality. This setting is NOT related to bandwidth selection but rather to EIS-specific settings such as the integration time. If higher speed is selected, lower integration times are used. If higher quality is selected, longer integration times are used for the AC signals

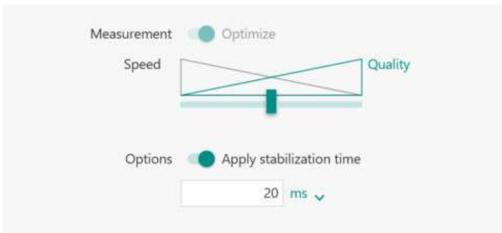


Figure 17 EIS measurement optimization option in the EIS frequency scan command. This option does NOT involve and is not related to any change in bandwidth selection.

4.4.2 Input impedance and stability

In real life, a voltage signal needs to be buffered by an amplifier to protect the cell from leakage currents. Additionally, any real life amplifier has a parasitic impedance including a capacitance. Therefore, the voltage follower (VF) input also contains a small capacitive load.

When working in Potentiostatic mode, if the capacitive part of the impedance between CE and RE in the electrochemical cell is comparatively larger than the input capacitance of the voltage follower, a phase shift between the output signal of the amplifier and the signal which is fed back to the amplifier will occur. When this phase shift is higher than a certain threshold, it can lead to instability problems.

If the impedance between the CE and the RE in the cell cannot be changed and oscillations are observed, it is recommended to select a *lower bandwidth for the PGSTAT control loop*. In this way, the system stability is increased. In general, the use of lower bandwidth leads to a more stable control loop, when compared to the case when high and very high PGSTAT control bandwidth is used.

To make use of the full potentiostat bandwidth, the impedance between CE and RE in the electrochemical cell has to be lower than 35 kΩ. This value is derived by testing. In galvanostatic mode, a large impedance between CE and RE will usually not lead to stability problems though, because of the current feedback regulation.

4.5 Resolution specifications

The *potential* and the *current*, both applied and measured, are the most important signals in electrochemical measurements. During a measurement, the potential and the current must be controlled and monitored and the precision and accuracy of these signals should not be the limiting factor of the experiment.

When modern instrumentation is used, a continuous conversion is needed between the analog signals (as measured from the electrochemical cell) and digital signals (as used by modern electronics and computers). The conversion is done by the Analog to Digital (ADC) and Digital to Analog converters (DAC).

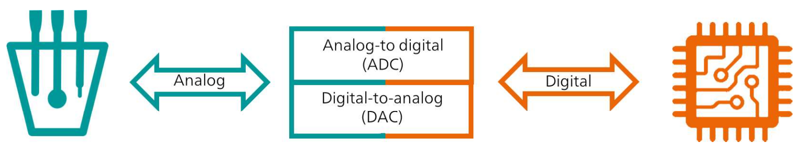


Figure 18 Basic representation of the signal path from the electrochemical cell (left) to the digital electronics of the instrumentation (right). Analog path - green, Digital path - orange.

One of the important specifications of the Analog to Digital (AD) or Digital to Analog (DA) converters is the *resolution*.

The *resolution* is given by number of available digital segments per total range of the analog signal. The smallest, physically detectable change in a signal is limited by the resolution of the measuring device. A higher resolution means that smaller changes of the signal can be detected

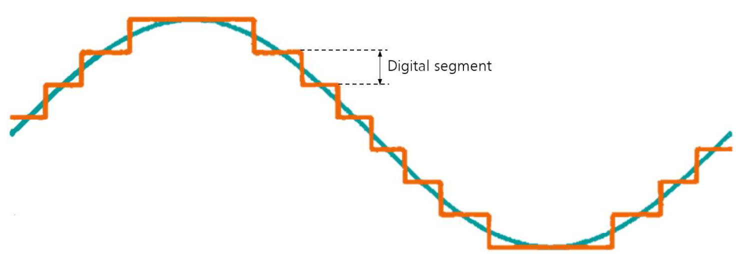


Figure 19 Analog signal (green, smooth) converted to a Digital signal (orange, staircase). The smallest digital segment (resolution) is shown.

The main factors which influence the signal resolution of an instrument are:

- The designed resolution specification of the ADC and DAC
- The input voltage range of the ADC and DAC
- Internal signal amplification possibilities (Gaining)
- Additional signal amplification circuits in the instrument
- Resolution enhancement by oversampling and averaging (DC sampling)

For VIONIC powered by INTELLO, the resolution specifications apply to the following signals:

Table 5 Type of signals in VIONIC powered by INTELLO

Signal/Type	Applied, DC	Applied, AC	Measured, DC	Measured, AC
Potential, (WE.Potential)	✓	✓	✓	✓
Second sense potential, (S2.Potential)	n.a.	n.a.	✓	✓
Current, (WE,Current)	✓	✓	✓	✓

In general, there is always a compromise between the resolution value of the ADC and DAC and the conversion speed. Using the highest resolution converters will limit the conversion speed. Therefore, for the user is important to understand the needed performance (resolution vs speed) and the limiting factors of the real experiment.

Having the *true parallel* feature, VIONIC allows for the *highest AD and DA conversion speed and the resolution enhancement through oversampling and averaging* (DC Sampling, see later in this chapter).

VIONIC is designed with a *true paraller* data aquisition. This means that there are dedicated AD and DA converters for the each measured and applied electrochemical signals: Potential, Second sense potential and Current which results in the highest sampling rates and highest synchronization accuracy between the measured and applied signals.

4.5.1 Potential resolution (WE.Potential)

The potential signal in INTELLO *(E, WE.Potential)* is the potential between the Reference (RE) and the Sense electrode (S) (V_S - V_{RE}).

The measured and applied potential range of the *WE.Potential* signal is ±10 V (i.e., a range of 20 V)

The AD and DC converters used for the *WE.Potential* signal have the following specifications:

Parameter	Value
Resolution specification of the ADC and DAC	18-bit (2^{18} digital words per range)
Input voltage range of the ADC and DAC	±2.5 V (5 V range)
Internal Gain factor *	0.2

* The ADC and DAC input range is ±2.5 V. Therefore a gain factor of 0.2 is internally used to reduce the ±10 V range of the *WE.Potential* signal to ±2 V range.

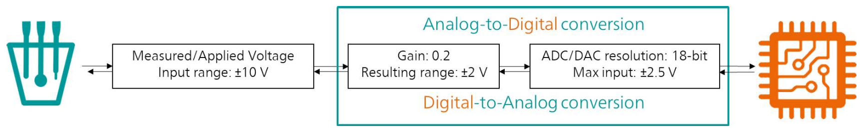


Figure 20 Schematic representation of the AD and DA conversion for the WE.Potential signal path with the applicable specifications and conversion factors.

DA and AD conversion resolution ($R_{E,DA/AD}$)

$R_{E,DA/AD}$ is the resolution of the measured and applied potential signal which results from the 18-bit AD and DA converters considering the specifications mentioned above. The resolution value is:

$$R_{E,DA/AD} = \frac{5\ V}{2^{18} \times 0.2} \cong 100\ \mu V$$

The above value is valid for both the **applied** and the **measured** potential.

Measured DC resolution ($R_{E,Meas,DC}$)

$R_{E,Meas,DC}$ is the resolution of the measured potential signal which results from the 18-bit AD converters considering the specifications mentioned above, which is further enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). The measured DC resolution (system DC resolution) value is:

$$R_{E,Meas,DC} = \frac{5\ V}{2^{24} \times 0.2} \cong 1.5\ \mu V$$

The above value is valid for the **measured, DC** potential signals. For CV staricase or Chrono methods techniques, the sampling interval in the procedure must be at least 16.4 ms (when at least 4096 points are aquired during a mains frequency period). When the sampling conditions are met, the measured potential signal resolution ($R_{E,DA/AD}$) is automatically enhanced to the measured DC resolution ($R_{E,Meas,DC}$).

Measured AC resolution ($R_{E,Meas,AC}$)

$R_{E,Meas,AC}$ is the resolution of the measured potential signal which results from the 18-bit AD converter considering the specifications mentioned above, with the measured potential signal being further amplified 128x by a dedicated amplification circuit (Zoom path). The AD resolution is also enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). The measured AC resolution (system AC resolution) value is:

$$R_{E,Meas,AC} = \frac{5\ \mathrm{V}}{2^{24} \times 0.2 \times 128} \cong 12\ \mathrm{nV}$$

The above value is valid for the **measured, AC** potential signals. For EIS techniques, the the maximum frequency where the Zoom path is used is 20 Hz. When the sampling conditions are met (measured AC signals, < 20 Hz), the measured potential signal resolution ($R_{E,DA/AD}$) is automatically enhanced to the AC resolution ($R_{E,Meas,AC}$).

There are no user selectable settings which are necessary to apply to achieve the best system resolution. When the sampling conditions are met, the measured potential signal resolution (ADC resolution) ($R_{E,DA/AD}$) is automatically enhanced to the best possible system resolution value.

4.5.2 Current resolution (WE.Current)

The current *(i, WE.Current)* signal in INTELLO is the current measured between the Counter (CE) and the Working electrode (WE).

The current (i) is measured with dedicated electronic circuits (current sensors) for each current range (CR) which also act as current-to-voltage converters. The voltage output of the CR circuits is proportional to the measured current with a maximim of 5V for the full scale current range.

The AD and DC converters used for the *WE.Current* signal have the following specifications:

Parameter	Value
Resolution specification of the ADC and DAC	18-bit (2^{18} digital Words per range)
Input voltage range of the ADC and DAC	±2.5 V (5 V range)
Internal Gain factor *	1

* In this case, no additional gaining factor is applied (Internal Gain factor = 1)

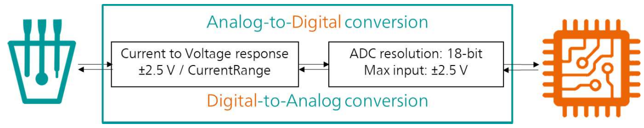


Figure 21 Schematic representation of the AD and DA conversion for the WE.Current signal path with the applicable specifications and conversion factors.

DA and AD conversion resolution ($R_{i,DA/AD}$)

$R_{i,DA/AD}$ is the resolution of the measured and applied current signal which results from the 18-bit AD and DA converters considering the specifications mentioned above. Considering the 1 nA (10^{-9}A current range, the current resolution for this current range is:

$$R_{i,DA/AD} = 10^{-9}[A/V] \times \frac{5\,[V]}{2^{18}} \cong 20\ fA$$

The above value is valid for both the **applied** and the **measured** current.

Measured DC resolution ($R_{i,Meas,DC}$)

$R_{i,Meas,DC}$ is the resolution of the measured current signal which results from the 18-bit AD converter considering the specifications mentioned above, which is further enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). Considering the 1 nA (10^{-9}A current range, the measured DC current resolution (system DC resolution) value is:

$$R_{i,Meas,DC} = 10^{-9}[A/V] \times \frac{5\,[V]}{2^{24}} \cong 300\ aA$$

The above value is valid for the **measured, DC** current signals. For CV staricase or Chrono methods techniques, the sampling interval in the procedure must be at least 16.4 ms (when at least 4096 points are aquired during a mains frequency period). When the sampling conditions are met, the measured current signal resolution ($R_{i,DA/AD}$) is automatically enhanced to the measured DC resolution ($R_{i,Meas,DC}$).

Measured AC resolution ($R_{i,Meas,AC}$)

$R_{i,Meas,AC}$ is the resolution of the measured current signal which results from the 18-bit AD converter (considering the conversion specifications mentioned above) with the measured current signal being further amplified 128x by a dedicated amplification circuit (Zoom path). The AD resolution is also enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). Considering the 1 nA (10^{-9}A current range, the measured AC current resolution (system AC resolution) value is:

$$R_{i,Meas,AC} = 10^{-9}[A/V] \times \frac{5\,[V]}{2^{24} \times 128} \cong 2.3\ aA$$

The above value is valid for the **measured, AC** current signals. For EIS techniques, the the maximum frequency where the Zoom path is used is 20 Hz. When the sampling conditions are met (measured AC signal, < 20 Hz), the measured current signal resolution ($R_{i,DA/AD}$) is automatically enhanced to the AC resolution ($R_{i,Meas,AC}$).

There are no user selectable settings which are necessary to apply to achieve the best system resolution. When the sampling conditions are met, the measured potential signal resolution (AD resolution) ($R_{i,DA/AD}$) is automatically enhanced to the best possible system resolution value.

4.5.3 Second Sense (S2) potential resolution (S2.Potential)

The Second Sense potential *(S2, S2.Potential)* signal in INTELLO is the measured potential between the Reference (RE) and the Second Sense electrode (S2) (V_{S2} - V_{RE}).

The Second Sense (S2.Potential) is always a measured signal. It is not possible to apply (i.e., control) the S2.Potential. For additional details about the functionality of the Second Sense (S2) and the possible cell connections, please see the dedicated pragraphs in this User Manual.

The maximum measured potential range (in High compliance mode) of the *S2.Potential* signal is ±50 V (i.e., a full range of 100 V)

The AD and DC converters used for the *S2.Potential* signal have the following specifications:

Parameter	Value
Resolution specification of the ADC and DAC	16-bit (2^{16} digital words per range)
Input voltage range of the ADC	±2.5 V (5 V range)
Internal Gain factor *	0.04

* The ADC input range is ±2.5 V. Therefore a gain factor of 0.04 is internally used to reduce the ±50 V range of the *S2.Potential* signal to ±2 V range.

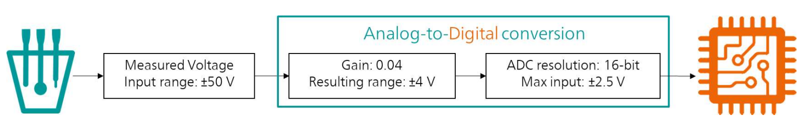


Figure 22 Schematic representation of the AD and DA conversion for the S2.Potential signal path with the applicable specifications and conversion factors.

AD conversion resolution ($R_{S2,AD}$)

$R_{S2,AD}$ is the resolution of the measured Second Sense potential *(S2.Potential)* signal which results from the 16-bit AD converters considering the specifications mentioned above. The resolution value is:

$$R_{S2,AD} = \frac{5\text{ V}}{2^{16} \times 0.04} \cong 2\text{ mV}$$

The S2.Potential signal is always a **measured** potential.

Measured DC resolution ($R_{S2,Meas,DC}$)

$R_{S2,Meas,DC}$ is the resolution of the measured *S2.Potential* signal which results from the 16-bit AD converter (considering the specifications mentioned above) which is further enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). The measured DC resolution (system DC resolution) value is:

$$R_{S2,Meas,DC} = \frac{5\text{ V}}{2^{24} \times 0.04} \cong 7.5\ \mu\text{V}$$

The above value is valid for the **measured, DC** *S2.Potential* signals. For CV staricase or Chrono methods techniques, the sampling interval in the procedure must be at least 262 ms (when at least 4096 points are aquired during a mains frequency period). When the sampling conditions are met, the measured potential signal resolution ($R_{S2,DA/AD}$) is automatically enhanced to the measured DC resolution ($R_{S2,Meas,DC}$).

Measured AC resolution ($R_{S2,Meas,AC}$)

$R_{S2,Meas,AC}$ is the resolution of the measured potential signal which results from the 16-bit AD converter (considering the conversion specifications mentioned above) with the measured potential signal being further amplified 128x by a dedicated amplification circuit (Zoom path). The AD resolution is also enhanced to a 24-bit resolution through DC sampling (oversampling and averaging). The measured AC resolution (system AC resolution) value is:

$$R_{S2,Meas,AC} = \frac{5\text{ V}}{2^{24} \times 0.04 \times 128} \cong 60\text{ nV}$$

The above value is valid for the **measured, AC** *S2.Potential* signals. For EIS techniques, the the maximum frequency where the Zoom path is used is 20 Hz. When the sampling conditions are met (measured AC signal, $<$ 20 Hz), the measured potential signal resolution ($R_{E,DA/AD}$) is automatically enhanced to the AC resolution ($R_{E,Meas,AC}$).

There are no user selectable settings which are necessary to apply to achieve the best system resolution. When the sampling conditions are met, the measured *S2.Potential* signal resolution (ADC resolution) ($R_{S2,DA/AD}$) is automatically enhanced to the best possible system resolution value.

4.5.4 Applied AC signal resolution

AC signals (i.e., sinusoidal signals) are used for the Electrochemical Impedance Spectroscopy (EIS) techniques and they have a dedicated signal processing path in VIONIC.

The applied AC signal range coincides with the range specified for the main potential and current signals.

The DA converters used to generate the applied AC signals have the following specifications:

Parameter	Value
Resolution specification of the DAC_{AC}	14-bit (2^{14} digital words per range)
Input voltage range of the DAC_{AC}	±2.5 V (5 V range)
Internal Gain factor (for AC Potential)	0.2
Signal attenuation	1/256

Applied AC potential resolution ($R_{E,Appl,AC}$)

This is the resolution of the applied AC potential signal used in EIS measurements and is the result of the 14-bit DA converter considering the specifications mentioned above. The resolution value is:

$$R_{E,Appl,AC} = \frac{5\ V}{2^{14} \times 0.2 \times 256} \cong 6\ \mu V$$

Applied AC current resolution ($R_{i,Appl,AC}$)

This is the resolution of the applied AC current signal used in EIS measurements and is the result of the 14-bit DA converter considering the specifications mentioned above. The voltage output of the Current range (CR) circuits is proportional to the measured current with a maximim of 5V for the full current range.The resolution value is:

$$R_{i,Appl,AC} = 10^{-9}\ [A/V] \times \frac{5\ [V]}{2^{14} \times 256} \cong 1\ fA$$

4.5.5 Overview of the resolution specifications

The table below gives a complete overview of the resolution specifications for all signals which can be measured or applied with VIONIC and INTELLO.

Table 6 Overview of the resolution specifications of VIONIC

Signal \\ Type	Applied DC signals (18-bit)	Applied AC signals (14-bit with 1/256 Attenuation)	Measured DC signals (24-bit)	Measured AC signals (24-bit with 128x Gain)
WE.Potential	100 µV	6 µV	1.5 µV	12 nV
S2.Potential	n.a.	n.a	7.5 µV	60 nV
WE.Current	20 fA	1 fA	300 aA	2.3 aA

There are no user selectable settings which are necessary to apply to achieve the best system resolution. Depending on the type of the signal and the sampling conditions, the best system resolution is used automatically.

When considering the experimental parameters and evaluating the results, the complete electrochemical setup must be considered including the potentiostat/galvanostat together with the electrochemical cell and electrodes. As a good practice, the limiting factor of the experiment must be identified as this will introduce the largest error in the measurement. Some examples of possible sources of errors can be: noise pickup and singal-to-noise ratio, signal drifts, signal accuracy, influence of contacts and connectors, geometrical dimesions of the electrodes, accuracy of solution concentration, impurities in the solution or in the electrode material etc.

The enhanced resolution values do not solve the problems and limitations created by external noise or interference or by inaccurate or unstable signals.

The immage below is the visual representation of high and low *Accuracy* and *Precission* for a signal with high and low *Resolution*.

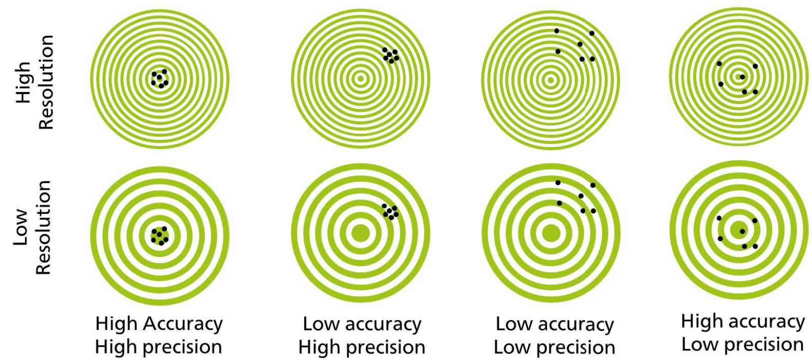


Figure 23 Visual representation of the corelation between Accuracy, Precission and Resolution

4.6 Power plot

The **electric power** (P, measured in Watt) is most commonly defined as the product between the voltage (V in Volts) and the current (i in Ampere). The power produced by an electric current (i.e. charge per unit of time) passing through an electric potential is:

$$P = i \times V = \frac{V \times Q}{t}$$

The **Power plot** is a two-dimensional representation of the maximum current and voltage which is applied or measured at a certain time.

In the case of electrochemical applications and instrumentations, a power plot gives an immediate indication on the *Maximum power* which can be *delivered to the cell* (for passive electrochemical cells) and the *Maximum power* which can be *dissipated from the cell* (for active electrochemical cells) showing the general overview of the power range in which the power amplifier of the instrument is capable to operate in safe conditions.

Please notice the difference between the **Power plot** and the **Power requirements**:

The **Power plot** indicates the power which can be delivered to or dissipated from the electrochemical cell by the instrument (through the cell cables)

The **Power requirements** (usually listed on the instrument label) indicates the electric power consumed when the instrument is switched ON and operated. This is the power delivered by the power grid of the building facility.

4.6.1 Distributed power

One of the important conditions for achieving the most accurate experimental results is to have the best possible match between the specifications of the instrument used and the requirements and particularities of the experiment and application. In other words, use the *right tool for the task.*. To enable this, VIONIC istrument has a *distributed power* offering the highest power and best accuracy for every type of electrochemical cells.

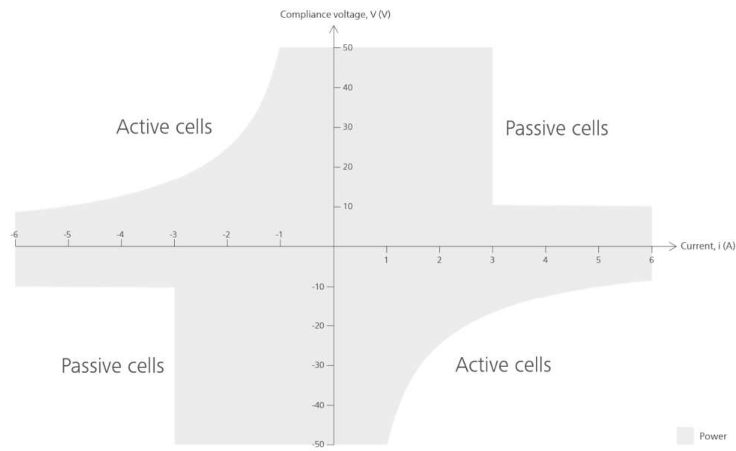


Figure 24 Power plot of VIONIC showing the areas which are relevant for passive and active electrochemical cells.

VIONIC can operate when the total power applied to the *passive* electrochemical cells or dissipated from *active* electrochemical cells is within the shaded area of the power plot.

4.6.2 Passive electrochemical cells.

In electrochemistry, the **passive cells** are the "typical", common electrochemical cells for which the potential or the current of the working electrode is controlled in order to generate and control the electrochemical process in the cell. For passive cells, the electrochemical cell "consumes" the electric power delivered by the PGSTAT and this power is actually converted into energy which drives the electrochemical reactions in the electrochemical cell. Therefore, in this case, the power delivered by the PGSTAT is positive which means that both the current and the potential in the cell have the same sign, as shown in the power plot. The total power delivered by the power amplifier of the PGSTAT is determined by the product between the *total cell voltage* (applied or measured) and the *measured/applied current*

The total cell voltage is the total voltage applied to the cell, between the counter electrode (CE) and the working electrode (WE) in order to achieve the user defined *applied voltage* between the working electrode (WE) and reference electrode (RE). The total cell voltage is limited by the compliance voltage of the PGSTAT.

The applied or measured current is the total current flowing between the counter electrode (CE) and the working electrode (WE). The applied and measured current is limited by the maximum current of the PGSTAT.

As the Power plot shows, VIONIC has a distributed power between *high compliance voltage* and *high current*. This allows VIONIC to be used in a wide range of applications with different power requirements.

- **High Compliance mode** - VIONIC can be set to High compliance mode whenever non-conductive (or high resistance) electrolytes and electrochemical cells are used in the experiments and/or the studied electrochemical process has a relatively low charge transfer resistance. In this case, the maximum deliverable power is 150W.
  Some typical examples of such experiments, when VIONIC should be used in high compliance mode are: electrochemistry in organic electrolytes, corrosion in oils and concrete, electrolysis etc. In this case, the maximum compliance voltage, the maximum applied and measured current and the maximum applied and measured potential ranges are:
  - Compliance voltage range: ±50V
  - Maximum applied and measured current range: ±3A
  - Maximum applied and measured potential range: ±10V
- **High accuracy mode** - VIONIC can be set to High accuracy mode whenever conductive (or low resistance) electrolytes and electrochemical cells are used in the experiments and/or the studied electrochemical process has a relatively high charge transfer resistance. Some typical examples of such experiments, when VIONIC should be used in high accuracy mode are: electrochemistry in aqueous acidic or basic electrolytes, corrosion in sea water, energy storage and generation research etc. In this case, the maximum compliance voltage, the maximum applied and measured current and the maximum applied and measured potential ranges are:
  - Compliance voltage range: ±10V
  - Maximum applied and measured current range: ±6A
  - Maximum applied and measured potential range: ±10V

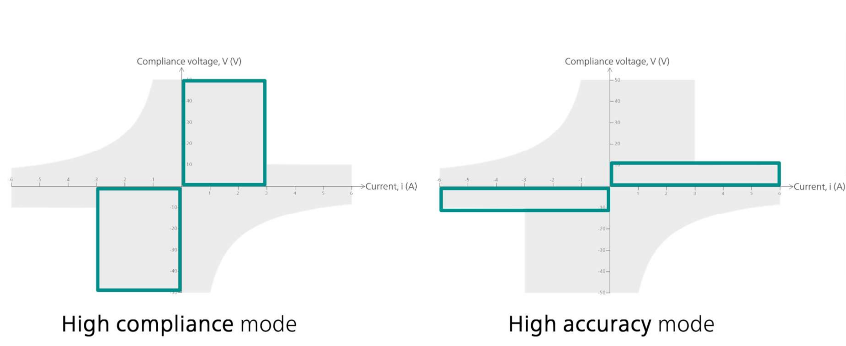


Figure 25 The High compliance and High accuracy region of the Power plot of VIONIC

If the Compliance voltage limit is reached during the electrochemical measurement, the yellow OVL indication will be lit up on the Dynamic interface. In this case, the use of the high compliance mode is necessary or, if already used, the electrochemical cell must be optimized. For more information and explanation of the compliance voltage, other specifications and parameters which can influence the electrochemical instruments, please see the existing supplementary documentation on *www.metrohm.com/electrochemistry* or contact your local Metrohm Autolab distributor.

Difference between High compliance vs High accuracy mode

The accuracy of the applied/measured potential value is always the same.

When using the **High accuracy** mode, the overall control of the electrochemical cell is faster and more accurate. The main difference between **High accuracy** mode and **High compliance** mode is the consequence of the additional gaining which must be used for the high compliance mode, when the voltage range is extended from ±10V (high accuracy mode) to ±50V (high compliance mode). Therefore, because less gaining is used when VIONIC is operated in High accuracy mode, there will be less overall noise in the signal, the control of the cell will be faster and there will be less ringing and overshooting when a signal is applied to the cell.

It is important to always select the instrument settings according to the experiment requirements. The use the high accuracy mode is recommended anytime high compliance is not needed.

4.6.3 Active electrochemical cells

In the case of **active cells**, the electrochemical process in the cell is spontaneous and *the cell delivers power* which needs to be dissipated by the PGSTAT. In this case, the power disipated by the PGSTAT is negative which means that both the current and the potential in the cell have opposite signs, as shown in the figure representing the Power plot of VIONIC. The total power which must be disipated by the power amplifier of the PGSTAT is determined by the product between the *total cell voltage* and the *measured (delivered) current* and is limited by the design of the electronics of the PGSTAT and heat sink of the electronics.

Some common examples of active cells which can deliver significant amount of power are the energy storage devices, measurements on fuel cells while in operating state or other energy generation devices.

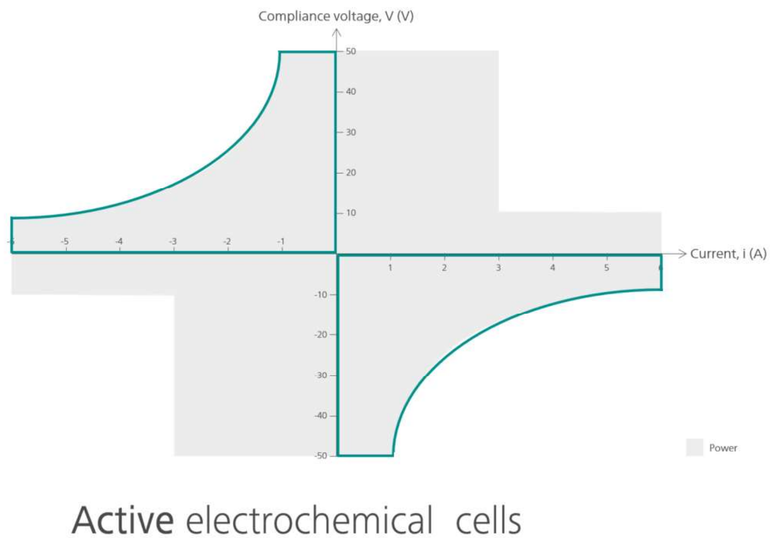


Figure 26 The active cell region of the Power plot of VIONIC

As shown by the Power plot of VIONIC, when active cells are connected, VIONIC can dissipate up to 50W (at 25 °C).

Active cells showing an absolute voltage, $|V_{Cell}|$, of less than 8 V between the working electrode (WE) and counter electrode (CE) are intrinsically safe. They may drive VIONIC into current limit but will not overload the power amplifier.

Active cells that have an absolute voltage higher than 8.3 V between the working (WE) and the counter electrode (CE) may only deliver a maximum current, i_{MAX} given by:

$$i_{MAX} = \frac{P_{MAX}}{|V_{Cell}|} = \frac{50W}{|V_{Cell}|}$$

Temperature overload

When the maximum dissipated power limit is reached, the power electronics of VIONIC might become overheated. In this case, the temperature overload protection circuit will be activated to protect the power electronics of the instrument.

During a temperature overload, the red T_{OVL} indication will be lit on the Dynamic interface of the instrument and the electrochemical cell will be automatically isolated (i.e. automatically disconnected) from VIONIC, for safety purposes. The measurement procedure will be also stopped. If a temperature overload (T_{OVL}) occurs, VIONIC can be recovered only after a complete reboot of the instrument.

As the power dissipation is made by converting power to heat, the maximum dissipated power depends on the operation (environmental) temperature of VIONIC.

VIONIC must be set in High Compliance mode to enable the highest dissipated power.

Maximum input voltage

The maximum voltage range which can be measured with VIONIC is ±10V. The differential electrometer of VIONIC contains an input protection circuitry which is activated when the measured voltage is outside of the ±10V interval. This is implemented to avoid electrometer damage. Please be aware that the OVL indicator, on the Dynamic interface, will not light up for this type of voltage overload. The measured voltage will be cutoff at an absolute value of ±10V.

When using high power active cells, do not try dissipate more than 50W with VIONIC. When active cells are used, always operate them at powers lower than 50W.

Always connect the electrochemical cell or device under test (DUT) to the correct terminals (cell cables) of VIONIC.

In case of any doubts, please contact your local Metrohm Autolab distributor for further guidance on how to connect and setup an electrochemical cell.

4.7 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an essential and powerful technique used for the investigation of the electrochemical processes, material properties and electrode reactions.

The Electrochemical Impedance (EIS) measurements are the result of the complete electrochemical setup including the electrochemical cell, connectors, the Pure Signal Bridge (cell cables), and the instrument (i.e. the potentiostat/galvanostat).

For details on the principles of the Electrochemical Impedance Spectroscopy (EIS) technique, please see the dedicated technical documentation on www.metrohm.com or contact your local Metrohm Autolab representative (https://www.metrohm.com/en/country-chooser/).

In this chapter, details about the EIS specifications and the measurements accuracy are presented.

4.7.1 EIS Contour plot

The measured electrochemical impedance is frequency dependent. Therefore, the errors in the measured impedance due to the stray effects in the experiment setup are also frequency dependent. Moreover, the performance of the electrochemical instrument used for the EIS measurement also plays a role in the accuracy and measurable impedance range. As a consequence, It is not possible to achieve the same measurement accuracy at any frequencies for any types of electrochemical cells (i.e. for any measured impedances).

The *EIS Contour plot* is a useful specification tool which correlates the accuracy of the EIS measurement with the frequency and the measured impedance value.

The EIS Contour plot is a log-log representation of the total impedance Z (Ω) versus the AC frequency (Hz).

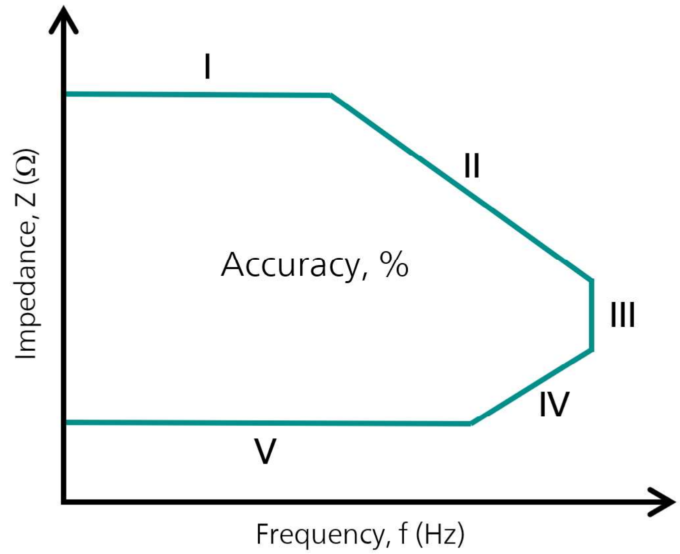


Figure 27 General representation of an EIS Contour plot

The area (contour) delimited by the green line in the plot above shows the accuracy of the measured impedance within a given frequency range. If the impedances measured at certain frequencies fall outside of the contour, the measurement can still be done but the accuracy of the measurement is not defined.

There are five specific regions in a typical EIS contour plot with the accuracy of the measurement being limited by different factors:

- **Region I** - **indicates the highest measurable impedance** within the given accuracy limit. In practice, the highest measurable impedance is reached at low frequencies where the parasitic capacitance contributions are negligible. The highest measurable impedance is limited by the instrument capability to measure low currents as well as the maximum AC amplitude which can pe applied during the EIS measurement.
- **Region II** - **indicates the capability of the instrument to measure high impedances at high frequencies (i.e. low capacitances)**. The effect of stray (i.e. parasitic) capacitances which are in parallel with the main sample impedance is more pronounced at high frequencies. As a result, for the same accuracy, the highest measurable impedance will decrease with the increasing frequency.
- **Region III - indicates the highest frequency** which can be used to measure the electrochemical impedance with a given accuracy. This is limited by the instrument capability to apply and measure AC signals up to the specified maximum frequency.

- **Region IV - indicates the capability of the instrument to measure low impedances at high frequencies**. The effect of the inductances (parasitic or due to a physical of chemical process) is more pronounced at high frequencies. Due to the parasitic inductances coming from the cables and electronics of the instrument, the lowest measurable impedance limit, measured with the same accuracy, will be higher at higher frequencies.
- **Region V - indicates the lowest measurable impedance** within the given accuracy limit. In practice, the lowest measurable impedance is reached at low frequencies where the parasitic inductance contributions due to cables and electronics are negligible. The lowest measurable impedance is limited by the instrument capability to measure high currents as well as the minimum AC amplitude which can pe applied during the EIS measurement.

Even though the instrument is capable of measuring impedances up to its maximum frequency, it is important to evaluate and take into consideration the limitations and experimental artifacts due to the electrochemical cell and setup. Most of the time, the electrochemical cell, cables and connectors will be the limiting factors for the maximum usable frequency in EIS measurements. For example, when wet reference electrodes are used in the setup (such as Ag/AgCl in 3M KCl), the maximum usable EIS frequency will be in the range of 100 - 500 kHz.

4.7.2 EIS Contour plot for VIONIC powered by INTELLO

The EIS measurement range in VIONIC and the corresponding accuracy of the results depends on the specific characteristics of the electrochemical system measured as well as the performance of the instrumentation.

The main impedance is always measured between the Reference (RE) and the Sense electrode (S). Therefore, all processes which occur between RE and S will have an influence on the measured results at certain frequencies.

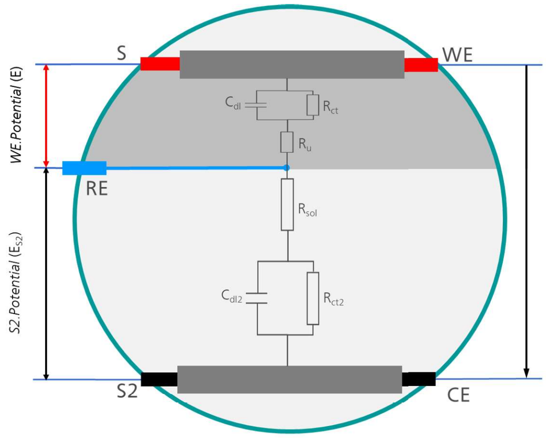


Figure 28 Visual representation (in darker shade) of the electrochemical cell parameters that contribute to the main EIS measurements (measured between RE and S).

In potentiostatic mode, the AC potential is controlled between the RE and S and the AC current response is measured between CE and WE.

In galvanostatic mode, the AC current is controlled between CE and WE and the voltage response is measured between RE and S and between RE and S2.

Table 7 Main EIS measurement specifications

Parameter	**Spefification**
Maximum EIS Frequency in Pstat mode	10 MHz
Maximum EIS Frequency in Gstat mode	1 MHz
Minimum EIS Frequency	10 µHz
Maximum AC amplitude in Pstat mode	10 V
Maximum AC amplitude in Gstat mode	6 A
Minimum AC amplitude in Pstat mode	0.1 mV
Minimum AC amplitude in Gstat mode	0.5 pA
Maximum measurable impedance (accuracy %)	25 GΩ (>99.75% accuracy) 100 GΩ (>99% accuracy) 1 TΩ (>90% accuracy)
Minimum measurable impedance (accuracy %)	4 mΩ (>99.75% accuracy) 1 mΩ (>99% accuracy) 100 µΩ (>90% accuracy)

The full contour plot of the main EIS measurements with VIONIC powered by INTELLO, (i.e., EIS measured between RE and S) is presented below. .

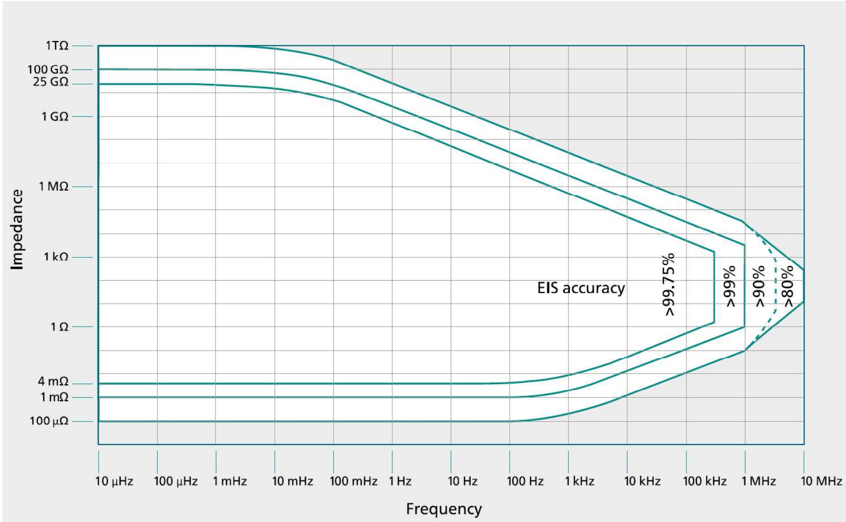


Figure 29 Contour plot of the main EIS measurements with VIONIC powered by INTELLO.

The presented accuracy applies for both the measured impedance and phase. During the measurements, S was connected to WE and the optimal measurement conditions were used.

4.7.3 EIS on S2 Contour plot for VIONIC powered by INTELLO

The impedance on the Second sense (EIS on S2) is always measured between the RE and the S2 electrode. Therefore, all processes that occur between RE and S2 will have an influence on the measured S2 impedance at certain frequencies.

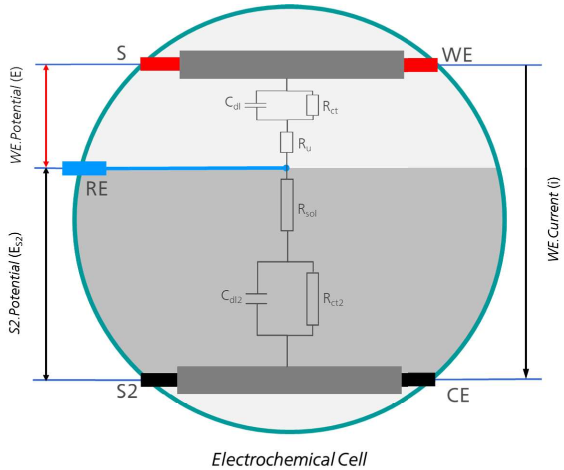


Figure 30 Visual representation (in darker shade) of the electrochemical cell parameters contributing to the EIS on S2 measurements (measured between RE and S2).

During the EIS on S2 measurements, the AC signal applied (either AC potential in potentiostatic mode or AC current in galvanostatic mode) is the same as the AC signal used for the main EIS measurements.

In potentiostatic mode, the AC potential is controlled between the RE and S but the voltage measured between the RE and S2 is used for calculating the EIS on S2. The AC current response is always measured between CE and WE.

In galvanostatic mode, the AC current is controlled between CE and WE and the AC voltage response is measured between RE and S2.

Table 8 EIS on S2 measurement specifications

Parameter	Spefification
Maximum EIS on S2 Frequency	100 kHz
Minimum EIS on S2 Frequency	10 µHz
Maximum S2 potential (AC + DC)	± 50V
Maximum measurable S2 impedance (accuracy %)	25 GΩ (>99.75% accuracy) 100 GΩ (>99% accuracy)
Minimum measurable S2 impedance (accuracy %)	40 mΩ (>99.75% accuracy) 10 mΩ (>99% accuracy) 5 mΩ (>97% accuracy)

The full contour plot of the EIS on S2 measurements with VIONIC powered by INTELLO, (i.e., EIS measured between RE and S2) is presented below.

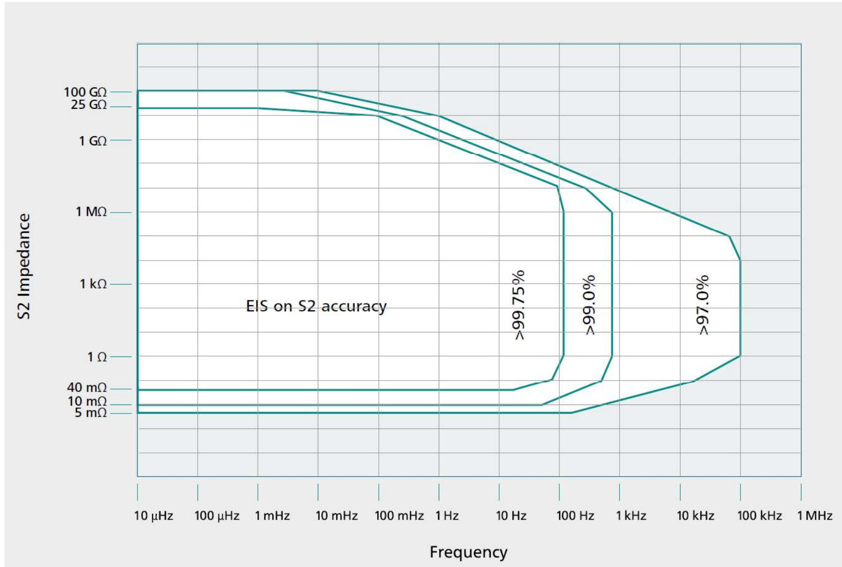


Figure 31 Contour plot of EIS on S2 measurements with VIONIC powered by INTELLO.

The presented accuracy applies for both the measured impedance and phase.

The optimal measurement conditions were used when building the contour plot. During the measurements, S2 was connected to the CE, $Z_{S2\text{-}RE}$ typical 10x $Z_{S\text{-}RE}$

The bandwidth of the second voltage follower (used to measure the potential difference between S2 vs RE) is lower due to its wider voltage range (i.e., ±50V) compared to the main voltage follower (used to measure the potential difference between S and RE, i.e., ±10V), and different gaining factors used. Therefore, the maximum frequency for EIS measurements on S2 is 100 kHz.

4.7.4 EIS measurements at High Frequencies

When electrochemical impedance measurements require the use of high frequencies (i.e., frequencies between 1 MHz and 10 MHz), it is very important to identify the limiting factor in the experimental setup. The vast majority of the electrochemical cells cannot be used for EIS measurements above 100 kHz or above 1 MHz as measured response will be highly influenced by factors other than the physical or electrochemical process itself.

VIONIC is capable of measuring electrochemical impedance up to 10 MHz on electrochemical cells which allow high frequency measurements for the investigation of the physical/chemical processes.

To achieve the highest stability and accuracy during EIS measurements at high frequencies, the special High Frequency (HF) Adaptive cables must be used for all EIS measurements above 1 MHz (item number 3500002750).

Figure 32 Adaptive cables used for high frequency measurements

The HF Reference (RE) and HF Sense (S) adaptive cables must be connected to the reference and sense electrodes in the electrochemical cell, respectively. The standard Working (WE) and Counter electrode (CE) adaptive cables are used to connect to working and counter electrode in the cell, respectively.

The Analog ground (AGND) and the Earth ground (EARTH) connections on the Pure signal bridge (Buffer and Splitter box) must be connected together using the special cable which is part of the HF Adaptive cable set.

EIS on S2 measurements are limited to a maximim frequency of 100 kHz and not available at high frequencies. For details on EIS on S2, please see the dedicated paragraph in this user manual.

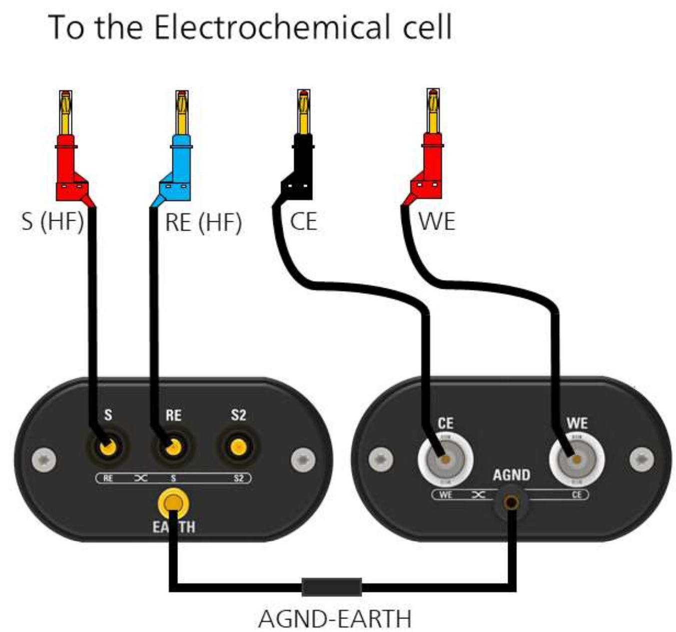


Figure 33 Pure signal bridge and Adaptive cable connections used for High Frequency (HF) EIS measurements.

4.7.5 Practical tips for stable and accurate EIS measurements

In practice, most of the time the overall accuracy of the EIS measurement is limited by the electrochemical cell and the connections of the instrument to the cell.

Here some practical tips to achieve the most stable EIS measurements and and the most accurate results:

- Use a frequency range for which the EIS response will not be limited by the reference electrode in the cell, by the cables nor by other accessories used in the setup. Be aware of the limiting factor in the experimental setup.
- Always make sure that the Stability, Linearity and Causality conditions are fulfilled during the EIS measurement
- Always use the original Adaptive Cables. Do not use any additional cables to connect VIONIC to the electrochemical cell. Make sure that the cables and connectors are not damaged.
- For low impedance measurement, use a 4-point connection measurement, also known as Kelvin probe.
- For EIS measurements at frequencies higher than 1 MHz, use the special High Frequency (HF) Adaptive cables
- Use a Faraday cage in noisy environments or for sensitive measurements (e.g. high resistance samples with a low current response such as high impedance coatings)

- Do not place the cell, cables nor the instrument in the close proximity of another electronic equipment or other noise generating devices.
- Choose wisely between potentiostatic and galvanostatic EIS as well as connecting and measuring EIS on S2 (if needed)

For further help and guidance, please see the existing technical documentation on www.metrohm.com or contact your local Metrohm Autolab support office (https://www.metrohm.com/en/country-chooser/)

4.8 Second Sense (S2)

The Second Sense (S2) functionality enables the measurement of a second voltage versus the Reference electrode (RE) within the same electrochemical cell.

The second voltage is measured with an additional voltage follower in VIONIC, with a dedicated *true parallel* signal aquisition path.

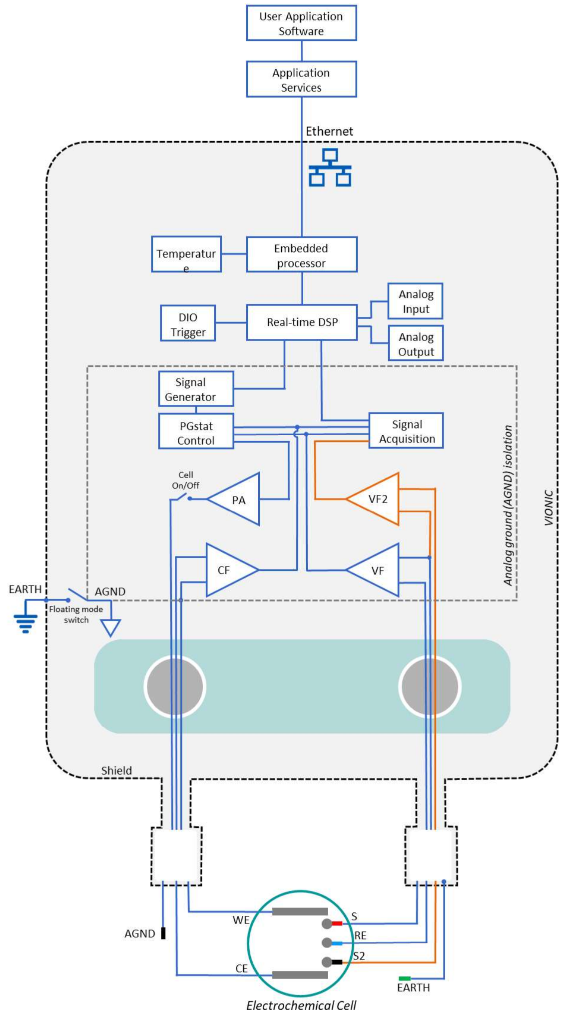


Figure 34 Second Sense (S2) voltage measurement path highlighted as part of the VIONIC block diagram

To connect the Second sense (S2) to the electrochemical cell, the S2 labeled Adaptive cable must be connected to the corresponding connector on the Pure signal bridge and to the corresponding electrode in the electrochemical cell.

Figure 35 Second Sense (S2) connection on the Buffer box of the Pure signal bridge

For details about the labeling and connectors on the Pure signal bridge, please see the dedicated chapter describing the Pure signal bridge and the Adaptive cables.

The standard cell connector of the Second sense (S2) adaptive cable is 4 mm banana plug. Different type of cell connectors are optionally available. For details, please see the dedicated chapter describing the optional Adaptive cables.

Measured potential signals

In INTELLO, there are two measured potential signals available:

- The *WE.Potential* is measured with the main voltage follower and is defined as:
  WE.Potential = S - RE
  i.e. the potential difference between the Reference electrode (RE) and the Sense (S).
- The *S2.Potential* is measured with the second voltage follower and is defined as:
  S2.Potential = S2 - RE
  i.e. the potential difference between the Reference electrode (RE) and the Second Sense (S2).

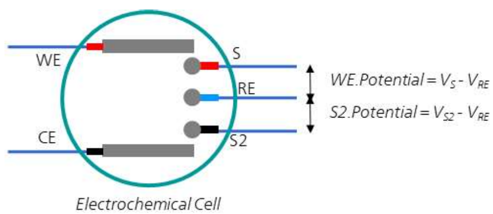


Figure 36 Representation of an electrochemical cell with 5 cell connections and the definitions of the two measured potential signals: WE.Potential and S2.Potential

There is always one current flowing through the electrochemical cell. The current, *WE.Current* (i) is measured or applied between the Counter (CE) and the Working electrode (WE)

The Second Sense (S2) can only measure potentials vs the Reference electrode (RE). It is not possible to apply or control a second potential in the electrochemical cell.

Due to the fact that the second voltage follower which is used to measure the voltage between the Second sense (S2) and the Reference electrode (RE) is galvanically isolated from the Earth ground, measurements with the Second sense (S2) are possible independently of VIONIC being set in floating or non-floating mode.

It is not possible to control or apply a potential with the Second Sense (S2). Therefore, S2 does not have the functionality of a second potentiostat channel nor the finctionality of a Bipotentiostat (BA). If a multichannel potentiostat of a BA functionality is needed for your application, please contact your local Metrohm Autolab representative for additional information and recommendations.

4.8.1 Second Sense (S2) connected to the Counter electrode (CE)

The functionality of the Second Sense (S2) electrode is probably most commonly used with the Second Sense (S2) connected to the Counter electrode (CE). In this case, the Second sense (S2) will monitor the voltage of the Counter electrode (CE) vs the Reference electrode (RE). The cell setup can be the standard three or four electrode setup

Three electrode setup

This experimental setup is helpul in monitoring the on-going secondary electrochemical processes at the Counter electrode (CE) simultaneously with the main electrochemical process at the Working electrode (WE) when using a typical three electrode setup.

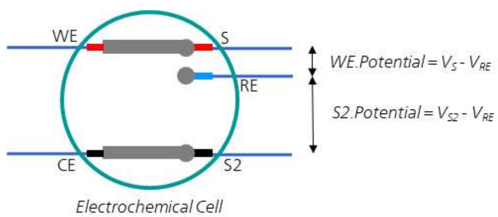


Figure 37 Electrochemical cell in three electrode configuration with S2 connected to CE.

Typical measurement examples are:

- Monitor the voltage on the Counter electrode (CE) vs the Reference electrode (RE): *S2.Potential* signal
- Monitor the total voltage difference between the Counter electrode (CE) and the Working electrode (WE): *S2.Potential - WE.Potential*
- Simultaneous Electrochemical impedance measurements on the Counter (CE) and Working electrode (WE) (anode and cathode) (when a stand-alone reference electrode is part of the electrochemical cell)

Four electrode setup

These type of electrochemical cell setups are used to investigate processes accross membranes or liquid-liquid interfaces.

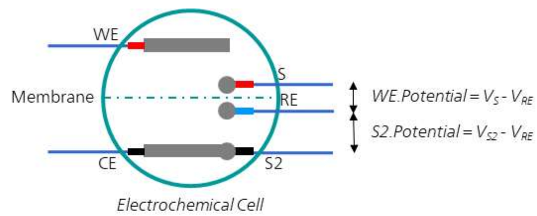


Figure 38 Electrochemical cell in four electrode configuration with S2 connected to CE.

The typical measurements are:

- Monitor the voltage on the Counter electrode (CE) vs the Reference electrode (RE): *S2.Potential* signal
- Monitor the total voltage difference between the Counter electrode (CE) and the Sense (S): *S2.Potential - WE.Potential*
- Simultaneous Electrochemical impedance measurements between the Counter (CE) vs Reference (RE) and Sense (S) vs Reference (RE) electrodes.

Please notice that in the case of the four-electrode cell setup, the Sense (S) is not connected to the Working electrode (WE). The *WE.Potential* signal is **always** the potential difference between the Sense (S) and the Reference electrode (RE).

When the Sense (S) is not connected to the Working electrode (WE), the difference between *S2.Potential - WE.Potential* will **not** be the voltage difference between the Counter electrode(CE) and the Working (WE) electrode nor the voltage difference between the Second sense (S2) and the Working (WE) electrode. (Remember that the *WE.Potential* signal is measured between RE and S)

4.8.2 Second Sense (S2) as stand alone probe in the cell

The Second Sense (S2) electrode can be used to monitor the potential difference between any point in the electrochemical cell versus the Reference electrode (RE). In this case, the Second sense (S2) is not connected to the Counter electrode (CE).

This experimental setup is helpul in monitoring the potential differences accross membranes or between well defined points in the electrochemical cell. The cell setup can be the standard three or four electrode setup.
In this case, the Second sense (S2) is connected to an additional probe (electrode) in the electrochemical cell.

Three electrode setup with stand alone Second Sense (S2)

This experimental setup is helpul in monitoring an additional potential difference versus the Reference electrode (RE) simultaneously with the potential of the main electrochemical process at the Working electrode (WE).

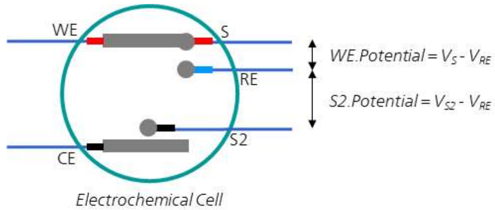


Figure 39 Electrochemical cell in three electrode configuration with S2 as stand alone probe in the cell.

Typical measurement examples are:

- Monitor the an addtitional voltage difference in the electrochemical cell vs the Reference electrode (RE): *S2.Potential* signal
- Simultaneous Electrochemical impedance (EIS) measurements between the Second Sense (S2) vs Reference (RE) and Sense (S) vs Reference electrode (RE) in the same electrochemical cell (cells with membranes or liquid-liquid interfaces)

Four electrode setup with stand alone Second Sense (S2)

These type of electrochemical cell setups are used to investigate processes accross membranes or liquid-liquid interfaces.

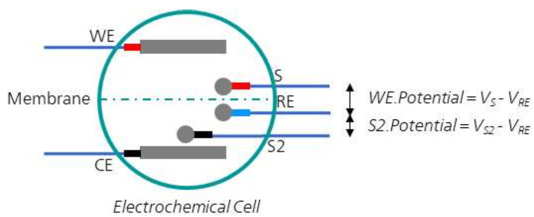


Figure 40 Electrochemical cell in four electrode configuration with S2 as stand alone probe in the cell.

The typical measurements are:

- Monitor the an addtitional voltage difference in the electrochemical cell vs the Reference electrode (RE): *S2.Potential* signal
- Simultaneous Electrochemical impedance (EIS) measurements between the Second Sense (S2) vs Reference (RE) and Sense (S) vs Reference electrode (RE) in the same electrochemical cell (cells with membranes or liquid-liquid interfaces)

Please notice that in the case of the four-electrode cell setup, the Sense (S) is not connected to the Working electrode (WE). The *WE.Potential* signal is **always** the potential difference between the Sense (S) and the Reference electrode (RE).

When the Sense (S) is not connected to the Working electrode (WE), the difference between *S2.Potential - WE.Potential* will **not** be the voltage difference between the Counter electrode(CE) and the Working (WE) electrode nor the voltage difference between the Second sense (S2) and the Working (WE) electrode. (Remember that the *WE.Potential* signal is measured between RE and S)

4.8.3 Second Sense (S2) and the cell parameters

Even though most of the time the electrochemical process of interest is taking place at the Working electrode (WE), the complete electrochemical cell including the counter electrode and the electrolyte is part of the process.

The example below is built considering a typical 3-electrode setup with the Sense (S) and Working electrode (WE) connected together and also with the Second sense (S2) connected to the Counter electrode (CE).

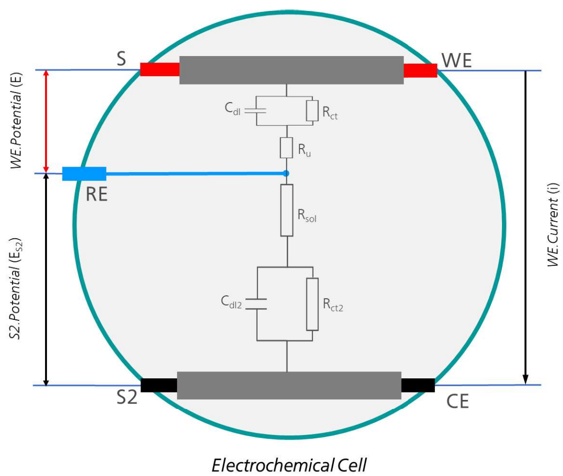


Figure 41 Schematic representation of an electrochemical cell and its signals and parameters in a typical 3-electrode setup with S2 connected to CE.

The electrochemical signals and parameters which are necessary to control and monitor the electrochemical processes in the cell are shown above in the figure:

- R_{sol} - solution resistance
- R_u - uncompensated resistance
- R_{ct1} - charge transfer resistance of the main electrochemical process at the WE

- R_{ct2} - charge transfer resistance of the secondary electrochemical process at the CE
- C_{dl1} - double layer capacitance of the main electrochemical process at the WE
- C_{dl2} - double layer capacitance of the secondary electrochemical process at the CE

4.8.4 Ohm's Law and the cell parameters for DC measurements

Using Ohm's Law, we can deduct the simple relationship between the applied and measured signals and the parameters specific to the electrochemical process. Understanding this relationships is helpful in further understanding how the electrochemical setup works and what are the signals which are actually applied and measured during the electrochemical measurement.

For DC measurements, the impedance of a capacitor is infinite:
$Z_C = 1/(\omega C)$
where ω is the frequency and C is the capacitance
Therefore, C_{dl1} and C_{dl2} will be disregarded in the examples presented here.

Ohm's Law: $E = i\,R$

$$\mathit{WE.Potential} = i\,(R_{ct1} + R_u) \Rightarrow i = \frac{E_{appl}}{(R_{ct1} + R_u)}$$

$$\mathit{S2.Potential} = i\,(R_{ct2} + R_{sol}) = \frac{E_{appl}}{(R_{ct1} + R_u)}(R_{ct2} + R_{sol})$$

$$\mathit{S2.Potential} = \mathit{WE.Potential}\,\frac{(R_{ct2} + R_{sol})}{(R_{ct1} + R_u)}$$

$$E_{WE} - E_{CE} = \mathit{WE.Potential} - \mathit{S2.Potential}$$

WE.Potential, S2.Potential and WE.Curret (i) are measured or applied signals available in INTELLO.
The total applied potential accross the cell (E_{WE} - E_{CE}) is not directly available as a measured signal in INTELLO. This can be calculated as shown above.

4.8.5 Second Sense and Electrochemical impedance (EIS) measurements

The impedance on the Second sense (EIS on S2) is always measured between the RE and the S2 electrode. Therefore, all processes which occur between RE and S2 will have an influence on the measured S2 impedance at certaing frequencies.

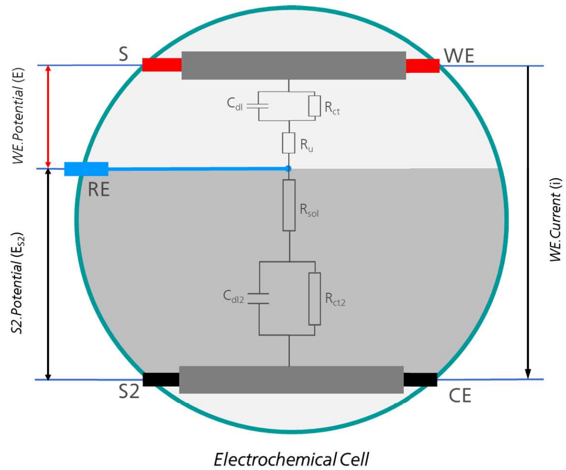


Figure 42 Visual representation of the electrochemical cell parameters which contribute to the EIS on S2 measurements (measured between RE and S2).

During the EIS on S2 measurements, the AC signal applied (either AC potential in potentiostatic mode or AC current in galvanostatic mode) is the same as the AC signal used for the main EIS measurements.

In potentiostatic mode, the AC potential is controlled between the RE and S but the voltage measured between the RE and S2 is used for calculating the EIS on S2. The AC current response is always measured between CE and WE.

In galvanostatic mode, the AC current is controlled between CE and WE and the AC voltage response is measured between RE and S2.

The EIS on S2 specifications and the full Contour plot of the EIS on S2 measurements with VIONIC powered by INTELLO, (i.e., EIS measured between RE and S2) are presented in the chapter dedicated to the EIS measuremnt and Contour plot details in this user manual.

4.9 VIONIC detailed specifications

The selected specifications of VIONIC powered by INTELLO are provided in the tables below.

The specified values are typical values which are reached in optimal working conditions at 25 °C. Specifications can change without notice.

Do not modify the the Adaptive cables and do not use any additional cables to connect to the electrochemical cell. The original Adaptive cables are designed for the best possible operation. Modifications of these connections, i.e. with other connectors, will lead to the loss of any warranty.

Compliance voltage, Applied potential and Current

Parameter	Specification
Compliance voltage	±50 V
Maximum applied potential	±10 V
Maximum applied current	±6 A (up to ±10 V compliance ±3 A (up to ±50 V compliance
Applied potential: Accuracy	±0.2% of setting ±2 mV
Applied potential: Resolution	100 µV
Applied current: Accuracy (10 nA current range or higher)	±0.2% of setting ±0.2% of current range
Applied current: Resolution (10 nA current range)	0.2 pA
Rise time (typical)	200 ns
Maximum control loop bandwidth (typical)	10 kHz / 100 kHz / 1 MHz, selectable

Measured potential (V_S - V_{RE})

Parameter	Specification
Maximum measured potential	±10 V
Measured potential: Accuracy	±0.2% of signal ±2 mV

Parameter	Specification
Measured potential: Resolution (ADC resolution)	100 µV
Measured potential: Resolution (system, DC signals)	1.5 µV (24-bit)
Measured potential: Resolution (system, AC signals, <20 Hz)	12 nV
Input impedance of the electrometer	>1 TΩ
Bandwidth of electrometer (-3 dB)	>10 MHz

Measured potential - Second sense (V_{S2} - V_{RE})

Parameter	Specification
Maximum measured S2 potential	±50 V
Measured S2 potential: Accuracy	±0.3% of signal ±5 mV
Measured S2 potential: Resolution (ADC resolution)	2 mV
Measured S2 potential: Resolution (system, DC signals)	7.5 µV (24-bit)
Measured S2 potential: Resolution (system, AC signals, <20 Hz)	60 nV

Measured current

Parameter	Specification
Maximum measured current	± 6 A
Measured current: Accuracy	±0.2% of signal ±0.2% of current range
Measured current: Resolution (ADC resolution, 1nA current range)	20 fA
Measured current: Resolution (system, DC signals, 1nA current range)	300 aA
Measured current: Resolution (system, AC signals, <20 Hz, 1nA current range)	2.3 aA
Lowest current range Lowest current range with internal gaining	10 nA 1 nA
Total number of current ranges	11

EIS - measured between S and RE

Parameter	Specification
Maximum frequency in Pstat mode	10 MHz
Maximum frequency in Gstat mode	1 MHz
Minimum frequency	10 μHz
Maximum AC amplitude, Pstat (top)	10 V
Maximum AC amplitude, Gstat (top)	6 A
Minimum AC amplitude, Pstat (top)	100 μV_{TOP}
Minimum AC amplitude, Gstat (top)	0.5 pA_{TOP}
Maximum measurable impedance (Accuracy, %)	25 GΩ (99.75% accuracy) 100 GΩ (99.0% accuracy) 1 TΩ (90.0% accuracy) See contour plot for additional details
Minimum measurable impedance (Accuracy, %)	4 mΩ (99.75% accuracy) 1 mΩ (99.0% accuracy) 100 μΩ (90.0% accuracy) See contour plot for additional details
Full EIS accuracy	See contour plot

General

Parameter	Specification
EIS	Yes
Analog scan	Yes
Floating mode	Selectable with 4 options

Parameter	Specification
Pure signal bridge	1 m fixed cables and 0.5 m removable Adaptive cables with 4 mm banana connectors
Mode switching time (Pstat/Gstat)	50 µs
Maximum scan rate (Analog scan)	10 kV/s_{TOP}
Minimum scan rate (Analog scan)	50 µV/s
Maximum scan rate (Staircase scan, 10 mV stem potential, 100 µs step duration)	100 V/s
Minimum scan rate (Staircase scan, 100 µV stem potential, 1 s step duration)	100 µV/s
Number of cell connections	5 (WE, CE, RE, S, S2)
Earth ground connection (EARTH)	Yes
Analog ground connection (AGND)	Yes
Maximum output power (applied / passive cells)	150 W
Maximum input power (dissipated / active cells)	50 W @ 25 °C
Cell isolation	Automatic
Dynamic interface	7-segment LED with collor signage
Connection type	Ethernet
True paraler data aquisition paths	Yes
Seamless measurements	Yes
Untethering (computer free operation)	Yes

Timing

Parameter	Specification
Time resolution	10 ns
Time gap between two seamless measurement commands	0 ns (no gap)
Lowest sampling interval (aquisition time) for i, E and S2	1 µs

Memory

Parameter	Specification
On-board memory for data buffer (sampling rate <10000 data points / s)	10 Milion data points
On-board memory for data buffer (sampling rate >10000 data points / s)	1 Milion data points

Dimensions

Parameter	Specification
Size (W x H x D), excluding cables	20 cm (W) x 27 cm (H) x 40 cm (D)
Weight	13 kg
Power requirement	300 W, 100..240 V, 50/60 Hz

Materials of exposed parts

Exposed part	Material
Front anel (transparent)	Polymethyl methacry-late (PMMA)
Back panel, bottom and green rims	Polypropylene (PP, 20% mineral filled)
Side and top pannels	Stainless steel (SS)
Fixed cables	Polyvinyl chloride nitrile (PVC Nitrile)
Buffer and Splitter box	Aluminium (Al), black anodized with silicone protective rings
Adaptive cables	Polyvinyl chloride (PVC) with Au-plated con-tacts
Test Cell	Acrylonitrile butadiene styrene (ABS)

Please be aware of the chemical and thermal resistance of the expost materials for the experimental conditions in which VIONIC is used.

4.9.1 Scope of delivery

The VIONIC instrument is supplied standard with the following items:

Item number	Description	Units
3500001080	VIONIC istrument with 1 m fixed Pure Signal Bridge including:	1 unit
	Adaptive cable *set* including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with *4 mm banana* cell connectors (supplied standard with VIONIC)	1 set
	Adaptive cable *set* for High frequency (HF) EIS measurements including, Reference (RE), Sense (S) electrode and Ground bridge cables, 0.25 m with 4 mm banana cell connectors	1 set
	Earth Ground cable (EARTH), 0.5 m with 4 mm / 4 mm banana connectors	1 pc.
	Autolab test cell	1 pc.
	Ethernet cable, 3 m	1 pc.
	Power cable	1 pc.
	Alligator clips, red	2 pcs.
	Alligator clips, black	3 pcs.
	Quality certificate	1 pc.
	Basic Safety and CE declaration	1 pc.
	INTELLO Software with EIS 1 MHz, EIS 10 MHz, S2, Analog scan licenses included	download

Optional accessories

The following accessories are optionally available for the VIONIC instrument

Item number	Description
3500002500	Adaptive cable *set* including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with *4 mm banana* cell connectors (supplied standard with VIONIC)
3500002510	Adaptive cable *set* including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with *2 mm banana* cell connectors
3500002530	Adaptive cable *set* including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with *Alligator clip* cell connectors
3500002540	Adaptive cable *set* including, Working (WE), Reference (RE), Counter (CE), Sense (S) and Second sense (S2) electrode cables, 0.5 m with *isolated BNC* cell connectors
3500002750	Adaptive cable *set* for High frequency (HF) EIS measurements including, Reference (RE), Sense (S) electrode and Ground bridge cables, 0.25 m with 4 mm banana cell connectors
3500002000	Earth Ground cable (EARTH), 0.5 m with 4 mm / 4 mm banana connectors
3500002010	Analog ground cable (AGND), 0.5 m with 2 mm / 4 mm banana connectors
3500002470	Autolab test cell
3500002880	Galvanostatic Floating Stabilization (GSTAT FLOAT Stabilization) box
3500001940	Ethernet cable, 3 m
ALL.CLIP.RED	Alligator clips, red
ALL.CLIP.BLACK	Alligator clips, black

For additional details, please contact your local Metrohm Autolab support office.

5 VIONIC in an extended Work system

Depending on the experimental and application requirements, additional devices such as rotating electrodes (RDE, RCE), thermocouples (TC), oscilloscopes etc. should be used together with the potentiostat.

A *work system* is a set of devices used together to run an electrochemical measurement by connecting it to an electrochemical cell (the electrochemical cell is not considered part of the work system). A *work system* reflects the physical set-up used, how the devices are connected to each other and the configuration of each device. The type of the devices and their role in the work system is user-configurable.

In its most basic form, a *work system* typically consists only of one VIONIC instrument, in the role of "main instrument". In this case, no additional devices are connected to VIONIC.

The status of the created work system is shown in INTELLO (e.g., available, claimed) and, if available, it can be claimed in order to connect the cell and run the procedure(s) without other users interfering.

To create a work system, in the work system editor window in INTELLO, the external devices from the *Known devices* list can be dragged-and-dropped to the field adjacent to the *Main instrument*.

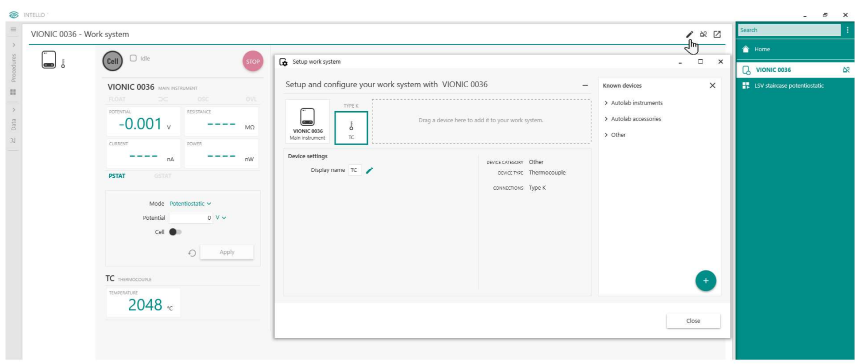


Figure 43 Example of the work system setup window in INTELLO. In this example, a VIONIC main instrument and K-type thermocouple are making up the work system.

The configuration and capabilities of a *work system* is also reflected in the possibility to define the *Required work system* in the procedure settings. This is necessary to specify the minimum work system required to run the respective procedure.

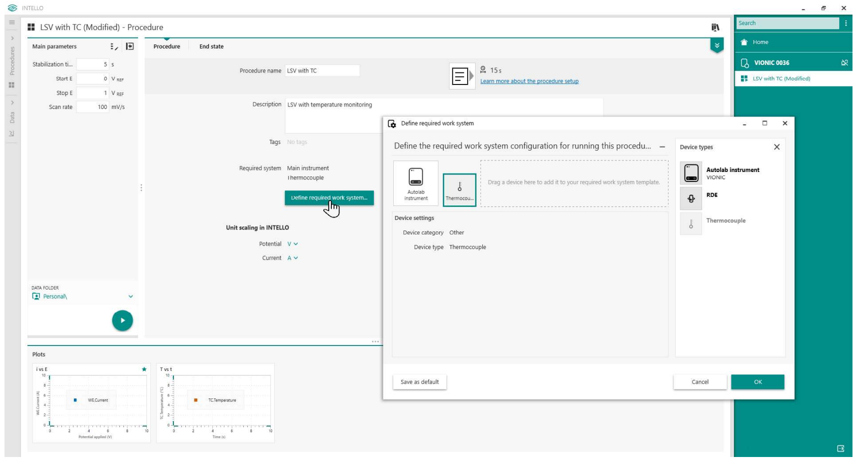


Figure 44 Example of a required work system definition in the procedure settings in INTELLO. In this example, a VIONIC main instrument and K-type thermocouple are making up the work system required for the measurement.

5.1 Work system for hydrodynamic measurements

For applications and experiments which require hydrodynamic measurements with rotating electrodes, a work system can be created by adding an Autolab Rotating Disk Electrode (RDE) or an Autolab Rotating Cylinder Electrode (RCE) to the VIONIC main instrument. The procedure of adding an RDE or and RCE to the work system is the same. Therefore, from now on, the general *Autolab Rotating Electrode* terminology will be used to describe both RDE and RCE.

The Autolab Rotating Electrode can be remotely controlled from VIONIC and INTELLO. For this the Remote Input on the back of the Motor Controller must be connected to one of the Analog output (A-OUT1 or A-OUT2) on the back panel of VIONIC by using a BNC cable.

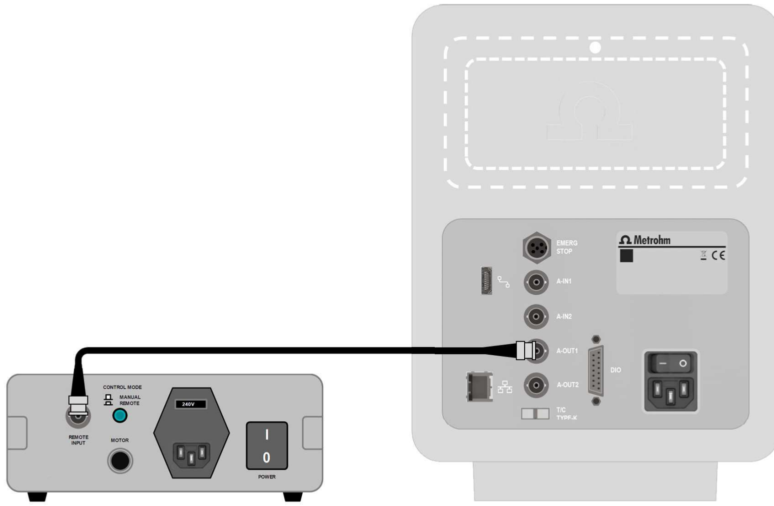


Figure 45 Connection between the Remote Input of the Motor Controller (left) and the Analog Output (A-OUT1) of VIONIC (right) using a BNC cable.

For additional details on the Autolab Rotating Electrode, please see the dedicated User Manual.

To remotely control the rotation rate of the Autolab Rotating Electrode, make sure that the Motor controller is in Remote operation mode.

5.1.1 Creating the work system with the Autolab Rotating Electrode in INTELLO

Once the Autolab Rotating Electrode is physically connected to the analog output of VIONIC, the work system can be created in INTELLO.

In INTELLO, in the work system editor window, add the Autolab RDE as an Autolab accessory. Once added, it should appear in the *Known devices* list, under the Autolab Accessories group.

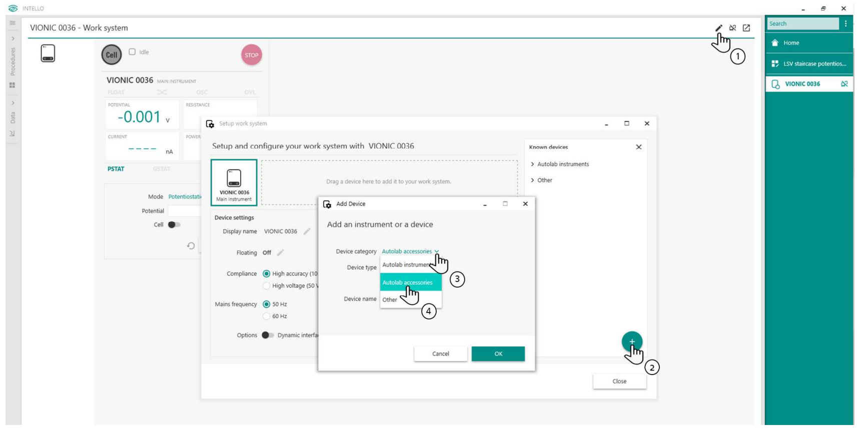


Figure 46 Adding an Autolab Rotating Electrode to the Known devices list in the Edit Work system window in INTELLO.

The newly created Autolab Rotating Electrode device can be dragged-and-dropped from the *Known devices* list to the field adjacent to the *Main instrument*, onto the same A-OUT connector to which the BNC cable is connected on the back panel of VIONIC.

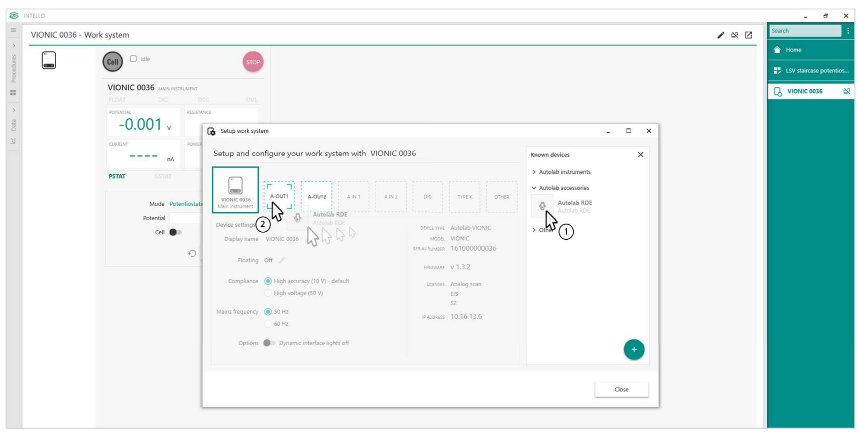


Figure 47 Adding an Autolab Rotating Electrode to the Work system in the Edit Work system window in INTELLO. In this example, the Motor controller is connected to the VIONIC's analog output 1 (A-OUT1).

Either analog outputs (A-OUT1 or A-OUT2) can be used in VIONIC. The configuration of the work system in INTELLO must correspond to the physical connection between the Autolab Rotating Electrode and VIONIC.

If a procedure is prepared offline (i.e., without having a work system connected and claimed) for an experiment which requires an Autolab Rotating Electrode connected to VIONIC, the required work system must be defined in advance in the Procedure setting tile of the respective procedure.

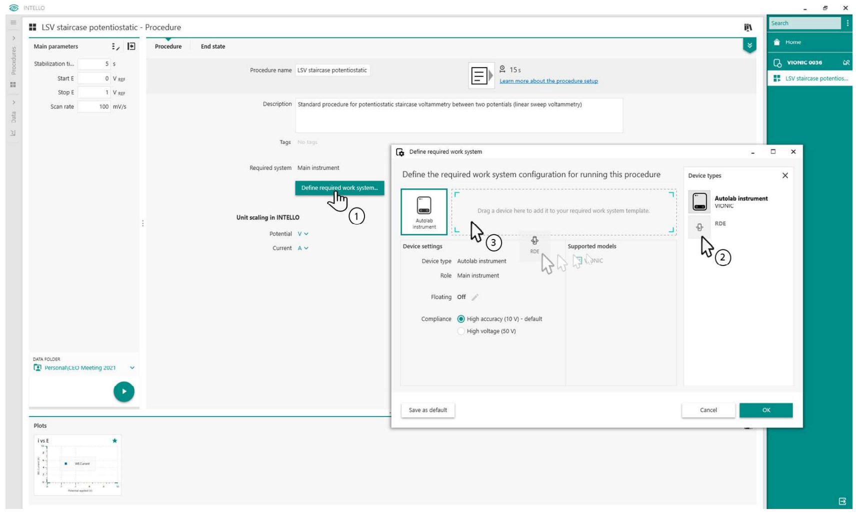


Figure 48   Adding an Autolab Rotating Electrode to the Required Work system in the Edit Work system window in INTELLO.

Once the Autolab Rotating Electrode is added to the required work system and the RDE command is used in the sequence, the RDE.Rotation rate can be selected for sampling in the Signals tab of the measurement commands.

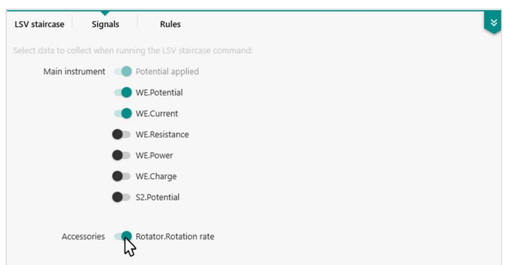


Figure 49   Selecting the RDE.Rotation rate in the Signals tab of the measurement command in INTELLO.

If a non-Autolab Rotating Electrode needs to be used in a work system, the same steps described above should be followed. The new device will be defined in the *Known devices* list under Other group.

5.2 Work system including a K-type Thermocouple (TC) for temperature monitoring

For applications and experiments which require temperature monitoring during the electrochemical measurements, a work system can be created by adding a K-type thermocouple (TC) to the VIONIC main instrument. The procedure of adding a K-type TC to the work system is described here.

As a first step, the K-type TC must be plugged into the connector labeled correspondingly on the back panel of VIONIC.

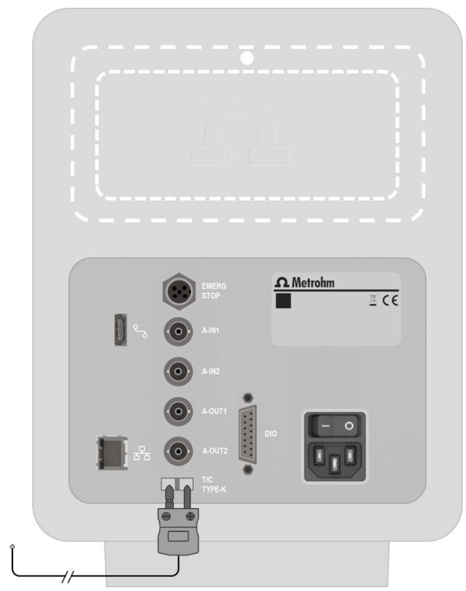


Figure 50 Connecting a K-type TC to the back of VIONIC.

Any TC with a standard K-type connectors can be connected to VIONIC. For the details specifications and characteristics of the TC, please check the specification sheet provided by the TC's manufacturer. For guidance on selecting an adequate TC for your experiment, please contact your local Metrohm Autolab support office.

5.2.1 Creating the work system with a K-type Thermocouple

Once the K-type TC is plugged into the connector on the back panel of VIONIC, the work system which includes a Main instrument and a TC can be created in INTELLO.

In INTELLO, in the work system editor window, add the Thermocouple (TC) as an Autolab accessory. Once added, it should appear in the *Known devices* list, under the Autolab Accessories group.

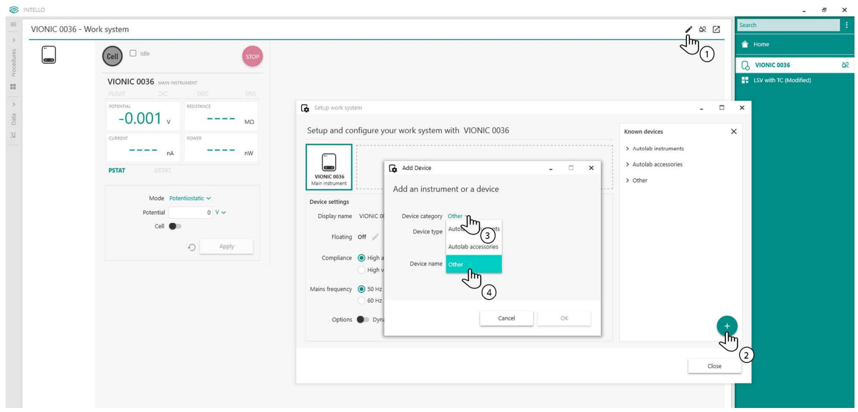


Figure 51 Adding the Thermocouple (TC) to the Known devices list in the Edit Work system window in INTELLO.

The newly created Thermocouple (TC) device can be dragged-and-dropped from the *Known devices* list to the field adjacent to the *Main instrument*, onto the TYPE K marked field.

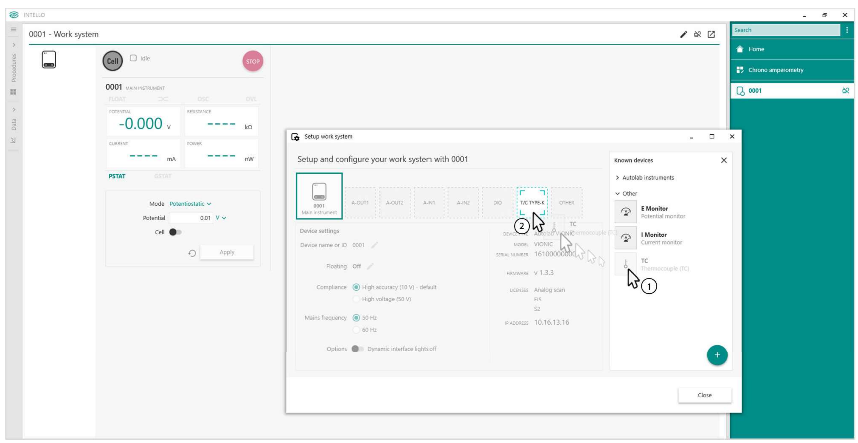


Figure 52 Adding a Thermocouple (TC) to the Work system in the Edit Work system window in INTELLO.

If a procedure is prepared offline (i.e., without having a work system connected and claimed) for an experiment which requires temperature monitoring with a K-type Thermocouple (i.e., a TC connected to VIONIC), the required work system must be defined in advance in the Procedure setting tile of the respective procedure.

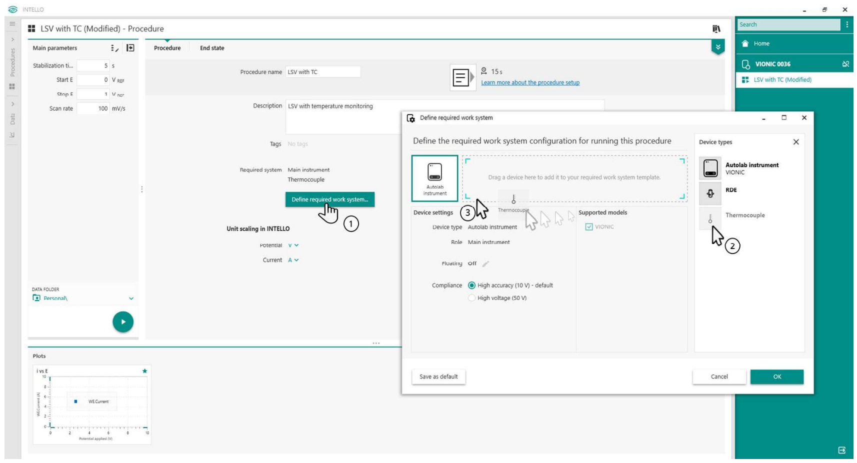


Figure 53 Adding a Thermocouple (TC) to the Required Work system in the Edit Work system window in INTELLO.

Once the Thermocouple (TC) is added to the required work system, the TC.Temperature signal can be selected for sampling in the Signals tab of the measurement commands.

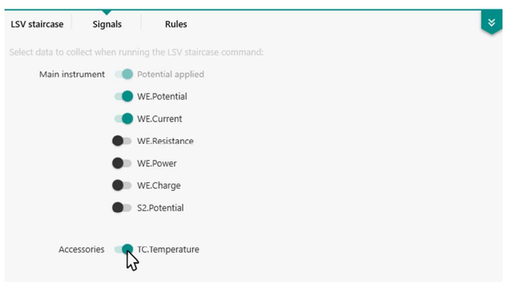


Figure 54 Selecting the TC.Temperature in the Signals tab of the measurement command in INTELLO.

If the Thermocouple will be placed **inside the electrochemical cell** during the electrochemical measurements (e.g., TC will be in contact with the electrolyte or any of the electrodes), an **insulated Thermocouple MUST be used**.

5.3 Work system for external monitoring of the measured electrochemical signals (E Monitor and I Monitor)

For applications and experiments which require external monitoring of the measured electrochemical signals (i.e., E and i) a Work system can be created by enabling an E Monitor and/or I Monitor output on the VIONIC main instrument. A common example when such a Work system would be used is the case when the measured potential and/or current needs to be monitored by an oscilloscope.

The E Monitor and/or I Monitor output on a VIONIC instrument are enabled through the A-OUT1 and/or A-OUT2 connectors on the back panel of VIONIC and by creating the corresponding Work system in INTELLO. Additionally, the corresponding A-OUT connectors (i.e., A-OUT1 and/or A-OUT2) on the back panel of VIONIC must be connected to the analog input connectors of the external device.

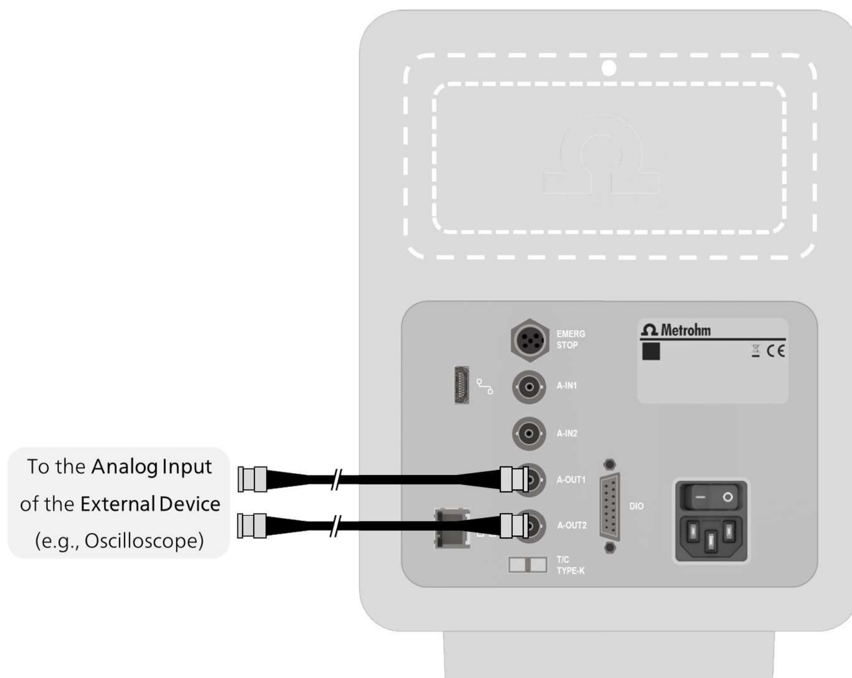


Figure 55 Connecting external devices to the Analog Outputs (A-OUT1 and A-OUT2) of VIONIC for monitoring the measured potential (E Monitor) and current (I Monitor).

5.3.1 Creating the Work system for external monitoring of the electrochemical signals (E Monitor and I Monitor)

Once the external device (e.g., the oscilloscope) is connected to the A-OUT1 and/or A-OUT2 of VIONIC, the corresponding Work system can be created in INTELLO.

E Monitor and I Monitor (i.e., the potential and current monitor) are always available In INTELLO, in the *Known devices* list of the Work system editor window, under the *Others* group.

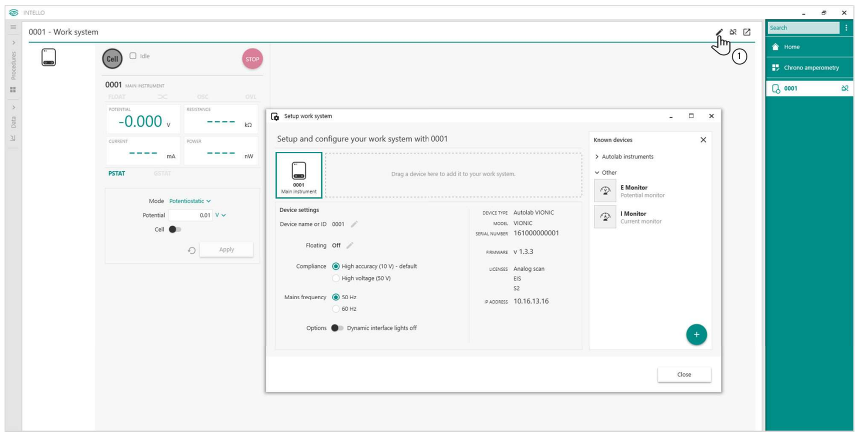


Figure 56 E Monitor and I Monitor in the list of the Known devices under the Others group.

To create a Work system for external monitoring of the electrochemical signals, E Monitor and I Monitor can be dragged-and-dropped from the *Known devices* list to the field adjacent to the *Main instrument*, onto the A-OUT field corresponding to the physical connection where the external device is connected to VIONIC.

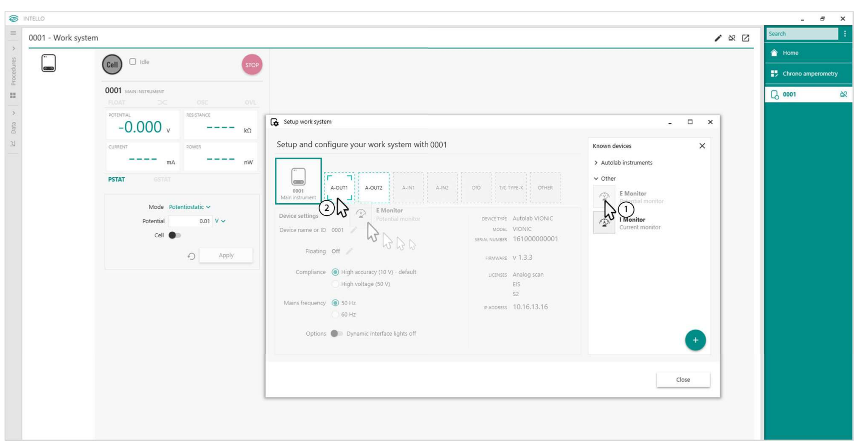


Figure 57 Adding E Monitor to the Work system in the Edit Work system window in INTELLO. In this example, E Monitor is

enabled on the VIONIC's analog output 1 (A-OUT1). The same procedure can be followed for enabling I Monitor.

On the external device, the E Monitor signal is a $V_{EMonitor}$voltage corresponding to the measured potential in the electrochemical cell:

$V_{EMonitor} = E_{meas}$.

The I Monitor signal is a $V_{IMonitor}$voltage proportional to the measured current in the electrochemical cell and it depends on the current range (CR) used for the measurement:

$V_{IMonitor} = i_{meas} / CR$

For example, if we measure 2 mA on the 10 mA $\cdot V^{-1}$ CR, the voltage on the I Monitor connector will be $V_{IMonitor} = (2\ mA) / (10\ mA \cdot V^{-1}) = 0.2\ V$

The output impedance of A-OUT1 and A-OUT2 on the back panel of VIONIC is 50 Ω with a maximum current of 20 mA and a maximum output potential of ±10V.

E Monitor and I Monitor can be enabled on either analog outputs (A-OUT1 or A-OUT2) on VIONIC. The configuration of the Work system in INTELLO must correspond to the physical connection between the VIONIC and the external device.

In a procedure sequence, there are no specific settings which need to be set or enabled for the external monitoring of the electrochemical signals. Therefore, when creating procedures offline (i.e., without having a VIONIC instrument claimed), there is no need to define a specific Work system in the procedure command of the procedure sequence. A procedure sequence used to monitor externally the electrochemical signals is not Work system specific as long as the A-OUT1 and/or A-OUT2 are configured according to the physical connection between VIONIC and the external devicxe.

5.4 Cell Protection

Cell protection limits can be specified in INTELLO, to protect the cell or DUT against overcurrents or overvoltages. These limits are checked by the instrument itself, and the cell is switched off as soon as one of them is reached. They are valid during and in between measurements (see details below) when activated. If no measurement is running, the cell is isolated and an error is displayed on the instrument and INTELLO. If triggered during a run, the cell is isolated (working electrode disconnected), the procedure paused, and can either be resumed (if the limit was reached by accident and the situation can be fixed by readjusting the cell or the cables: disconnected cable, or contact issue between the cable and the, an issue with the reference electrode, etc.) or stopped.

The cell protection settings are accessible in the work system view, or at the procedure level, in the procedure tile, and the cell protection tab.

Work System: in the work system overview, an E and I symbols are visible next to cell button and display the state of the cell protection on the work system. Clicking on these opens a dialog where the values can be specified. When the triangles around the "E" and "i" are grey: no limits are defined.

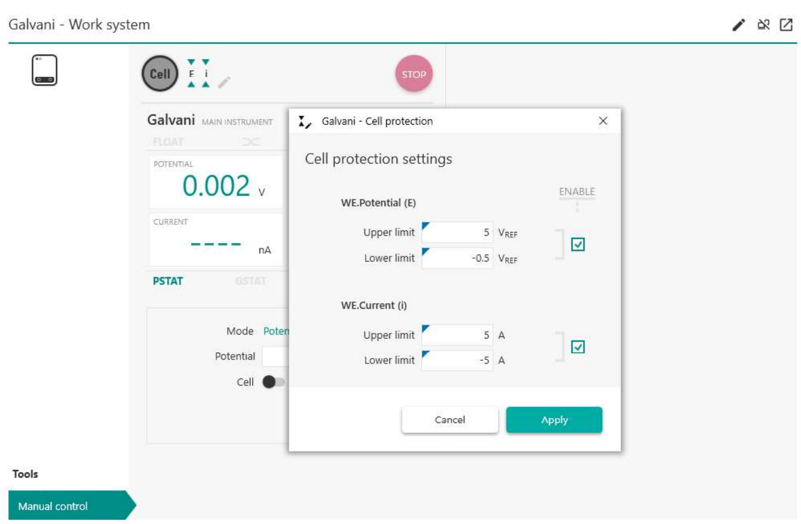


Figure 58 Cell protection settings in the Work system view. The green triangles around E and i next to the cell button indicate that cell protection is active on both signals.

Cell protection tab in the procedure settings: limits input in a procedure are watched by the instrument as soon as the procedure starts and until a new procedure with different cell protection settings is run, or the settings of the work system are modified. The option to "Apply new cell protection settings when starting a run" is by default toggled off, meaning that no cell protection is active unless defined in the work system.

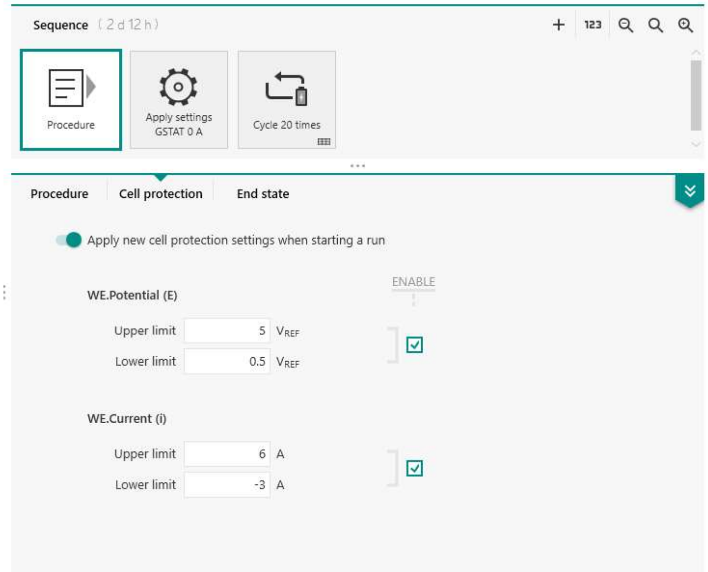


Figure 59 Cell protection settings in the procedure tile of a procedure.

The protection limits defined in the work system apply as long as the system is on unless specified otherwise in a procedure, or disabled later in the Work System. In case a procedure is started with different settings than specified in the work system, a warning is displayed with the possibility to overwrite the settings of the work system or stop and edit one or the other.

ℹ It is recommended to only apply the cell protection when a cell is connected to the VIONIC with (at least) the S and RE leads, especially when a limit on potential is appplied at the work system level. If no cell is connected, the fluctuations of potential when the S and RE are not connected could trigger the cell protection center of VIONIC.

When a limit is crossed, the Work system is isolated and the cell switched off: no current can flow through the cell anymore. In the work system view, one of the triangles next to the cell button indicates which limit was reached*(see "Cell Protection", chapter 5.4, page 96)*. If the limit was reached accidentally (bad connection, for example), the cell button must be pressed to reactivate the cell control and before resuming the procedure.

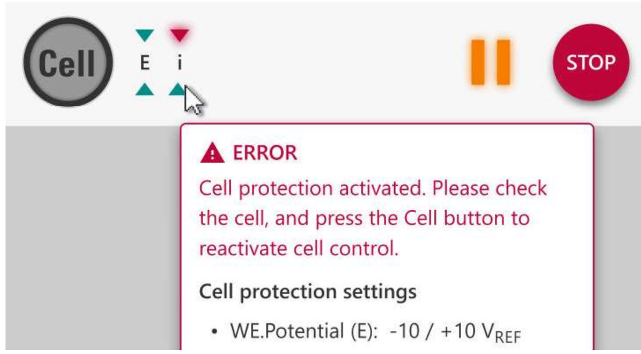


Figure 60 Cell protection triggered on the higher limit of the WE.Current.

6 Experimental setup considerations

Specific aspects concerning possible experimental setups with different types of electrochemical cells and connections, the correct use of the Faraday cage as well as the factors which can influence the quality of experimental (measurement) results are presented here.

6.1 Cell connections

As described in the dedicated chapter, the connection between VIONIC and the electrochemical cell is realized with the Pure signal bridge and the Adaptive cables. These allow different connection modes of VIONIC to the electrochemical cell, depending on the application.

Independently of the cell connection mode, when VIONIC is connected to an electrochemical cell, the potential is always controlled or measured between the Reference (RE) and Sense electrode (S) leads and the current is always measured or controlled between the Working (WE) and the Counter electrode (CE) leads. It is also important to know that the Second sense (S2) can only *measure* the potential with regard to the Reference electrode (RE). It is not possible to control or apply a potential by using the Second sense (S2) feature.

The standard Adaptive cables included with VIONIC are equipped with 4 mm male banana connectors. Please check the *Instrument description* chapter for details about optional Adaptive cables with different type of connectors.

The connections (leads) available on the Adaptive cables of VIONIC are labeled as follows:

- **Working (or indicator) electrode:** WE (red)
- **Sense electrode:** S (red)
- **Reference electrode:** RE (blue)
- **Counter electrode:** CE (black)
- **Second sense:** S2 (black)
- **Earth ground:** EARTH (green)
- **Analog ground:** AGND (black)

The Adaptive cables must be connected to the pure signal bridge by following the corresponding labeling.

Figure 61 Connectors and labeling on the Pure signal bridge (Buffer (1) and Splitter (2) boxes).

Independently of the cell connection mode, the potential is always controlled or measured between the reference (RE) and sense electrode (S) leads and the current is always measured or controlled between the working (WE) and the counter electrode (CE) leads.

There are a large variety of electrochemical applications which use different types of electrochemical cells. The main differences between these types of electrochemical cells are give by:

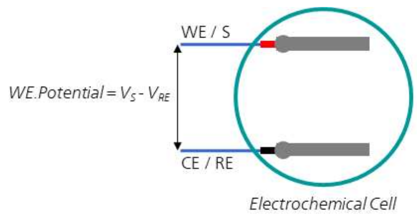
- The number of connection points (electrodes) to the cell:
  - 2-electrode cell setup
  - 3-electrode cell setup, with and without monitoring a second voltage (S2)
  - 4-electrode cell setup, with and without monitoring a second voltage
- Based on the grounding state of the cell:
  - non-grounded cells
  - grounded cells
- Based on the power requirements of the cell:
  - Passive cells
  - Active cells

Further details on how to connect the Pure signal bridge and adaptive cables of VIONIC to the electrochemical cell is presented individually for each type of electrochemical cell.

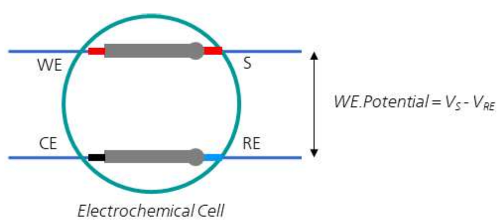
If you have any doubts on how to connect VIONIC to your eletrochemica cell, please contact your local Metrohm Autolab distributor for advice.

6.1.1 Cell connections: 4-connectors mode (No S2)

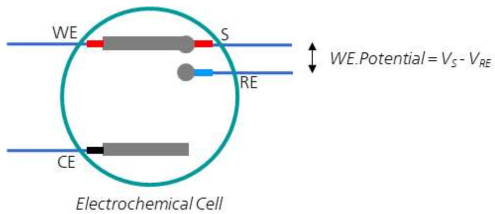
- **Two electrode mode, 2-point connection:** in this mode, the Counter (CE) and Reference electrode (RE) Adaptive cables are connected together to one electrode (e.g. negative electrode of a battery) while the Working (WE) and Sense electrode (S) cables are connected to the other electrode (e.g. positive electrode of a battery). The current is always measured between the CE and the WE and the potential difference is measured between the RE and the S. This mode is commonly used for the characterization of energy storage and conversion devices like batteries, fuel cells, solar cells and supercapacitors, in electrolysis or whenever the use of a stand-alone reference electrode is not possible.



- **Two electrode mode, 4-point connection:** in this mode the Counter (CE) and the Reference electrode (RE) Adaptive cables are connected separately to the same electrode (e.g. negative electrode of a battery) and the Working (WE) and the Sense electrode (S) cables are connected separately on the other electrode (e.g. positive electrode of a battery). This connection mode is highly recommended for high current and/or low impedance applications. Furthermore, it is recommended to place the RE and S as close as possible to the electrodes in the cell. This will reduce ohmic losses coming from the connections. This connection mode is particularly important for electrochemical impedance spectroscopy (EIS) characterization of low impedance devices such as batteries and fuel cells.

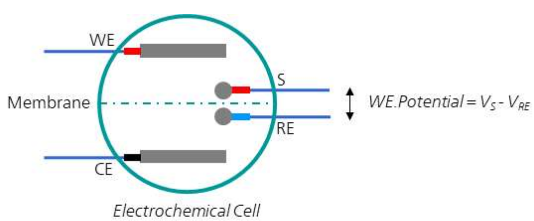


- **Three electrode mode:** in this mode, the Counter (CE) and Reference (RE) electrodes of the Adaptive cables are connected to a counter and reference electrode of the cell, respectively. The The Working (WE) and Sense electrode (S) cables are connected to the working electrode in the cell. The current is measured between the CE and the WE and the potential difference is measured between the RE and the S. This is the most common mode of connecting an electrochemical cell and is used for the characterization most electrochemical systems in which a separate reference electrode is used.

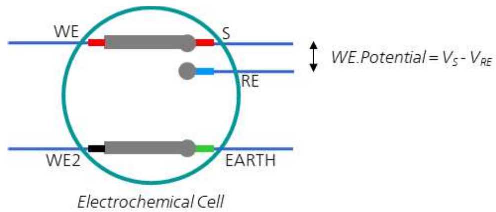


It is common practice to place the Reference electrode (RE) as close as possible to the Working electrode (WE) to reduce the uncompensated resistance and reduce the ohmic losses arising from this resistance. This can be achieved by physically placing the reference electrode close to the working electrode or by using a *Luggin-Haber* capillary.

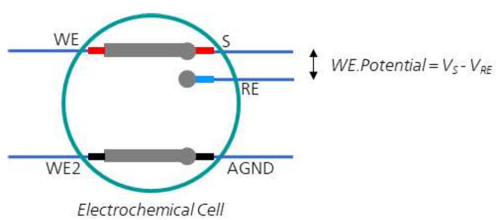
- **Four electrode mode:** in this mode, each Adaptive cable is connected to its own electrode in the cell. The difference when compared with the three electrode setup mentioned above is that the Sense electrode (S) lead is connected to a second reference electrode or innert probe in the electrochemical cell. The Four electrode setup is used for measurements accross membranes or liquid-liquid interfaces generated by two non miscible solvents. The current is measured between the CE and the WE and the potential difference is measured between the RE and the S. This mode is commonly used for the characterization of membranes and liquid-liquid interfaces.



- **Zero Resistance Ammeter (ZRA), non-floating mode:** in this mode, the Working (WE) and Sense (S) electrodes of the Adaptive cables are connected to the first working electrode (WE1), the Reference electrode (RE) cable is connected to the reference electrode in the cell and the additional ground cable (EARTH) is connected to the second working electrode (WE2) in the cell. When this connection mode is used, the current is monitored in non-invasive way as no external perturbation is applied to the electrochemical cell. This connection mode is used for monitoring the potential and current fluctuations (electrochemical noise, ECN) that arise directly from the electrochemical reactions taking place on the electrode surface. For this configuration, the first working electrode (WE1) and/or the cell cannot be connected to Earth.



- **Zero Resistance Ammeter (ZRA), floating mode:**in this mode, the Working (WE) and Sense (S) electrode of the Adaptive cables are connected to the first working electrode (WE1), the reference electrode (RE) lead is connected to the reference electrode in the cell and the additional analog ground cable (AGND) is connected to the second working electrode (WE2) in the cell. When this connection mode is used, the current is monitored in non-invasive way as no external perturbation is applied to the electrochemical cell. This connection mode is used for monitoring the potential and current fluctuations (electrochemical noise, ECN) that arise directly from the electrochemical reactions taking place on the electrode surface *only when ZRA (or ECN) measurements are done with a grounded first working electrode (WE1) or a grounded cell.*



Please notice that in the case of the four-electrode mode the Sense (S) is not connected to the Working electrode (WE). The *WE.Potential* signal is **always** the potential difference between the Sense (S) and the Reference electrode (RE).

When the Sense (S) is not connected to the Working electrode (WE), the difference between *S2.Potential - WE.Potential* will **not** be the voltage difference between the Counter electrode (CE) or the Second Sense (S2) and the Working electrode (WE).

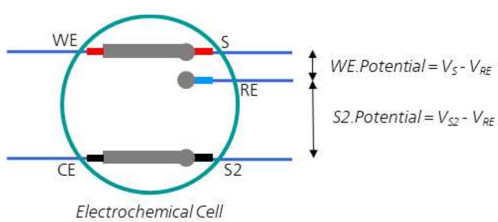
The Analog ground Adaptive cable (AGND) is not included in the standard list of accessories which are delivered with VIONIC. For additional information, please contact your local Matrohm Autolab support office.

6.1.2 Cell connections: 5-connectors mode (with S2)

By using the Second sense (S2) connection , VIONIC provides the possibility of measuring an additional voltage in the electrochemical cell with regard to the Reference electrode (RE). The following cell connection modes are possible when the Second sense (S2) is used:

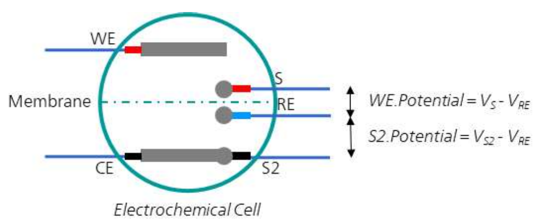
Second Sense (S2) connected to the Counter electrode (CE)

- **Three electrode mode with the Second sense (S2) connected to the Counter electrode (CE):** This is a typical three electrode setup with the Second sense (S2) and the Counter electrode (CE) Adaptive cables connected together to the counter electrode in the cell. The Reference electrode (RE) cable is connected to the reference electrode and the Working (WE) and Sense electrode (S) leads are connected to the working electrode in the cell. The current is measured between the CE and the WE. The S and S2 leads are used to measure the potential difference between WE and CE versus RE, respectively. This is the most common mode of connecting an electrochemical cell and is used for the characterization the electrochemical systems in which a separate reference electrode is used and additionally the voltage of the counter electrode is monitored.

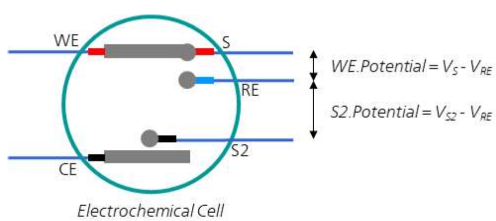


It is common practice to place the reference electrode as close as possible to the working electrode to reduce the uncompensated resistance and reduce the ohmic losses arising from this resistance. This can be achieved by physically placing the reference electrode close to the working electrode or by using a *Luggin-Haber* capillary.

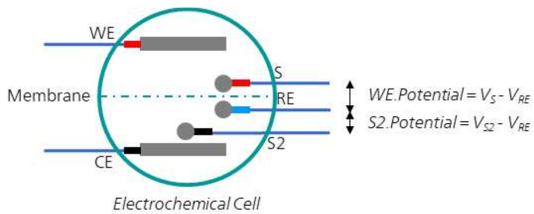
- **Four electrode mode with the Second sense (S2) connected to the Counter electrode (CE):** in this mode, the Second sense (S2) and the Counter electrode (CE) Adaptive cables are connected together to the counter electrode in the cell. The Reference (RE), Working (WE) and Sense electrode (S) Adaptive cables are connected to an individual electrode or innert probe in the cell. The Four electrode setup is used for measurements accross membranes or liquid-liquid interfaces generated by two non miscible solvents. The current is measured between the CE and the WE and the potential difference is measured between the RE and the S. By using the Second sense (S2) connected to the Couner electrode (CE), the potential of the CE versus the Reference electrode (RE) can be monitored. This mode is commonly used for the characterization of membranes and liquid-liquid interfaces.



- **Three electrode mode with stand alone Second sense (S2):** this is the same as a typical three electrode setup but with the Second sense (S2) Adaptive cable connected to a stand alone probe in the cell. The Counter electrode (CE) cable and the Reference electrode (RE) Adaptive cables are connected to the counter and reference electrodes if the electrochemical cell, respectively. The Working (WE) and Sense electrode (S) Adaptive cables are connected together to the working electrode in the cell. The current is measured between the CE and the WE. The potential difference between S and RE (i.e. the potential difference between WE and RE) and the potential difference between S2 and RE can be monitored.



- **Four electrode mode with stand alone Second sense (S2):**this is the same as a typical four electrode setup but with the Second sense (S2) Adaptive cable connected to a stand alone probe in the cell.Therefore, in this case, all Adaptive cables are connected to an individual electrode or innert probe in the cell. The Four electrode setup is used for measurements accross membranes or liquid-liquid interfaces generated by two non miscible solvents. The current is measured between the CE and the WE. The potential difference between S and RE and the potential difference between S2 and RE can be monitored. This mode is commonly used for the characterization of membranes and liquid-liquid interfaces.



Please notice that in the case of the four-electrode mode the Sense (S) is not connected to the Working electrode (WE). The *WE.Potential* signal is **always** the potential difference between the Sense (S) and the Reference electrode (RE).

When the Sense (S) is not connected to the Working electrode (WE), the difference between *S2.Potential - WE.Potential* will **not** be the voltage difference between the Counter electrode (CE) or the Second Sense (S2) and the Working (WE) electrode.

When the electrochemical cell is connected in **two electrode mode**, either in 2 point or 4 point connection, the use of S2 to measure the voltage of the CE will not bring any additional information because S2, CE and RE are connected together (i.e. the potential difference between S2 and RE will be always zero). If the application requires independent monitoring of the electrochemical processes occuring at the annode and cathode of an energy storage device, a **three electrode** connection mode is required by using a stand-alone reference electrode in the electrochemical cell.

For grounding a Faraday cage or when a ground connection is required within the work system which includes the VIONIC instrument, always the **EARTH connector** of the cell cables must be used. This applies either when the instrument operates in non-floating mode or in floating mode. The EARTH connector is directly connected to the Earth ground of the instrument. Please see details in the dedicated section which describes how to connect a Faraday cage.

6.2 Grounded and non-grounded electrochemical cells

VIONIC is equipped with the *selectable floating* feature which allows to connect VIONIC to any type of electrochemical cells, grounded or not grounded. With a software controlled switch, VIONIC has the possibility work in "normal" or non-floating (grounded) mode and also in floating mode. The floating/non-floating mode selection is available in the Work system editor in INTELLO

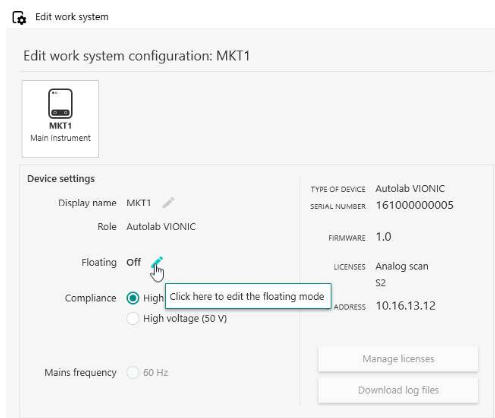


Figure 62 The floating mode selection in the Work system editor in INTELLO

For more details about the Work system editor in INTELLO, please see the dedicated paragraph in the User manual.

In *grounded (non-floating) mode*, the control and measurement electronics of VIONIC is connected to the protective Earth ground and, during operation, it uses the Earth ground (EARTH) as the ground reference.

In *floating mode*, the control and measurement electronics of VIONIC is disconnected from the protective Earth ground and, during operation, uses a floating analog ground (AGND) as reference ground.

To achieve the best possible measurement performance, it is very important to select the correct operation mode of VIONIC (i.e. floating or non-floating) for the type of the electrochemical cells used in the experiment .

The electrode connection modes are described in the dedicated section of the User manual and they apply for both grounded and non-ground electrochemical cells.

6.2.1 Non-grounded electrochemical cells

The vast majority of the electrochemical experiments use a classical, non-grounded electrochemical cell. This means that the electrochemical cell, including the cell vessel, electrodes and electrolyte are totally isolated from Earth (i.e. they are not grounded). In this case, for the best measurement performance, the instrument must be set in non-floating mode (i.e VIONIC should not be set in floating mode).

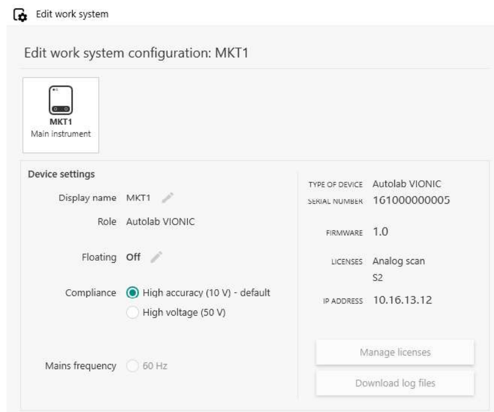


Figure 63 VIONIC set up in non-floating mode (i.e. Floating set Off)

If VIONIC was used in floating mode and must be switched to non-floating mode (non-grounded cells are used in the experiment), the corresponding selection must be made in the Work system editor selection guide.

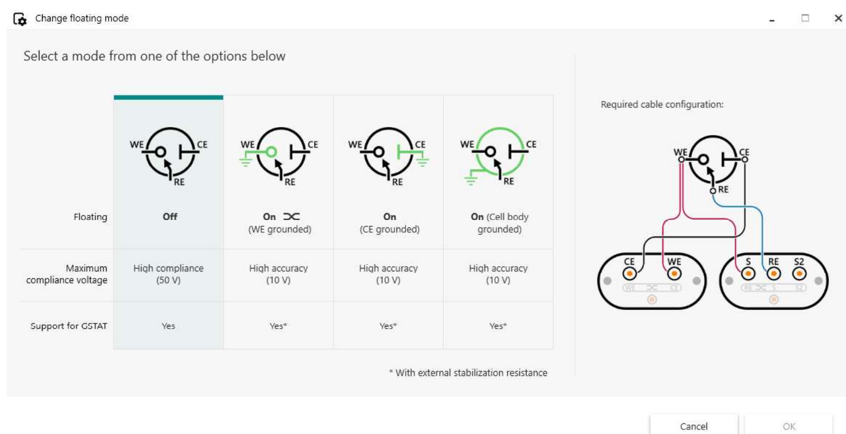


Figure 64 Non-floating selection and connection guide in the Work system editor in INTELLO for electrochemical cells which are not grounded.

- The Adaptive cables must be connected to the Pure signal bridge by following the main labeling.

- VIONIC can be used in both High accuracy (±10V compliance voltage range) and High compliance mode (±50V compliance voltage range)
- VIONIC can be used in both Potentiostatic and Galvanostatic mode without any additional limitations, within the specifications.

When VIONIC is switched on, the default state will be non-floating mode.

In general, a grounded electronics is always more stable and less noisy than a floating electronics. Therefore, the floating mode should be used only when needed. When VIONIC is connected to general, non-grounded electrochemical cells, it is recommended to use the normal, non-floating (grounded) mode for VIONIC.

Please note that not only a short circuit or a resistance can make a connection to earth, but also a capacitance is capable of providing a conductive path (for AC signals). When a non-floating instrument is used to measure on a grounded cell, an undefined current will flow through the PGSTAT control loop when the electrode connections from the PGSTAT are connected to the cell (i.e. current will leak to the ground) and measurements will not be possible.

When VIONIC operates in non-floating mode, the analog ground of the electronics (AGND) is connected to the Earth. In this case, **AGND** and **EARTH** are internally connected to each other and to the Earth. The use of **ANGND** connection and cable is not needed. More details about the Earth and Analog ground switch is available in the chapter describing the block diagram of the instrument.

Please check the Faraday cage connection section for details on how to connect correctly a Faraday cage.

6.2.2 Grounded electrochemical cells

For some specific electrochemical applications and experiments, a grounded electrochemical cell must be used. An electrochemical cell is grounded in one of the following cases:

- The working electrode (or sample) is or must be connected to the Earth
- The counter electrode (auxiliary electrode or current collector) is or must be connected to the Earth
- The cell vessel (container) is or must be connected to the Earth

Figure 65 Graphical representation of different types of grounded cells with the grounding point.

Due to the *selectable floating* feature, VIONIC can be connected and used with any of the above mentioned grounded cell types for both potenstiostatic and galvanostatic measurements.

Depending on the type of the electrochemical cell used in the experiment, the corresponding floating mode of VIONIC must be selected in the Work system editor and cell must be connected accordingly. The Work system editor in INTELLO includes a comprehensive guidance for the user to select the apropriate floating mode depending on the type of the the grounding point in the cell. A clear indication of the connections on the Pure signal bridge is also shown in at the moment of the floating mode selection in INTELLO.

Please notice the labeling on the Pure signal bridge. When the Cross Floating mode must be used, please make sure you connect the Adaptive cables according to the labeling corresponding to the sign on the Pure signal bridge.

Grounded Working electrode (WE)

In this case, the Working electrode (WE) in the electrochemical cell is directly connected to the Earth ground.

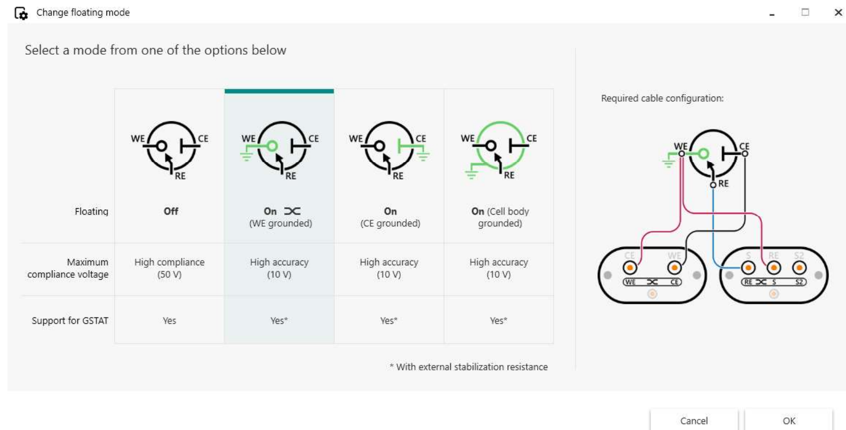


Figure 66 *Cross Floating mode selection and connection guide in the Work system editor in INTELLO for electrochemical cells with grounded Working electrode (WE).*

- VIONIC must be set in Cross Floating mode by following the guide in the Work system editor in INTELLO. The FLOAT together with the sign will be shown on the dynamic interface.
- The Adaptive cables must be connected to the Pure signal bridge by following the labeling corresponding to the sign.
- VIONIC can be used in High Accuracy mode only (±10V Compliance voltage range).
- In case of measurements done in Galvanostatic mode, the use of the external Stabilization resistance box is required.

Grounded Counter electrode (CE)

In this case, the Counter electrode (CE) in the electrochemical cell is directly connected to the Earth ground.

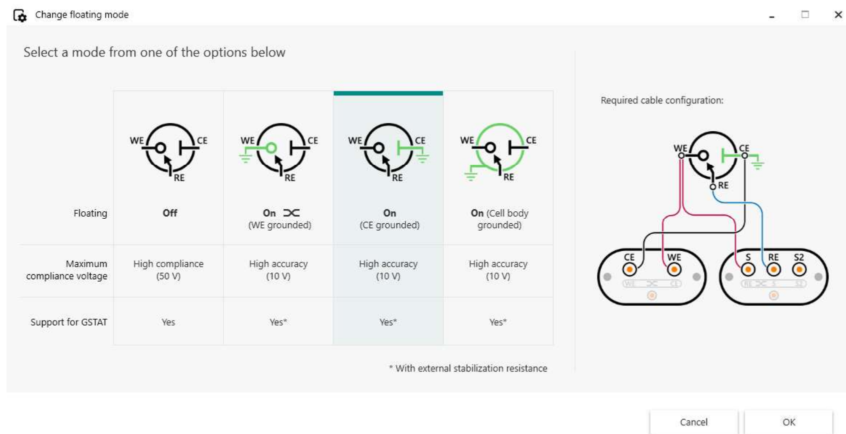


Figure 67 Floating mode selection and connection guide in the Work system editor in INTELLO for electrochemical cells with grounded Counter electrode (CE).

- VIONIC must be set in Floating mode by following the guide in the Work system editor in INTELLO. The FLOAT sign will be shown on the dynamic interface.
- The Adaptive cables must be connected to the Pure signal bridge by following the main labeling.(same as for the non-floating mode).
- VIONIC can be used in High Accuracy mode only (±10V Compliance voltage range)
- In case of measurements done in Galvanostatic mode, the use of the external Stabilization resistance box is required.

Grounded cell vessel

In this case, the electrically conductive electrochemical cell vessel is directly connected to the Earth ground.

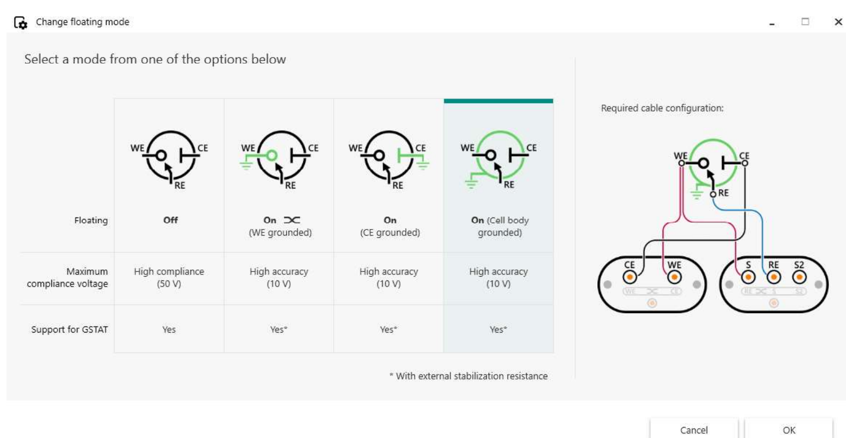


Figure 68 Floating mode selection and connection guide in the Work system editor in INTELLO for electrochemical cells with grounded cell vessels.

- VIONIC must be set in Floating mode by following the guide in the Work system editor in INTELLO. The FLOAT sign will be shown on the dynamic interface.
- The Adaptive cables must be connected to the Pure signal bridge by following the main labeling (same as for the non-floating mode).
- VIONIC can be used in High Accuracy mode only (±10V Compliance voltage range)
- In case of measurements done in Galvanostatic mode, the use of the external Stabilization resistance box is required.

From the instrument perspective, the floating mode and the cell connections are the same when electrochemical cells have a grounded Counter electrode or a grounded cell vessel.

Please note that not only a short circuit or a resistance can make a connection to earth, but also a capacitance is capable of providing a conductive path (for AC signals). When a non-floating instrument is used to measure on a grounded cell, an undefined current will flow through the PGSTAT control loop when the electrode connections from the PGSTAT are connected to the cell (i.e. current will leak to the ground) and measurements will not be possible.

When VIONIC operates in floating mode, the analog ground of the electronics (AGND) is disconnected to the Earth. In this case, **AGND** and **EARTH** are internally disconnected from each other. The EARTH connection is still connected to the protective Earth and to the frame of the instruments. The use of **ANGND** connection is needed only for very specific applications such as Zero Resistance Ammeter (ZRA) (or Electrochemical noise (ECN)) measurements in floating mode. More details about the Earth and analog ground switch is available in the paragraph describing the block diagram of the instrument

Because the analog electronics of VIONIC is isolated from the external input/output board, it is still possible to connect grounded external devices to the external inputs and outputs of VIONIC (I/O board) even when VIONIC is used in floating mode.

When using a Faraday cage with VIONIC set in any of the floating modes, the EARTH connection on the Pure signal bridge must be used for grounding the Faraday cage. Please check the Faraday cage connection section for more details on how to connect correctly a Faraday cage.

If the instrument is set in Floating mode and the measured current is zero or VIONIC indicates an overload on the Dynamic interface (OVL), please make sure that the analog ground is not connected to Earth and the type of floating mode and cable connections correspond to the type of cell used.

If you have any doubts on the type of floating mode and connections, please contact your local Metrohm Autolab distributor for advice.

6.2.3 Galvanostatic measurements on grounded cells

The **GSTAT FLOAT Stabilization** resistor (see figure below) must be used only for galvanostatic measurements with VIONIC operating in floating mode. The external GSTAT FLOAT stabilization is a pure resistor which must be connected in series with the electrode on which the current measurement is done in the electrochemical cell (i.e., the electrode which is NOT connected to ground).

The role of the external GSTAT FLOAT Stabilization resistor is to achieve the most *stable and accurate galvanostatic control when VIONIC is operated in floating mode,* for any type of electrochemical cells (see previous paragraph) having a wide range of properties (i.e. grounded WE, grounded CE or grounded cell vessel in the electrochemical setup, high and low impedance etc).

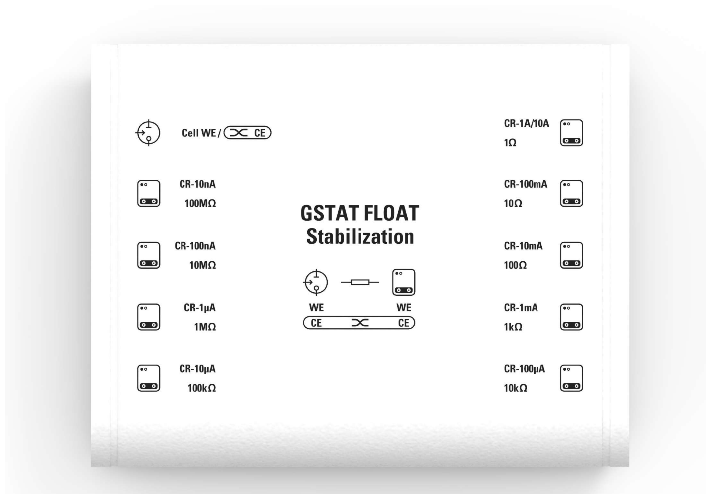


Figure 69 GSTAT FLOAT Stabilization box.

Connecting the GSTAT FLOAT Stabilization box

Depending on the the grounding point of the electrochemical cell, the GSTAT FLOAT Stabilization box should be connected as follows:

Counter electrode (CE) grounded - connect the Working electrode (WE) to the  labeled connector on the GSTAT FLOAT Stabilization box and the WE Adaptive cable of VIONIC to the connector labeled with the  pictogram which corresponds to the current range (CR) used for the measurement.

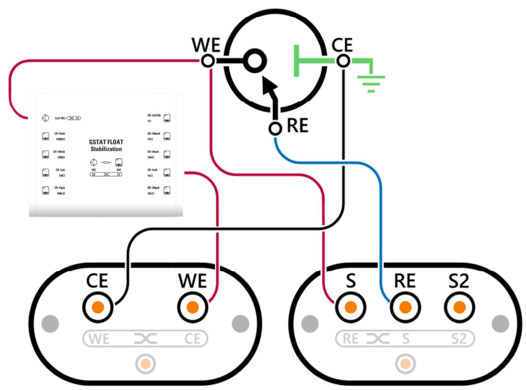


Figure 70 GSTAT FLOAT Stabilization box connection for electrochemical cells with CE grounded.

Cell body grounded - connect the Working electrode (WE) to the  labeled connector on the GSTAT FLOAT Stabilization box and the WE Adaptive cable of VIONIC to the connector labeled with the  pictogram which corresponds to the current range (CR) used for the measurement.

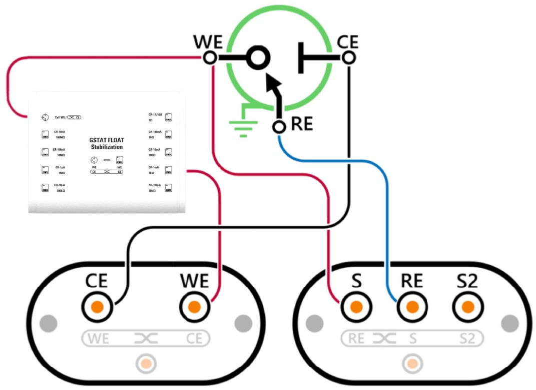


Figure 71 GSTAT FLOAT Stabilization box connection for electrochemical cells with the Cell body grounded.

Working electrode (WE) grounded- connect the Counter electrode (CE) to the labeled connector on the GSTAT FLOAT Stabilization box and the CE Adaptive cable of VIONIC to the connector labeled with the pictogram which corresponds to the current range (CR) used for the measurement. In this case, the *cross mode* floating configuration is used and the labeling corresponding to the symbol must be followed)

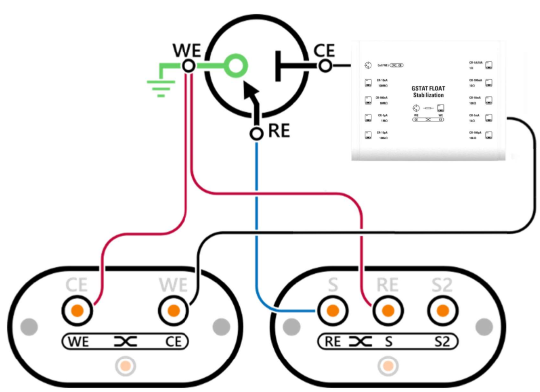


Figure 72 GSTAT FLOAT Stabilization box connection for electrochemical cells with WE grounded.

Electrochemical cell not grounded - do not use the GSTAT FLOAT Stabilization resistance in this case.

The external stabilization resistor which should be used (i.e the position of the connection labeled with the pictogram) depends on the current range in which the galvanostatic measurements is executed and it is $R_{stab}(\Omega) = 1\ (V) / [CurrentRange\ (A)]$, where R_{stab} is the value of the external stabilization resistance and*CurrentRange (A)* is the fixed current range in Ampere used in VIONIC. As a consequence, one specific stabilization resistence must be used for each current range used.

When the external stabilization resistance is used, the Sense (S) and the Reference (RE) Adaptive cables of VIONIC are always connected directly to the respective electrodes in the cell and not to the external stabilization resistor box. Therefore, the potential measurement (always measured between the Reference (RE) and the Sense electrode (S)) will not be influenced by the external stabilization resistor.

The 1 nA current range is not supported in Galvanostatic mode. In case of applications which require control of very low currents, the use of the 10 nA current range is recommended.

The GSTAT FLOAT Stabilization box is offered optionally and therefore, it is not included in the standard list of accessories delivered the VIONIC. For additional details and comercial information, please contact your local Metrohm Autolab representative.

6.3 Passive vs Active electrochemical cells.

This paragraph presents specific details related to the use of **passive** and **active** electrochemical cells and the corresponding VIONIC specifications.

6.3.1 Passive electrochemical cells.

In electrochemistry, the **passive cells** are the "typical", common electrochemical cells for which the potential or the current of the working electrode is controlled in order to generate and control the electrochemical process in the cell. For passive cells, the electrochemical cell "consumes" the electric power delivered by the PGSTAT and this power is actually converted into energy which drives the electrochemical reactions in the electrochemical cell. Therefore, in this case, the power delivered by the PGSTAT is positive which means that both the current and the potential in the cell have the same sign, as shown in the power plot. The total power delivered by the power amplifier of the PGSTAT is determined by the product between the *total cell voltage* (applied or measured) and the *measured/applied current*

The total cell voltage is the total voltage applied to the cell, between the counter electrode (CE) and the working electrode (WE) in order to achieve the user defined *applied voltage* between the working electrode (WE) and reference electrode (RE). The total cell voltage is limited by the compliance voltage of the PGSTAT.

The applied or measured current is the total current flowing between the counter electrode (CE) and the working electrode (WE). The applied and measured current is limited by the maximum current of the PGSTAT.

As the Power plot shows, VIONIC has a distributed power between *high compliance voltage* and *high current*. This allows VIONIC to be used in a wide range of applications with different power requirements.

- **High Compliance mode** - VIONIC can be set to High compliance mode whenever non-conductive (or high resistance) electrolytes and electrochemical cells are used in the experiments and/or the studied electrochemical process has a relatively low charge transfer resistance. In this case, the maximum deliverable power is 150W.
  Some typical examples of such experiments, when VIONIC should be used in high compliance mode are: electrochemistry in organic electrolytes, corrosion in oils and concrete, electrolysis etc. In this case, the maximum compliance voltage, the maximum applied and measured current and the maximum applied and measured potential ranges are:
  - Compliance voltage range: ±50V
  - Maximum applied and measured current range: ±3A
  - Maximum applied and measured potential range: ±10V
- **High accuracy mode** - VIONIC can be set to High accuracy mode whenever conductive (or low resistance) electrolytes and electrochemical cells are used in the experiments and/or the studied electrochemical process has a relatively high charge transfer resistance. Some typical examples of such experiments, when VIONIC should be used in high accuracy mode are: electrochemistry in aqueous acidic or basic electrolytes, corrosion in sea water, energy storage and generation research etc. In this case, the maximum compliance voltage, the maximum applied and measured current and the maximum applied and measured potential ranges are:
  - Compliance voltage range: ±10V
  - Maximum applied and measured current range: ±6A
  - Maximum applied and measured potential range: ±10V

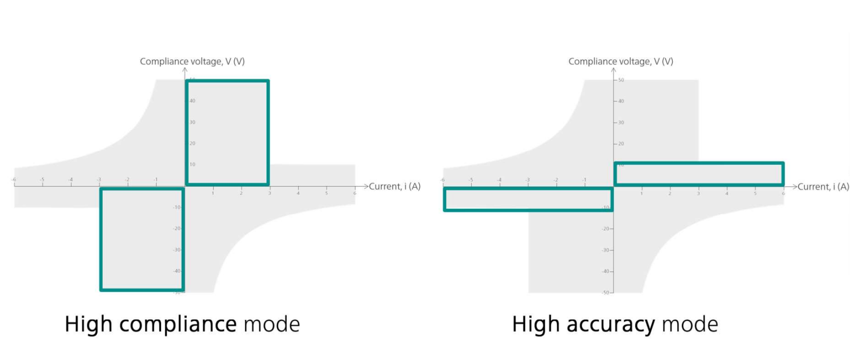


Figure 73 The High compliance and High accuracy region of the Power plot of VIONIC

If the Compliance voltage limit is reached during the electrochemical measurement, the yellow OVL indication will be lit up on the Dynamic interface. In this case, the use of the high compliance mode is necessary or, if already used, the electrochemical cell must be optimized. For more information and explanation of the compliance voltage, other specifications and parameters which can influence the electrochemical instruments, please see the existing supplementary documentation on *www.metrohm.com/electrochemistry* or contact your local Metrohm Autolab distributor.

Difference between High compliance vs High accuracy mode

The accuracy of the applied/measured potential value is always the same.

When using the **High accuracy** mode, the overall control of the electrochemical cell is faster and more accurate. The main difference between **High accuracy** mode and **High compliance** mode is the consequence of the additional gaining which must be used for the high compliance mode, when the voltage range is extended from ±10V (high accuracy mode) to ±50V (high compliance mode). Therefore, because less gaining is used when VIONIC is operated in High accuracy mode, there will be less overall noise in the signal, the control of the cell will be faster and there will be less ringing and overshooting when a signal is applied to the cell.

It is important to always select the instrument settings according to the experiment requirements. The use the high accuracy mode is recommended anytime high compliance is not needed.

6.3.2 Active electrochemical cells

In the case of **active cells**, the electrochemical process in the cell is spontaneous and *the cell delivers power* which needs to be dissipated by the PGSTAT. In this case, the power disipated by the PGSTAT is negative which means that both the current and the potential in the cell have opposite signs, as shown in the figure representing the Power plot of VIONIC. The total power which must be disipated by the power amplifier of the PGSTAT is determined by the product between the *total cell voltage* and the *measured (delivered) current* and is limited by the design of the electronics of the PGSTAT and heat sink of the electronics.

Some common examples of active cells which can deliver significant amount of power are the energy storage devices, measurements on fuel cells while in operating state or other energy generation devices.

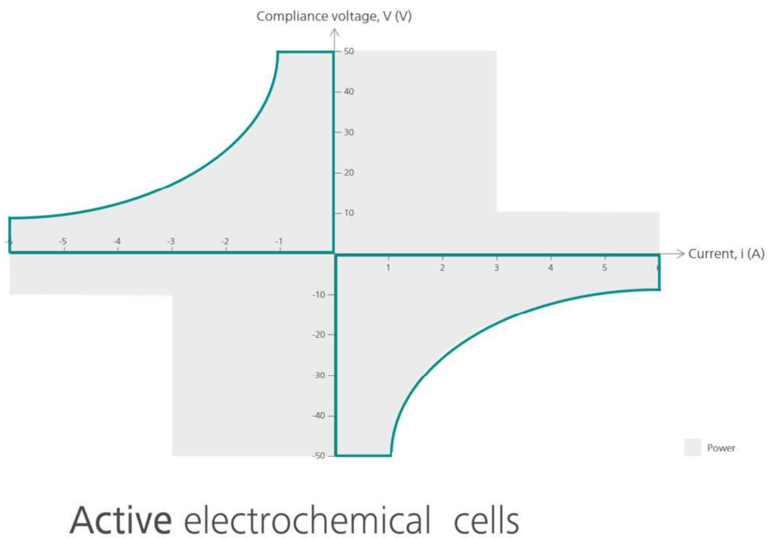


Figure 74 The active cell region of the Power plot of VIONIC

As shown by the Power plot of VIONIC, when active cells are connected, VIONIC can dissipate up to 50W (at 25 °C).

Active cells showing an absolute voltage, $|V_{Cell}|$, of less than 8 V between the working electrode (WE) and counter electrode (CE) are intrinsically safe. They may drive VIONIC into current limit but will not overload the power amplifier.

Active cells that have an absolute voltage higher than 8.3 V between the working (WE) and the counter electrode (CE) may only deliver a maximum current, i_{MAX} given by:

$$i_{MAX} = \frac{P_{MAX}}{|V_{Cell}|} = \frac{50W}{|V_{Cell}|}$$

Temperature overload

When the maximum dissipated power limit is reached, the power electronics of VIONIC might become overheated. In this case, the temperature overload protection circuit will be activated to protect the power electronics of the instrument.

During a temperature overload, the red T_{OVL} indication will be lit on the Dynamic interface of the instrument and the electrochemical cell will be automatically isolated (i.e. automatically disconnected) from VIONIC, for safety purposes. The measurement procedure will be also stopped. If a temperature overload (T_{OVL}) occurs, VIONIC can be recovered only after a complete reboot of the instrument.

As the power dissipation is made by converting power to heat, the maximum dissipated power depends on the operation (environmental) temperature of VIONIC.

VIONIC must be set in High Compliance mode to enable the highest dissipated power.

Maximum input voltage

The maximum voltage range which can be measured with VIONIC is ±10V. The differential electrometer of VIONIC contains an input protection circuitry which is activated when the measured voltage is outside of the ±10V interval. This is implemented to avoid electrometer damage. Please be aware that the OVL indicator, on the Dynamic interface, will not light up for this type of voltage overload. The measured voltage will be cutoff at an absolute value of ±10V.

When using high power active cells, do not try dissipate more than 50W with VIONIC. When active cells are used, always operate them at powers lower than 50W.

Always connect the electrochemical cell or device under test (DUT) to the correct terminals (cell cables) of VIONIC.

In case of any doubts, please contact your local Metrohm Autolab distributor for further guidance on how to connect and setup an electrochemical cell.

6.4 Faraday cage connection

When the electrochemical application requires low current measurements or the external noise from the experimental environment (laboratory) interferes with the electrochemical measurement, the use of a Faraday Cage is advised.

The role of the Faraday cage is to shield the electrochemical cell from any external electromagnetic interference. For the best performance, the Faraday cage should create a common shield around the electrochemical instrument and the cell cables.

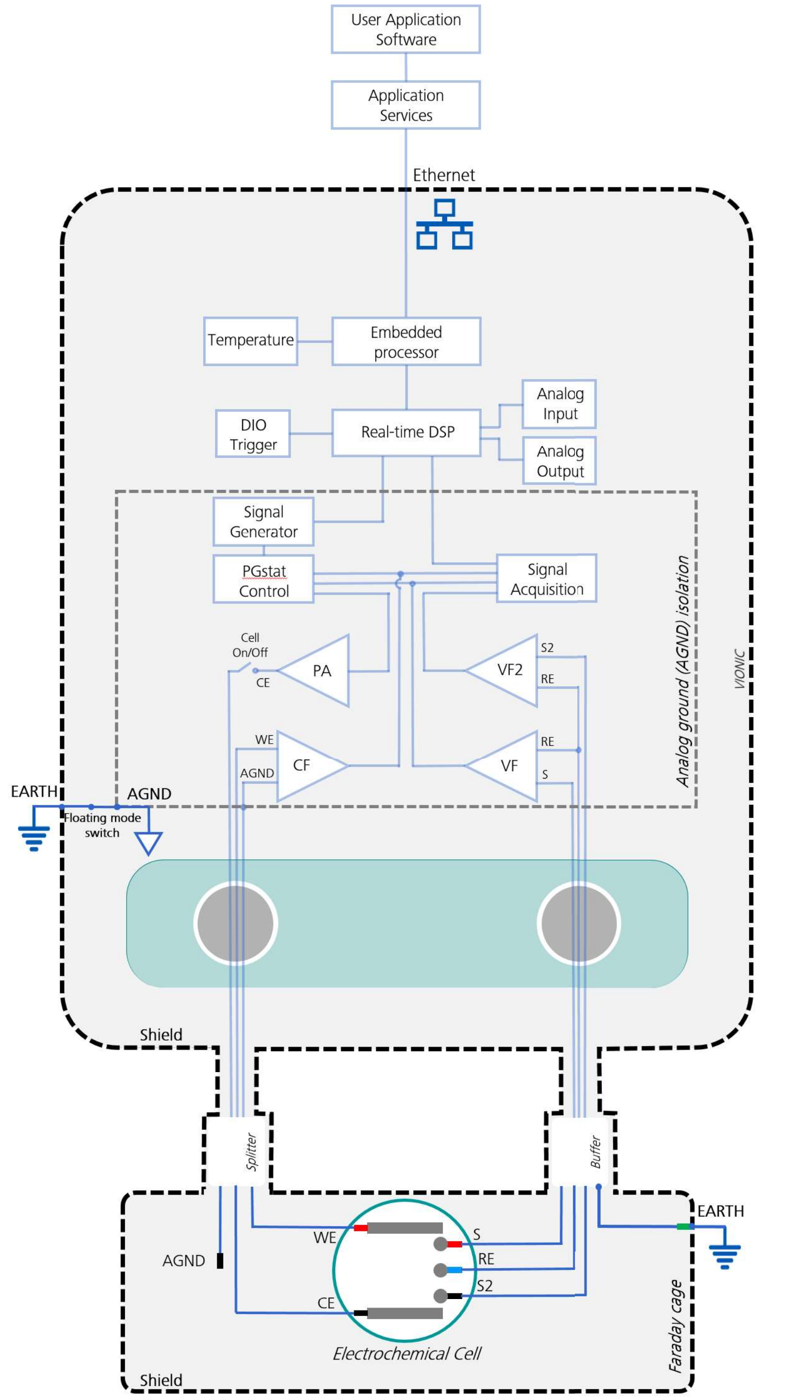


Figure 75 *Faraday cage connection and representation of the electromagnetic shielding (in thick dashed line). In this representation, the Autolab instrument is operated in non-floating mode.*

For the Faraday cage to be effective, it must be connected to the EARTH connector on the Pure signal bridge of the VIONIC instrument and the removable Adaptive cables (between the Buffer/Splitter boxes and the electrochemical cell) should be as much as possible inside the Faraday cage.

VIONIC must be always plugged into a grounded power socket. The EARTH connector on the Pure signal bridge is directly connected to the Earth and, beside the electromagnetic shielding, it also plays an important role in the safety of the users.

The same guidance applies for using and connecting a Faraday cage when VIONIC operates in *floating mode*.

When VIONIC is operated in**floating mode**, the analog ground connector (AGND) on the Pure signal bridge must not have electric connection to the Earth. The AGND connector should not be connected to the Faraday cage nor to the EARTH connector on the Pure signal bridge.

The **Analog ground connector (AGND)** is used only for *Zero Resistance Ammeter (ZRA)* (or electrochemical noise (ECN) measurements done in *floating mode*.

6.5 Maximum input voltage

The maximum voltage range which can be measured between the Sense (S) and the Reference electrode (RE) with VIONIC is ± 10 V. The differential electrometer of VIONIC contains an input protection circuitry which is activated when the measured voltage is outside the ± 10 V interval. This is implemented to avoid electrometer damage.

Also, an overload detection circuit is implemented for the voltage measurements between the Second sense (S2) and the Reference electrode (RE) with the only difference that the maximum measurable voltage in this case is ± 50 V.

Depending on the cell properties, the galvanostatic control of the cell could lead to a potential difference between the Reference (RE) and the Sense electrode (S) larger than ± 10 V. This situation will also trigger the overload detection circuit to prevent overloading the differential amplifier.

Whenever the measured voltage is outside of the acceptable limits, the **OVL** indicator on the Dynamic interface will be lit indicating the voltage overload .

6.6 Environmental operating conditions

VIONIC may be used at temperatures between 0 to +40 °C. The instrument is calibrated at 25 °C and will have the highest accuracy at this temperature. The ventilation holes on the bottom plate and on the rear panel may never be obstructed, nor should the instrument be placed in direct sunlight or near other sources of heat.

VIONIC is rated for use only in laboratory conditions with relative humidity lower than 80% and at a maximum altitude of 2000 m.

VIONIC is not intended to be used inside a glovebox. The cooling conditions in the glove box environment might not be satisfactory for the safe operation of the instrument and the performance specifications of the instrument are not guaranteed.

If the experimental conditions require the use of a glovebox, the use of an isolated feedthrough connection is recommended (the feedthrough connector ground cannot have an electrical connection with the enclosure of the glovebox). In this way, VIONIC will be operated outside of the glovebox and will connect to the electrochemical cell through the isolated feedthrough connector.

VIONIC cannot be used in vacuum or in low pressure environment. The cooling conditions of the electronics cannot be reached and therefore the overheating of the instrument (temperature overload) is imminent.

6.6.1 Instrument temperature overload

When VIONIC operates at high power (delivered or dissipated), the cooling fan of the instrument will switch to a second stage. This is an normal behavior and is noticeable from the higher intensity sound of the cooling fan.

As a safety precaution, VIONIC is equipped with a circuit that monitors the temperature of the internal power electronics. A temperature overload is indicated by a *red flashing* light (3 Hz pulsing) on the power button together with the **Error11** code on the alphanumeric display on the Dynamic interface of VIONIC.

The temperature overload is considered an instrument error and therefore, when the temperature overload occurs, the electrochemical cell is isolated from the instrument. It is not possible to continue to work with the instrument until the temperature of the electronics has fallen to an acceptable level. For using the instrument again, VIONIC must be rebooted by switching it off and on again.

During normal operation, the temperature should never become extremely high and no temperature overload will occur. If this does happen, the origin of the temperature overload must be identified:

- Is the room temperature unusually high?
- Was VIONIC oscillating? (OSC indication shown on the display)
- Is the fan inside the instrument working and are all the ventilation holes on the back and at the bottom of the instrument unobstructed?
- Was the cell delivering a considerable amount of power to the instrument? Please see the power plot of VIONIC for the maximum acceptable power in case of active cells.
- Are the Working (WE) and Counter electrode (CE) cables shorted? Please make sure they are not.
- Are the Adaptive cables connected correctly to the Pure signal bridge and t the electrochemical cell?

VIONIC is equipped with a variable speed control for the cooling fan. It is a normal behavior when the speed of the cooling fan changes depending in the power requirement during the measurement.

If a temperature overload occurs repeatedly, for no obvious reason, please contact your local Metrohm Autolab service representative.

7 INTELLO installation

This section contains information relating to the installation of INTELLO on a host computer.

7.1 Computer and network requirements

This section describes the computer and system requirements that are necessary for INTELLO to work with the expected behavior and performance.

Software requirements

- Operating system: Windows 10 (64 bit), Windows 11
- Additional software: .NET framework 4.7.2 or newer

Computer requirements

- Processor (CPU): core i5 or equivalent AMD processor
- Physical memory (RAM): 8 GB
- Screen resolution: Full HD (1920x1080) or higher
- Hard disk space (HD) / storage capacity:
  - Minimum for installation: 200 MB
  - Recommended for data storage: 320 GB

A typical CV measurement produces approximately 600 KB of data. A typical EIS measurement produces approximately 150 KB of data.

- Video card / GPU: DirectX11 level graphics adapter or newer with DirectX11 compatible graphics hardware.
- Ethernet port: Recommended

Network and accessory requirements

- Network (recommended):
  - Ethernet: 1 Gbit/s with cable category 5 (Cat 5e cable)
  - Router or LAN: 1 Gbit/s, stable and permanent
  - DHCP server: present
  - Communication: via TCP/IPv4
- Network (alternative):
  - Direct connection between the computer and VIONIC instrument: ethernet cable category 5 (Cat 5e cable)
  - Ethernet to USB adapter (only if necessary): USB 2.0 (minimum) or USB 3.0 with 1 Gbit/s (recommended)
- Pointing device: Use of a mouse is recommended for the best experience and ergonomics. Use of a touch screen is possible.

The following ports are used by the embedded software of VIONIC:

Port	IP	Protocol	Description
1900	UDP	SSDP	Multicast port used by SSDP protocol, used for automatic discovery of VIONIC instruments in the network
6001...6009	TCP	Proprietary	Used by different Autolab specific services running on VIONIC, such as measurement execution, claiming, etc.
7890	TCP	Proprietary	Used by update service

7.2 Metrohm Autolab INTELLO Software License Agreement

Introduction

Please read this document thoroughly before ordering, downloading, installing or using the INTELLO Software. This End-User License Agreement (**EULA**) is a legal agreement between you whether an individual user or a business entity of a customer, (either further referred to in this document as CUSTOMER) and Metrohm Autolab B.V., a private company with limited liability, incorporated and existing under the Laws of the Netherlands, having its registered office at Woudwetering 3-5, 3543 AV Utrecht, the Netherlands, registered with the trade register of the Dutch chamber of commerce under number 30128927 (further referred to as METROHM AUTOLAB) that governs your use of the software as specified at the order form or the ordering document (including any updates or upgrades thereof (further referred to as SOFTWARE). You indicate your acceptance of and you agree to be bound by this EULA by ordering, downloading, installing, or using the SOFTWARE. If you do not accept or agree to this EULA, do not order, download, install, or use the SOFTWARE and return the SOFTWARE to your reseller or to METROHM AUTOLAB. If you are accepting this EULA on behalf of any corporation, partnership or other entity, you represent and warrant that you are authorized to legally bind such entity to this EULA.

1. **Software license**
   a. Subject to CUSTOMER's compliance with this EULA and payment of the fees, METROHM AUTOLAB hereby grants CUSTOMER a non-transferrable and non-exclusive right to use this SOFTWARE. The SOFTWARE is licensed, not sold to you by METROHM AUTOLAB. METROHM AUTOLAB reserves any rights not expressly granted to you.
   b. Except as expressly permitted under this EULA, CUSTOMER is not entitled to (a) modify, alter or translate the SOFTWARE or any copy of it in any form to any third party nor create any derivative works from it; (b) remove from or change in the SOFTWARE any designation concerning copyrights, trademarks or other intellectual property rights, including any indications concerning the confidential nature of the SOFTWARE (c) decompile, reverse engineer, disassemble, or seek to reconstruct or discover any humanly readable form of code of the SOFTWARE except to the extent allowed by applicable law (d) attempt to disable or circumvent any of the licensing mechanisms within the SOFTWARE, or (e) rent, lend, lease, assign, sub-license, resell, redistribute the SOFTWARE or otherwise pass it on to third parties except in conjunction with its use with analysis devices of the Metrohm Group and only if the third party expressly agrees to the terms of this EULA in writing.
   c. CUSTOMER may only make copies of the SOFTWARE in a reasonable number and only for backup or archival purposes consistent with this EULA. CUSTOMER shall include METROHM AUTOLAB's copyright, trademarks and other proprietary rights notices, as contained in the original copy of the SOFTWARE, on every copy CUSTOMER makes of the SOFTWARE.
   d. CUSTOMER undertakes to (a) monitor and control the use of the SOFTWARE in accordance with the terms of this EULA and (b) to maintain accurate and up-to-date-records of number of registered users of the SOFTWARE.
   e. Third Party Materials. The SOFTWARE may include certain open source software and/or other third party software, data or other materials (further referred to as THIRD PARTY MATERIALS) that are separately licensed to CUSTOMER by the respective owners or licensors. CUSTOMER's use of such THIRD PARTY MATERIALS is subject to the applicable open source or third party license terms and conditions and not this EULA. The applicable license terms and conditions and other information related to such THIRD PARTY MATERIALS (including any available source codes) are described in the SOFTWARE under 'About'.

f. Feedback. If CUSTOMER chooses to provide METROHM AUTOLAB with ideas or suggestions regarding the SOFTWARE, CUSTOMER agrees that METROHM AUTOLAB is free to use any such ideas and suggestions for any purpose, including, without limitation, developing, improving and marketing the SOFTWARE, without any liability or payment of any kind to METROHM AUTOLAB.

2. **Fees and payment**

   a. In consideration of the license granted under this EULA, CUSTOMER shall pay the reseller the applicable Fees as specified in the order form or ordering document. The Fees shall be paid in accordance with the payment terms specified in the order form or ordering document of its reseller.

3. **Intellectual property rights**
   a. All copyrights and all other intellectual property regarding the SOFTWARE as well as all parts and copies thereof shall remain solely vested in METROHM AUTOLAB or its licensors and shall not be assigned to CUSTOMER or any third party. CUSTOMER acknowledges these rights and shall refrain from any form of direct or indirect violation of these rights and shall not remove from or change in the SOFTWARE any designation concerning copyrights, trademarks or other intellectual property rights, including any indications concerning the confidential nature of the SOFTWARE.
   b. METROHM AUTOLAB shall have no liability for any claim of infringement of any intellectual property rights that is based on: (i) the use of other than the latest version of SOFTWARE, if such infringement could have been avoided by the use of the latest version; (ii) the use or combination of the SOFTWARE with software, hardware or other materials not approved by METROHM AUTOLAB, (iii) use of the SOFTWARE in a manner other than that for which it was designed or contemplated; (iv) any modification of the SOFTWARE made by CUSTOMER or a third party; or (v) any THIRD PARTY MATERIALS.
   c. In the event that a judgement or any injunction shall be obtained against CUSTOMER's use or possession of the SOFTWARE, METROHM AUTOLAB shall, at its expense and option, promptly (i) replace the SOFTWARE with a compatible, functionally equivalent, non-infringing software product; (ii) modify the SOFTWARE or take other action so that the SOFTWARE becomes non-infringing while maintaining the equivalent functionality; (iii) procure the right of CUSTOMER to continue using the SOFTWARE; or (iv) terminate the license and CUSTOMER's use of the SOFTWARE.
   d. Any further liability of METROHM AUTOLAB regarding the infringement of third party intellectual property rights is explicitly excluded.

4. **Confidentiality**
   a. The SOFTWARE is and contains valuable confidential information of METROHM AUTOLAB. Confidential information means non-public technical and non-technical information relating to the SOFTWARE, including, without limitation, trade secret and proprietary information, and the structure and organization of the SOFTWARE.
   b. CUSTOMER shall keep confidential the SOFTWARE or any part or any copy thereof and CUSTOMER shall not disclose the same to third parties without the prior written consent of METROHM AUTOLAB.
   c. CUSTOMER shall take all necessary measures to safeguard the confidentiality of the SOFTWARE or any part or any copy thereof and to prevent the disclosure, use, copying, publication or dissemination of the same to a third party.
5. **Updates**
   a. METROHM AUTOLAB may from time to time in its sole discretion develop and make available updates, which may include bug fixes, patches, security updates, enhancements and other error corrections and/or new features (further referred to collectively, including related documentation as UPDATE(S)). UPDATES may also modify or delete in their entirety certain features and functionalities of the SOFTWARE and METROHM AUTOLAB has no obligation to provide or enable any particular features or functionalities.
   b. CUSTOMER will receive a notification to download and install UPDATES when available. In addition to such notifications, METROHM AUTOLAB recommends to regularly check the SOFTWARE to see whether UPDATES are available. Before installing an UPDATE CUSTOMER should make a back-up of the information and/or data processed with the SOFTWARE.
   c. CUSTOMER shall download and install the UPDATES as they are made available and acknowledges and agrees that the SOFTWARE or portions thereof may not properly operate should CUSTOMER fail to download and install the UPDATES. All UPDATES will be deemed part of the SOFTWARE and be subject to all terms and conditions of this EULA.

6. **Term and termination**
   a. This EULA shall run for the initial term specified in order form or ordering document. If no initial term is specified in the order form or the ordering document, the initial term shall be one (1) year. After the initial terms this EULA will automatically renew for subsequent terms of one (1) year unless either party terminates this EULA at the end of the then current period by giving a three (3) months written notice. CUSTOMER may terminate this EULA by notifying METROHM AUTOLAB thereof and removing the SOFTWARE from its devices and providing written notice to METROHM AUTOLAB. METROHM AUTOLAB may at any time immediately terminate this EULA and CUSTOMER’s use of the SOFTWARE if CUSTOMER breaches any term of this EULA and CUSTOMER fails to cure such breach within 30 days of METROHM AUTOLAB’s written notice describing such breach. Upon such termination, CUSTOMER shall cease using the SOFTWARE and remove all copies of the SOFTWARE and any part of the SOFTWARE from any and all computer storage devices and destroy the SOFTWARE.

7. **Limited warranty and limitation of liability**
    a. The SOFTWARE and related documentation are provided "AS IS". METROHM AUTOLAB warrants that the SOFTWARE (i) will substantially conform to the documentation accompanying the SOFTWARE and, when operated properly and in compliance with this EULA and the documentation, (ii) is suitable for the specified use with electrochemical instrumentation from METROHM AUTOLAB or compatible external instrumentation. METROHM AUTOLAB expressly disclaims all other warranties, whether express, implied, or statutory including without limitation any implied warranties of merchantability, satisfactory quality, fitness for a particular purpose, accuracy, timeliness, title, or non-infringement of third-party rights, to the fullest extent authorized by law.
    b. CUSTOMER is responsible for the use of the SOFTWARE, the information and/or data processed with the SOFTWARE and for the decisions that CUSTOMER may make by using the SOFTWARE. CUSTOMER is recommended to make a backup of the information and/or data processed with the SOFTWARE on a regular basis.
    c. In no event will METROHM AUTOLAB be liable for any loss or damages whatsoever, resulting from CUSTOMER's use of the SOFTWARE, including without limitation third-party damage or consequential damage, damages to equipment, loss of samples, loss of use, loss of data, loss of profits, interruption of business, except for any loss or damages that (i) have been caused by willful intent or gross negligence of METROHM AUTOLAB or (ii) that cannot be excluded by law.
    d. METROHM AUTOLAB will have no warranty obligations and/or liability with respect to (i) SOFTWARE which has been modified by CUSTOMER or on behalf of CUSTOMER; (ii) malfunctions caused by CUSTOMER's use or operation of the SOFTWARE with any hardware, software or media not authorized by METROHM AUTOLAB or not in accordance with this EULA or the documentation; or (iii) any THIRD PARTY MATERIALS.
8. **Governing law and disputes**
    a. This EULA and all disputes arising from it will be governed by the laws of the Netherlands.
    b. The parties shall use their best efforts to negotiate in good faith and settle amicably any dispute that may arise out of or relate to this EULA or breach thereof. If the parties cannot reach an amicable settlement, all disputes arising in connection with this EULA shall be referred to the competent civil court in the Netherlands.

9. **Miscellaneous**

   a. Severability and invalidity. If parts of this EULA prove to be null and void or legally ineffective now or in the future, the remainder of this EULA continues to apply. This EULA must then be interpreted and applied so that the intended purpose of the ineffective section is nevertheless achieved to the greatest extent possible.
   b. Entire agreement. This EULA together with any order form or ordering document constitute the entire agreement between METROHM AUTOLAB and CUSTOMER regarding the use of the SOFTWARE and supersedes all prior agreements and understandings. No distributor, reseller, partner, sales person, employee or other person is authorized to modify this EULA or to make any representation, warranty or promise that is different from, or in addition to, this EULA. METROHM AUTOLAB is not in any way or manner bound to such representations, warranties or promises.
   c. Changes to EULA. METROHM AUTOLAB may change this EULA from time to time in its sole discretion. CUSTOMER's continued use of the SOFTWARE after notification of any changes has been provided to CUSTOMER or posted on METROHM AUTOLAB's or Metrohm Group website constitutes CUSTOMER's acceptance of such changes.
   d. No assignment. CUSTOMER shall not assign or delegate or otherwise deal with all or any of its rights or obligations under this EULA. METROHM AUTOLAB shall have the right to assign or otherwise delegate all or any of its rights or obligations under this EULA to any person or entity.
   e. Publicity. CUSTOMER hereby grants METROHM AUTOLAB the right to list CUSTOMER as a CUSTOMER of METROHM AUTOLAB along with other customers in marketing materials such as the METROHM AUTOLAB or Metrohm Group web site, presentations and press releases.
   f. Contact Information. All notices required or authorized under this EULA must be in writing and shall be sent to Metrohm Autolab B.V. at:
      Metrohm Autolab B.V.
      Woudwetering 3-5
      3543 AV Utrecht
      The Netherlands
      We can be reached by email at *autolab@metrohm.com* or by telephone at +31 030 289 3154.

8 Release notes

This chapter describes the release notes of the current and previous versions of INTELLO. The release notes are provided in reverse chronology. The following versions have been released:

- **Version 1.0:** the original major release of INTELLO *(see "Version 1.0 release", chapter 8.1, page 137)*. This version was released on March 1st 2021.
- **Version 1.1:** Minor update of INTELLO 1.0 *(see "Version 1.1 release", chapter 8.2, page 137)*
- **Version 1.2:** This new version was released on September 16th 2021 *(see "Version 1.2 release", chapter 8.3, page 138)*
- **Version 1.2.1:** This new version was released on October 18th 2021 *(see "Version 1.2.1 release", chapter 8.4, page 139)*
- **Version 1.3:** This new version was released on March 16th 2022 *(see "Version 1.3 release", chapter 8.5, page 139)*
- **Version 1.3.3:** This new version was released in April 2022 *(see "Version 1.3.3 release", chapter 8.6, page 140)*
- **Version 1.3.4:** This new version was released in August 2022 *(see "Version 1.3.4 release", chapter 8.7, page 141)*
- **Version 1.4:** This new version was released in January 2023 *(see "Version 1.4 release", chapter 8.8, page 141)*
- **Version 1.5:** This new version was released in September 2023 *(see "Version 1.5 release", chapter 8.9, page 142)*
- **Version 1.6:** This new version was released in October 2024 *(see "Version 1.6 release", chapter 8.10, page 144)*
- **Version 1.7:** This new version was released in September 2025 *(see "Version 1.7 release", chapter 8.11, page 147)*
- **Version 1.7.1:** This new version was released in December 2025 *(see "Version 1.7.1 release", chapter 8.12, page 148)*

8.1 Version 1.0 release

INTELLO 1.0 is the new generation software from Metrohm Autolab that is bursting with time-saving features that optimize any workflow.

The research and development of VIONIC powered by INTELLO was based upon over 30 years of customer insight. Each feature was created to meet the requirements of electrochemical research and improve your day-to-day discoveries.

- **Simply better procedures**: INTELLO provides workflows for both exploratory and routine measurements.
- **Procedure sequence editor**: Create your unique procedure with easy-to-use command tiles and avoid errors by displaying your experiment sequence from the first settings to the end state, and every step inbetween. INTELLO displays real-time command progress and state during your run.
- **Main parameters**: Displays only the parameters you choose; streamlining your workflow and making it easy to perform and delegate routine measurements.
- **Insight plots**: Customize the multi-plot overview by combining plots from different command tiles with a simple drag and drop. INTELLO provides automatic coloring of new series and iterative data.

8.2 Version 1.1 release

In INTELLO 1.1 several bugs were corrected and the following functionality and improvements were implemented:

- **Extract procedures from the runs**. A button has been added to INTELLO
- **Accept option is added to the OCP measurement.** The OCP measurement can be accepted anytime by using the **Accept** button in the measurement window.
- **Step height corrected to the resolution of the instrument**. For CV and LSV staircase commands, the step height is corrected to the actual value given by the resolution of the instrument. A tooltip is added to the user interface to show the corrected values.
- **User defined number of visible cycles / iterations in a plot.**The number of visible cycles / iterations in a plot is now limited to 100 by default. This can be set to any number in plot settings panel by the user. (e.g. if set to 5, only the last 5 cycle / iterations will be visible in the plot)

- **Improved plotting performance.** The plotting performance is improved significantly. It is now possible to start measurements with a high number of iterations / cycles without a significant delay in displaying the plots.
- **Signal-to-noise in linear CV and linear LSV.** The signal-to-noise in linear (analog) scan techniques was improved.
- **Performance of the high speed chrono methods.** The performance of high speed chrono method technique was improved.

8.3 Version 1.2 release

In INTELLO 1.2 the general user experience and performance of were improved, several bugs were corrected and the following functionalities and improvements were implemented:

New functionalities

- **Repeat for multiple values**: this new repeat type is used to repeat one or several command with variable parameters for each iteration
- **Pause measurement**
- **Copy and paste command tiles**: in a sequence one or multiple commands can be copied (Ctrl+C) and pasted elsewhere in the sequence (Ctrl+V) while preserving (or not) the input parameters and links of the copied tiles
- **Export EIS data to ZView and RelaxIS**: these two formats are available to export EIS data
- **Activity log**: a new tab is added to the runs with logged events, warnings and errors, and command states
- **Plot from group and repeat command**: plots can be created from a group of commands and repeat commands
- **Export image**: plot views can be exported as images with the export image tool on top of each plot
- **Dynamic interface lights (On/Off)**: the Dynamic Interface lights can now be turned off using the button in the Device Settings for light sensitive measurements
- **Filter procedures by technique**: procedures in the procedures drawer can be sorted by type of technique (impedance, chrono methods, voltammetry)

Improvements

- INTELLO displays now a **data transfer state** when the procedure is over but data is still being transferred from the Work System
- **The Cell Off command is seamless**: the cell is turned off instantaneously at the end of the previous command regardless of the data transfer state

- **Rules on charge**: creating a rule based on the measured charge is now possible.
- **Fast measurements**
  - Data transfer speed is improved for fast measurements
  - S2 signals can be acquired in high speed measurements

8.4 Version 1.2.1 release

In INTELLO 1.2.1 several bugfixes were implemented.

8.5 Version 1.3 release

INTELLO 1.3 was released on 2022, March 1st. The following functionalities and improvements were implemented:

New functionalities

- **Temperature monitoring**: a thermocouple (type K) can be connected to VIONIC and added to the work system in INTELLO. It allows the monitoring of the temperature of the cell by recording one additional signal in the procedures. The temperature can also be monitored in the Manual control window.
- **Rules on temperature**: with the possibility to monitor the temperature with a thermocouple, it is now possible to add rules based on the temperature.
- **Potential and current monitoring**: the measured current and potential can be monitored by an external device connected to one or two of the A-OUT ports on the back of VIONIC. The I monitor and E monitor must be added to your work system configuration.
- **Rotator control**: the motor controller of a rotating electrode (RDE, RCE) can be controlled by VIONIC. A new Rotator control command was added to INTELLO allowing for change of the rotation rate at any point of a procedure. The rotation rate can also be manually modified and monitored in the Manual control window.
- **Hydrodynamic LSV default procedure**: a new default procedure was added to the Autolab library. An LSV is repeated at different rotation rates for hydrodynamic measurements (RDE or RCE). This procedure allows for further hydrodynamic analysis with the dedicated IN2NOVA tool. This procedure can easily be modified to meet the requirements of the user experiments.
- **Repeat for multiple values**: a square root distribution was added to generate values for a parameter (column).

- **Data explorer**: new filters were added to the data explorer to help the user find runs based on the measurement date or the date of the last modification. It is possible to display runs created or modified today, this week, this month, this year or over a personalized period of time (range).

Improvements and bugfixes

- **Repeat for multiple values**: linking parameters of the repeat table to commands is now possible from the repeat table itself (header of the column) and from the nested command.
- **IN2NOVA**: when several commands have the same name in the INTELLO procedure they are now made unique and fully exported to NOVA for analysis with IN2NOVA.
- **Copy and paste**: pasting commands now preserves the order of the copied commands.
- **Invalid data points**: to avoid erroneous interpretation, invalid data points (measured during current overload, or voltage overload) are not displayed for EIS measurements. It is recommended to use automatic current ranging in EIS measurements to ensure no saturation of the current follower and avoid invalid measured datapoints with the EIS command.

8.6 Version 1.3.3 release

INTELLO 1.3.3 was released in April 2022. The following new functionality was added:

Invalid data points toggle in procedures, data tables and plots

To avoid erroneous interpretation, invalid data points are, by default, not displayed in plots and tables in INTELLO. For AC techniques (EIS frequency scan and single frequency), points measured during current or potential overload are invalid, due to the invalidity of the calculated complex impedance. To minimize the occurrence of invalid data points during EIS measurements, it is recommended to use automatic current ranging in potentiostatic mode. For DC techniques (CV, LSV, chrono methods), points sampled exactly during a current range switch in VIONIC are considered to be invalid due to the time required to change the current range in VIONIC. For measurements at high scan rates or low sampling intervals, it is recommended to use a fixed current range. This option allows for displaying all contingent invalid data points in plots and tables for this procedure.

8.7 Version 1.3.4 release

INTELLO 1.3.4 was released in August 2022. It is a minor release containing a bugfix.

8.8 Version 1.4 release

INTELLO 1.4 was released in January 2023. It includes the following new functionalities:

- **iR compensation**: iR (Ohmic drop) compensation can be enabled in the *Apply settings* command of a procedure, in the *more* section. A definition of the Ohmic drop and how it can be compensated can be found in *Chapter 12.16.6.1*.
  The value of the uncompensated resistance (R_u) can be input by the user along with the percentage of this value that must be compensated (e.g., for a R_u = 80 Ω, with 80 % compensation, the potential will be corrected by *- I (in A)* × *64 (Ω) V*. This value can also be determined by a command and further applied to the rest of the procedure.
- **iR drop measurement**: this command uses Electrochemical Impedance single frequency to determine the value of the uncompensated resistance. When placed before an *Apply settings* command, the measured value will be automatically input in the iR compensation section and compensated in the rest of the procedure (see *Chapter 12.16.6.3*).
- **Normalized signals**: the surface area or the mass of the material at the working electrode can be input as an option in the Procedure tile. This value is used when the procedure is run to calculate the normalized current (current density), charge or power. In the Signals tab of each measurement command of the procedure, the different normalized signals can be toggled on for sampling and plotting. See *(see "Normalized signals", chapter 9.5, page 153)*
- **Automatic export command**: it is possible to export automatically any data table of a procedure by using the new Export command. The export file can be in ASCII/CSV, Excel for all tables and, additionally, Relaxis and ZView for EIS data. The command must be placed beside the table to export and data will be exported automatically after the procedure is run. The file and folder names can be customized with metadata from the procedure (date, time, name of the procedure or command tile, main parameters, etc.). The exported signals, their order and name can be customized. More details can be found in *Chapter 12.6*

- **Custom frequency distribution for EIS**: beside the linear and logarithmic distribution of frequencies, the EIS can be performed with a custom list of frequencies. It is for example possible to change the number of frequencies per decade only in a specific frequency range or add/remove specific frequencies from an existing table. More details can be found in *Chapter 12.7.1*
- **Customized data tables**: data tables can be customized prior to or after the procedure is run. The following elements can be changed: order, visibility, units, notation, precision.

8.9 Version 1.5 release

INTELLO 1.5 was released in September 2023. It includes the following new functionalities:

- **Direct control of DIO ports** - The DIO (Digital In/Out) port on the back panel of VIONIC can be controlled and set directly in INTELLO. The Out Pins on the back of the instrument can be used to control external devices. New commands (Set DIO and DIO Pulse) are available after enabling the direct DIO port control in the required work system of a procedure (*Procedure* tile). Pulses can also be sent during LSV and CV staircase measurements (synchronization option). Only the Digital Output is made available.
- **Corrosion rate analysis** - Corrosion rate analysis (Tafel method) is possible on I vs. E plots in INTELLO. It enables the calculation of the corrosion rate of a material (in mm/year), corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_a, b_c) and other parameters from a polarization curve. The analysis can be performed from the plot itself (new icon on the plot) or by dragging and dropping a command near the data table of an LSV in a procedure or a run.

- Eight new default procedures were added to the Autolab library
  - **Hyphenated EC-Raman (LSV)**: this procedure requires a B&WTek I-Raman instrument connected to VIONIC via the Metrohm Autolab DIO trigger cable. This procedure runs an LSV between two given potentials and is set to send synchronisation pulses every 100 mV during the LSV: this allows for acquiring Raman spectra every 100 mV during the LSV. The number of pulses can be edited in the LSV command. This procedure can be used in combination with a Timeline in BWSpec. Please contact your local Metrohm representative for support and additional information.
  - **Hyphenated EC-Raman (Chrono steps)**: this procedure requires a B&WTek I-Raman instrument connected to VIONIC via the Metrohm Autolab DIO trigger cable. This procedure consists of several potential steps during which a trigger is sent after a stabilization time to start the acquisition of a Raman spectrum at each potential step. The number of steps and the value of the applied potential can be modified by editing the table of the Repeat for Multiple potentials command. The duration of the stabilization, spectrum acquisition (measurement step) can also be modified in the main parameters. This procedure can be used in combination with a Timeline in BWSpec. Please contact your local Metrohm representative for support and additional information.
  - **Staircase potentiostatic EIS**: this procedure runs EIS scans at different potentials. Each potential is applied for a stabilization time of 5 seconds (editable) before running each EIS scan. The number of potential steps and their individual offset can be edited in the Repeat for multiple values command tile.
  - **Mott-Schottky (staircase potentiostatic EIS)**: this procedure runs EIS scans at different potentials and automatically exports the EIS data for further analysis in NOVA (contact your local Metrohm representative for more details). The number of potential steps and their individual offsets (DC potential) can be edited in the Repeat for multiple values command tile. The folder location for data export must be specified (Export command) before running the procedure.
  - **CV linear potentiostatic at different scan rate**: CV (linear scan) is repeated at different scan rates. The number and distribution of the scan rates (linear, square root) can be edited in the repeat for multiple scan rates command.
  - **CV staircase potentiostatic at different scan rate**: CV (staircase) is repeated at different scan rates. The number and distribution of the scan rates (linear, square root) can be edited in the repeat for multiple scan rates command.

- **Linear polarization**: this procedure measures the OCP of the cell (no current or potential applied) and runs an LSV with potential limits defined versus the OCP. The polarization curve and Tafel plot are displayed.
- **Linear polarization (Tafel analysis)**: this procedure measures the OCP of the cell (no current or potential applied) and runs an LSV with potential limits defined versus the OCP. The polarization curve and Tafel plot are displayed. Additionally, a Tafel analysis command allows for extraction of the corrosion rate of the material, the Tafel slopes (b_a, b_c), the corrosion current and potential.

Additionally, some bugs were solved.

8.10 Version 1.6 release

INTELLO 1.6 was released in October 2024. It includes the following new functionalities:

- **Battery Cycling capabilities**: a new battery cycling command was implemented which allows for executing galvanostatic (constant-current, CC) charge-discharge cycles, with potential limits, CC followed by constant voltage (CV) charge-discharge also known as CC-CV cycling. This command integrates various new functionalities and cycling analysis capabilities:
  - automatic determination of **charge and discharge capacity (mAh)** and plotting for each cycle
  - **Σ Capacity (Ah)**, the **total capacity** of the cell over the entire set of cycles. This value is set to 0 only at the beginning of a new cycle command.
  - **Coulombic efficiency (CE, %)** determination and plotting for each cycle
  - **Capacity retention (CR, %)** or relative capacity determination and plotting for each cycle
  - **dQ/dE (differential capacity)** calculation and plotting
  - **CC (constant current) and CV (constant voltage)** commands were implemented to run galvanostatic charge and discharge cycles with or without potential limits, and constant voltage steps after CC steps, with or without current limits. These commands can be used inside a battery cycling command or outside for pre/post-conditioning of the cell.
  - **(WE-S2).Potential**: in a three-electrode configuration, the total voltage across the cell (WE and S connected to one pole of the battery, and CE and S2 to the other one) can be sampled in CC, CV and Rest commands.
  - **C-rate** input for current set points and limits: the current applied in CC commands and used as limits in CV commands can be defined as C-rate if a cell capacity is specified in the cell properties (main parameters)
  - **Rest** to monitor the voltage of the cell (OCP/OCV) while the cell is off between CC and/or CV steps
  - End conditions for the cycling command on total cycling duration, individual cycle duration or Coulombic efficiency.
- **EIS commands (frequency scan and single frequency) now contain an optional DC control part** where the DC setpoint and stabilization times can be defined, making the EIS command able to be used without a prior apply or apply settings command
- **Cell properties**: in the main parameters, a new section was added to edit properties of the cell used for the measurement (surface area or mass for normalization, theoretical or nominal capacity of a battery, cell ID for easy data identification)
- **New rule action to exit repeats**: a new rule action is available in the **Rules** tab of measurement commands nested inside repeats. This action allows INTELLO to end all commands inside the repeat loop and execute the next command, one level up, in the sequence

- **Automatic current ranging in GSTAT for all battery testing commands (CC charge and discharge, EIS)** available in the apply settings command. With other commands (LSV, CV staircase, chrono methods, record signals, and apply), it is necessary to select the most appropriate current range for the measurement using the current range slider.
- **Pulse techniques**
  - **Square-Wave Voltammetry (SWV)** is available as a new measurement technique
  - **Differential-Pulse Voltammetry (DPV)** is available as a new measurement technique
- **Automatic export command of repeated commands**: the automatic export command was modified to enable the export of individual files for data generated by repeated commands (nested in Repeat or repeat for multiple values).
- **Corrosion rate analysis**
  - **Butler-Volmer fit**: Tafel analysis allows for fitting polarization curves with the Butler-Volmer equation
  - **Polarization resistance** determination (Stern-Geary method) is available to determine corrosion rate from polarization curves
- Several **new default procedures** were added to the Autolab library:
  - **Corrosion**: ASTM G5, ASTM G59, ASTM G61, Linear polarization with polarization resistance analysis, Linear polarization with polarization resistance and Tafel analysis
  - **Battery testing**: CC Charge-discharge, CC-CV charge-discharge, CC charge-discharge with differential capacity analysis (dQ/dE), Galvanostatic Intermittent Titration Technique (GITT), Potentiostatic Intermittent Titration Technique (PITT), C-Rate capability testing (CC charge-discharge at different C-rates), EIS at different states of charge (SOC)
  - **Pulse techniques**: Square-Wave Voltammetry (SWV), Differential Pulse Voltammetry (DPV). Both these procedures have a version named (IME) which can be used in combination with the Metrohm Autolab IME663, used to control the Metrohm 663 VA Stand.

8.11 Version 1.7 release

INTELLO 1.7 was released in September 2025. It includes the following improvements and new functionalities:

- **UI Update:** A number of general improvements to the UI were made, including introduction of folders in the procedure drawer, improved display of meta data for a procedure or run, a new data tab, a redesigned events tab and a large number of smaller changes and bug fixes were made.
- **Cell Protection:** Cell safety protection limits were implemented. This is an instrument or procedure level setting that protects the connected cell by isolating it when the measured voltage and/or current exceeds limits set by the user. As an example, these limtits can protect a battery from overcurrents or overvoltages. The settings can be made to persist across different procedures, providing an additional layer of safety.
- **EIS Fitting:** The ability to fit measured EIS data to equivalent circuits was implemented. This feature allows the user to complete the analysis of EIS data by fitting the data, using a Levenberg-Marquardt algorithm, to an equivalent circuit. The circuit can either be taken from a library of prebuilt circuits or composed/modified by the user. The fit and sim tool supports circuits containing any number of different elements including Resistors, Capacitors, Inductors, Constant Phase Elements (CPE), Warburg (Normal, Open and Short Circuit), Bisquert & Gerischer. The elements can be arranged in series or parallel to build an equivalent circuit which best represents the system under study. The goodness of the fit can be analysed by the chi-square value. Weighted and non-weighted options for the fitting are available. Export of the data and the fitted values is possible.

Additionally, a number of previously known issues were fixed:

- In some cases the data transfer between the instrument and the host PC was slower than expected: this was improved.
- Signals from accessories (Thermocouple, Rotator) are now supported during fast measurements (sampling interval < 0.1 ms)
- Fast Chrono Methods under repeat commands don't apply the correct potential in the first repeat iteration
- In command rules, the "AND" operator between conditions of the same rule was previously treated as an "OR". This is now fixed. An "OR" is used between two separate rules (different rule tiles) in the same command.

8.12 Version 1.7.1 release

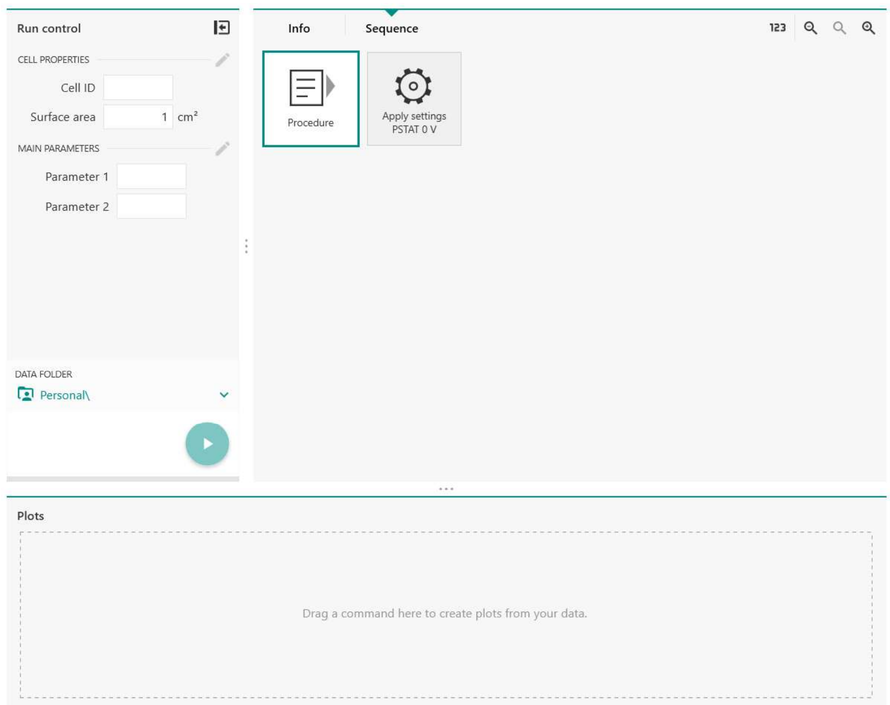
In INTELLO 1.7.1 several bug fixes were implemented

9 Procedures

This section describes Procedures in INTELLO.

9.1 Procedure view

The **Procedure** view is one of the most used screens in the software. The view is divided into three panels:



- The **Run control** panel at the left ensures that the most important parameters and monitored values are always in view. It contains both cell properties (cell ID, surface area or mass, etc.) and main parameters described further in the dedicated section. At the bottom of the run control panel, the data folder specifies the location where the data from the run will be saved in the INTELLO database.
- The **Plots ribbon** at the bottom displays the plots associated with the procedure. To add plots, a measurement command, repeat command or group command can be dragged and dropped in this section. Plots are automatically updated as soon as data is available when the procedure starts.

- The **Procedure** panel is the main part of this screen. It serves several purposes and exists on three different levels:
  - At the first level, **Procedure information** tile about the selected procedure is provided in the procedure tab. It contains an overview of the procedure settings and the possibility to edit settings specific to each procedure (required work system, signal normalization, etc.).
  - The **Procedure editor**: here the procedure sequence is displayed as a series of tiles and changes can be made by adding, removing, or moving tiles.
  - At the third level there is a specific **Command editor** view for each tile which is reached by opening the command tile (double click).

9.2 Main Parameters

The panel at the left side of the procedure view is dedicated to Main Parameters. Main Parameters offer a mechanism to ensure that the most important parameters are always visible in the procedure, run, and in the Procedure and Data Explorer tabs. The items on the Main Parameters panel can be viewed or altered quickly and easily, they function as quick glimpses or shortcuts into the procedure or run.

Suggested Use:

- **Repetitive measurements**: When running repetitive measurements, typically only a few of the parameters are altered (for example, the scan rate or second vertex potential of a CV profile). First, optimize the procedure for the electrochemical system by ensuring that all parameters in the commands are appropriate, then designate the parameters that will be altered frequently as Main Parameters.
- **Meta data**: Create custom fields for meta data in the Main Parameters panel to ensure that necessary information such as Sample ID, mass or volume of the sample, etc. are kept with the run.
- **Shared procedures**: When creating a procedure to be used by another person, designate Main Parameters to draw attention to the most important parameters. When creating procedures for less experienced users, the Main Parameters offer a way of giving focus to parameters that should be modified and keeping the other parameters that are not of immediate interest out of view.

Main Parameters are always visible in the procedure and in the data run. In the Procedure Explorer or the Data Explorer the Main Parameters are displayed and can be used to quickly identify a procedure or measurement.

9.3 Cell properties

Cell properties can be used to log identifiers and properties of the cell. Like main parameters, they can be linked to parameters in the procedure (e.g. mass or surface area of the electrode).

When a battery specific command (CC, CV, Rest, Cycle) is added to the procedure, a cell Capacity field is automatically added to the cell properties so that C-rate can be defined in the CC and CV commands instead of current in Ampères. This value is also used to calculate the relative capacity (capacity retention) in the battery analysis of the cycle command.

When a mass or surface area is specified in the Procedure tile for normalization (current, charge), the value is also added to the cell properties. When input in a procedure, current setpoints can be defined as current density setpoints. The nomalization factor can be used before or after the procedure was started to normalize the relevant signals.

9.4 Procedure settings

The procedure settings tile is used to specify settings relevant from the start of the procedure until its end.

General

- **Procedure name** and **Description** allow additional information about the procedure to be added to identify the procedure later on.
- **Tags**: Tags may be added to quickly categorize a procedure. The tags are visible in the **Procedure explorer** and can be used to locate and filter procedures.
- **Required work system**: opens a new window where it is possible to define the minimum work system that is required to run this procedure. Accessories (RDE, thermocouple, external devices) and settings (floating mode, compliance) required to run the procedure have to be defined here.
  When an accessory is added to the required work system, new signals can be recorded in different commands of the procedure. For example, when a thermocouple is added, the TC.Temperature signal is enabled in the whole procedure and toggled on by default where possible.
  When **saved by default**, the required work system will be present by default in all the procedures created later on. It can be edited at any time.

- **Default run name**: as soon as a procedure starts, INTELLO creates a run file combining the procedure and the measured data. The default name of this run can be defined in this field.
  - Automated: by default, the run has the same name as the procedure that was used. The name of the run can be automated and made unique for each run by inserting metadata, cell properties or the value of main parameters in the name of the run. For example, the name of a run created from the default CV procedure could be set to automatically include the Cell-ID, the procedure name, the scan rate used, the upper and lower vertices and more.
  - Manual: the preferred name of the run can be entered without any reference to the procedure or metadata. Runs will have the same name, but remain distinguishable by referring to the run number, date, time, user and work system which are always logged in the events tab and data folder.
- **Normalized signals**: the mass or surface area of the Working Electrode can be input here: this value is used in the rest of the procedure to normalize the measured or applied current (current density), measured Charge, Power. The additional normalized signals can be sampled, added to data tables and plotted when toggled on in the Signals tab of each measurement command tile. *(see "Normalized signals", chapter 9.5, page 153)*
- **Unit scaling**: the order of magnitude selected here will be used to scale inputs and displayed units in command tiles and plots throughout the procedure. These settings are provided for convenience and do not have technical influence on how the signals are applied or acquired.
  - **Potential**: can be scaled to V or mV.
  - **Current**: can be scaled to A, mA, or µA.

Invalid data points

To avoid erroneous interpretation, invalid data points are, by default, not displayed in plots and tables in INTELLO.

- For *AC techniques* (EIS frequency scan and single frequency), points measured during current or potential overload are invalid, due to the invalidity of the calculated complex impedance. To minimize the occurrence of invalid data points during EIS measurements, it is recommended to use automatic current ranging in potentiostatic mode.
- For *DC techniques* (CV, LSV, chrono methods), points sampled exactly during a current range switch in VIONIC are considered to be invalid due to the time required to change the current range in VIONIC. For measurements at high scan rates or low sampling intervals, it is recommended to use a fixed current range. This option allows for displaying all contingent invalid data points in plots and tables for this procedure.

End state

The End state refers to the state of the work system when the procedure is completed. It will also be applied if the procedure is aborted deliberately, due to an error, or due to the execution of a rule.

Main instrument End state

- **Mode**: potentiostatic or galvanostatic. It is necessary to define the set point when the mode is changed. This is indicated by a merge symbol placed beside these settings.
- **Potential / Current**: Input for the potential or current set point. This field will be automatically adjusted for input in potential or current, depending on the **Mode** setting.
- **Cell**: by default, the cell is switched off (CE disconnected). When the toggle is enabled, the cell will remain or be switched on when the procedure reaches the end state.

RDE end state

The rotation of the RDE at the end of the procedure can be defined here. The default value is 0 rpm. *This field is visible only if a RDE is defined in the required work system.*

DIO end state

The state of the pins on the DIO port at the end of the procedure can be defined here. The default state is 0 on all pins or the last known state at the end of the procedure. *This field is visible only if a DIO direct control is enabled in the required work system.*

9.5 Normalized signals

Data collected by VIONIC can be normalized by the surface area or the mass of the working electrode.

In the procedure tile, at the beginning of a procedure, it is possible to add information about the wroking electrode: mass or surface area. See the table below for available signals and their normalization.

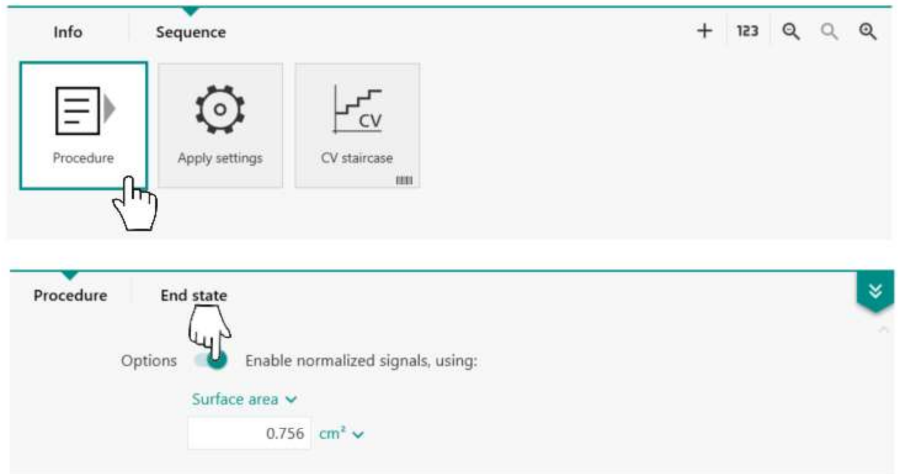


Figure 76 Normalized signals are enabled by inputting a surface area or mass in the Procedure information tile.

Table 9 Signal normalization in INTELLO

Signal (default unit)	**Normalization**	**Normalized signal (default unit)**
i, WE.Current, (A)	*i*/Area	*j*, current density (A/m²)
	i/mass	*j*, current density (A/g)
Q, WE.Charge, (C)	*Q*/Area	Q, normalized charge (C/m²)
	Q/mass	Q, normalized charge (C/g)
W, WE.Power, (W)	*W*/Area	W, normalized power (W/m²)
	W/mass	Q, normalized power (W/g)
Q+, *Q*-, |*Q*|, Charge, Discharge, Σ Capacity (Ah)	*Q*/Area	*Q*, normalized capacity (Ah/m²)
	Q/mass	*Q*, normalized capacity (Ah/g)

Some battery analysis results (charge and discharge capacity) can also be normalized. These values are automatically added to the data table of the battery analysis command if normalized signals are enabled, and normalized capacity is sampled in all battery cycling commands *(see "Battery Analysis", chapter 12.12.5, page 185)*.

When a mass or area value is input, and the option toggled, the normalized signals are accessible in each measurement command (signals tab) and can be plotted. The normalization factor is automatically added to the cell properties in the run control pane *(see "Cell properties", chapter 9.3, page 151)*.

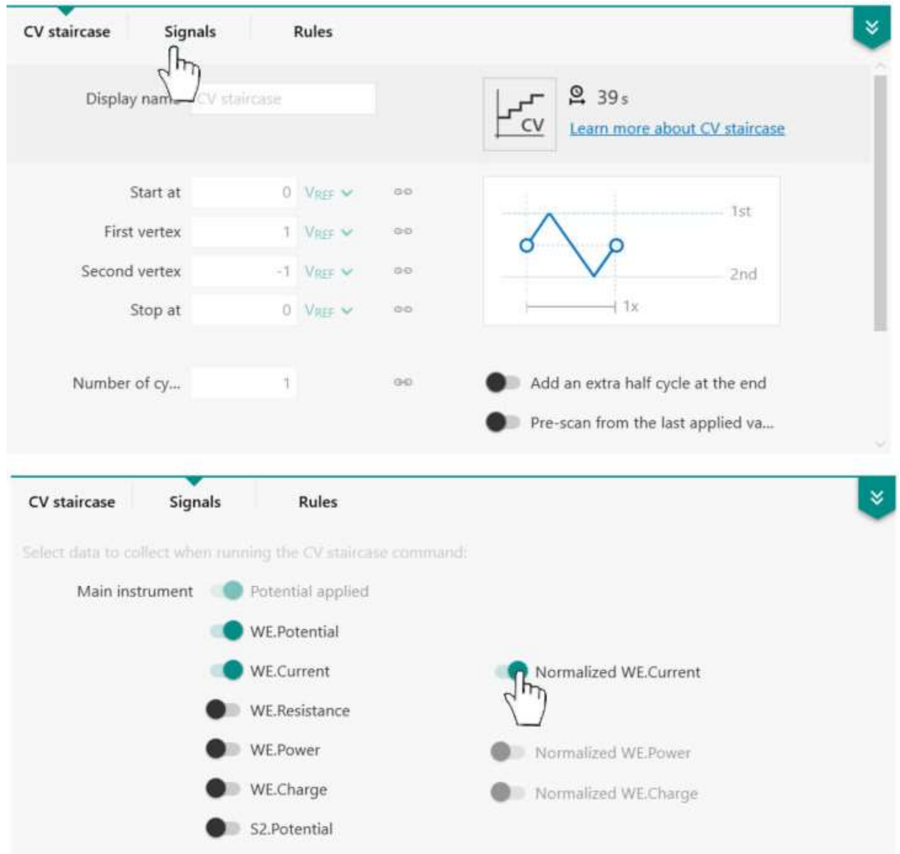


Figure 77 Sampling of the normalized signals is accessible from the measurement tiles, in the Signals tab

Only sampled signals can be normalized. For example, in the previous figure, the normalized WE.Charge would be accessible only if the WE.Charge is also sampled.

10 Data explorer and Procedure library

The data explorer and procedure library are accessible from the left ribbon in INTELLO and allow for easy access to all run and procedures stored in the database

10.1 Data explorer

The data explorer, accessible from the data drawer on left bar in INTELLO, is where runs (data collected from procedures) can be found and organized. All runs are saved in the INTELLO database, which is made accessible via this explorer (along with the procedure drawers for saved procedures). At the highest level, there are two main folders:

- The **personal** data folder: this folder contains runs accessible only to the current user. This is the default location when no other location is specified before starting a procedure. All runs imported into INTELLO (.irf files) are also automatically stored in this location (and the database).
- The **shared** data folder: this folder contains runs accessible to all users of the same instance of INTELLO in their respective data explorer. Runs can be moved to the shared folder for collaborating users.

Additionally, when a **run is deleted** from the data explorer, it is not instantaneously removed from the database, but temporarily moved to the **deleted items (shared or personal)**. Items are stored in the deleted items folder for 30 days, during which time they can be recovered. After that period of time, they are also deleted from the database. It is also possible to permanently delete a run from that location by using the dedicated button in the top bar menu.

The following actions are available to organize and search the data explorer:

- Create **folders and subfolders**. After the name of the folder, the number of individual runs in the folder is displayed.
- **Import runs from files (.irf)**: runs are then imported in the active location
- **Export runs and folders to files**: individual or multiple runs can be selected to be exported to .irf files in the windows explorer.
- **Filtering**: use the filters on tags, color markers of the runs, work system, user, techniques used in the procedure/run, date (specific date, or range)
- **Sort**: runs and folders can be sorted, by name, measured date, last modified time or session.

- The **search bar** is a useful tool to search the entire database for a specific run or set of runs

The list can be made compact where only the run name, the tags, comments and last modified date are visible in one line. The expanded view provides a more complete overview with the main plot visible, as well as some additional meta data and the list of main parameters.

Use the **drag and drop function to easily transfer runs, procedures and folders between INTELLO and the windows explorer**. Dragging from INTELLO to a location in the Windows explorer has the same functionality as exporting. Dragging from Windows to INTELLO has the same functionality as importing. Note that if folders or several folders are selected and contain subfolders, then the folder and subfolder structure is preserved. This can be useful to archive part of a database.

10.2 Procedure library

The procedure library, accessible from the procedures drawer on left bar in INTELLO, is where procedures can be found and organized. All procedures are saved in the INTELLO database, which is made accessible via this explorer (along with the data drawers for saved runs). At the highest level, there are three main folders:

- The **personal** library: this folder contains library created by and accessible only to the current user. This is the default location when no other location is specified after saving a procedure.
- The **shared** data folder: this folder contains procedures accessible to all users of the same instance of INTELLO in their respective library. Procedures can be moved to the shared folder for collaborating users.
- The **Autolab Library**: this library contains folders organized by application and technique where predesigned procedures can be found. These procedures are provided by Metrohm Autolab to start easily and can either be used as is, by simply editing the main parameters to match experimental needs or be used as a starting point to elaborate more advanced sequences. When an Autolab procedure is edited beyond the main parameters, it is possible to save it in the user's library as a new procedure. This library can be searched and filtered but cannot be edited. Its content is enhanced with new releases of INTELLO.

Additionally, when a **procedure is deleted** from the procedure library, it is not instantaneously removed from the database, but temporarily moved to the **deleted items (shared or personal)**. Items are stored in the deleted items folder for 30 days, during which time they can be recovered. After that period of time, they are also deleted from the database.

It is also possible to permanently delete a run from that location by using the dedicated button in the top bar menu.

The following actions are available to organize and search the procedure library:

- Create **folders and subfolders**. After the name of the folder, the number of individual runs in the folder is displayed.
- **Import procedures from files (.ipf)**: runs are then imported in the active location.
- **Export procedures and folders to files**: individual or multiple procedures can be selected to be exported to .ipf files in the windows explorer.
- **Filtering**: use the filters on techniques used in the procedure
- **Sort**: procedures and folders can be sorted, by name, last used or last modified date.
- The **search bar** is a useful tool to search the entire database for a specific procedure.

Use the **drag and drop function to easily transfer runs, procedures and folders between INTELLO and the windows explorer**. Dragging from INTELLO to a location in the Windows explorer has the same functionality as exporting. Dragging from Windows to INTELLO has the same functionality as importing. Note that if folders or several folders are selected and contain subfolders, then the folder and subfolder structure is preserved. This can be useful to archive part of a database.

11 INTELLO Runs

A run is a file created by INTELLO as soon as a procedure starts its execution. It contains the data collected, metadata such as a copy of the procedure structure and settings (Sequence), as well as a log of all events that occurred during the execution of the procedure (Events). Data is added to the run while measuring and can be plotted in real time.

A typical view for a run is shown in *(see "INTELLO Runs", chapter 11, page 159)*

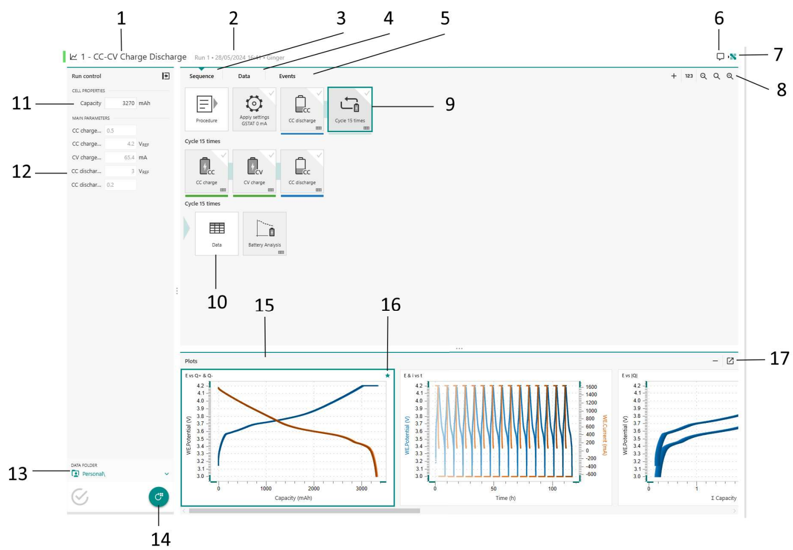


Figure 78 General view of a run in INTELLO (see main text for a description of the different sections and elements)

The run is composed of 4 main sections: the run name and information (1,2), the run control with the cell properties and main parameters used to run the procedure, the sequence itself (3) or the data tab when selected (4) and the events tab (5) and the plot ribbon at the bottom.

At the top of each run, a bar (**1**) indicates

- a **color** tile which can be used to easily recognize runs and changed at any time by clicking on the tile. This color is visible in the navigation pane of INTELLO as well as in the database.
- the **run name**. By default the run name is the one specified in the procedure tile before starting the measurement. This name can include metadata in order to make the name unique (e.g.: include the cell ID, material, date etc.), see the dedicated section *(see "Procedure settings", chapter 9.4, page 151)* for more details. The run name can be edited directly by clicking on it in the title bar.

- the run number, date and work system name are also indicated in gray (**2**)
- a button to add **run notes** and **tags** (**6**). A pop-up window appears and it allows to add **comments or remarks** during or after the measurement, tags for future data sorting, or to edit the run name or color.
- **IN2NOVA** (**7**): this button converts the run into a .nox file which can be opened in NOVA for additional data analysis

The sequence view is visible by clicking on the sequence tab and displays the complete structure of the procedure used to run the measurement. It is comprised of a series of tiles, with possible nested commands (such as in this example where the CC charge, CV charge, and CC discharge are nested into the cycle command). It is possible to zoom in and out, display the commands number or add analysis commands by selecting the option in the top ribbon (**8**). Navigating between the different commands is possible by clicking on them. The selected tile is highlighted (**9**) and its data table is accessible (**10**).

The cell properties (**11**) *(see "Cell properties", chapter 9.3, page 151)* and main parameters (**12**) *(see "Main Parameters", chapter 9.2, page 150)* are visible on the left for easy reference to the most important parameters (customizable in the procedure).

Runs are saved into the database in the location specified by the user in "Data folder" (**13**) which can be changed at any time before, during or after the run.

A run can be converted into a procedure by using the convert-to-procedure button (**14**).

The plot ribbon (**15**) contains all plots created and can be rearranged and modified at any time. Double clicking on one of the plots enlarges the plot and gives access to additional plot editing tools (coloring, cycle selection, etc.). One plot (with a green star) is the favorite plot (**16**): this plot is displayed in the database as a mini plot for easier recognition. Plots can be popped out (**17**).

The data view is visible by clicking on the data tab and provides an overview of, and easy access to, the data table(s) of every command within the run. During the measurement, this view also tracks the progress of each command during the sequence with its own progress bar. From this view, exporting the data to .csv or excel file is more convienent. If no command is selected, clicking on the export data table button in the top right will export all the data in the run into seperate files in the designated location. If one or more commands are selected, clicking on the button will export just the selected data tables.

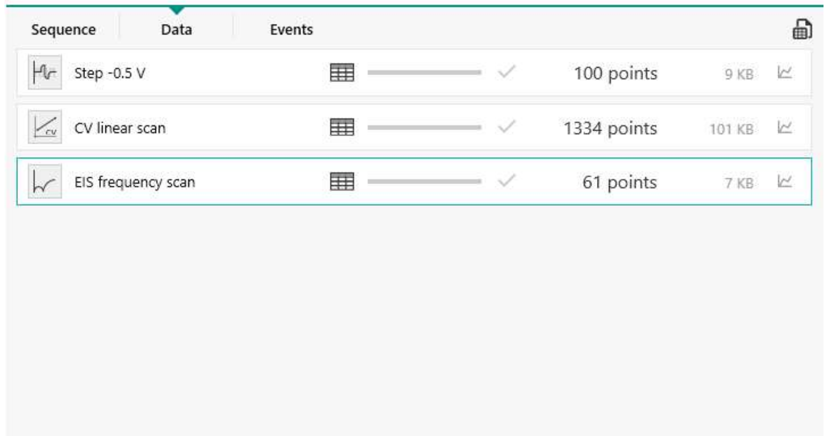


Figure 79 Data view of an INTELLO run

The events view is visible by clicking on the events tab and provides access to the events log, a time-stamped overview of every event that occured as the sequence was executed. An 'event' can take a variety of forms, including among others, the start and finishing time of the measurement, a rule execution, or errors such as current or voltage overload detection and premature abortion of the measurement. This is a useful view for troubleshooting and optimizing measurement conditions.

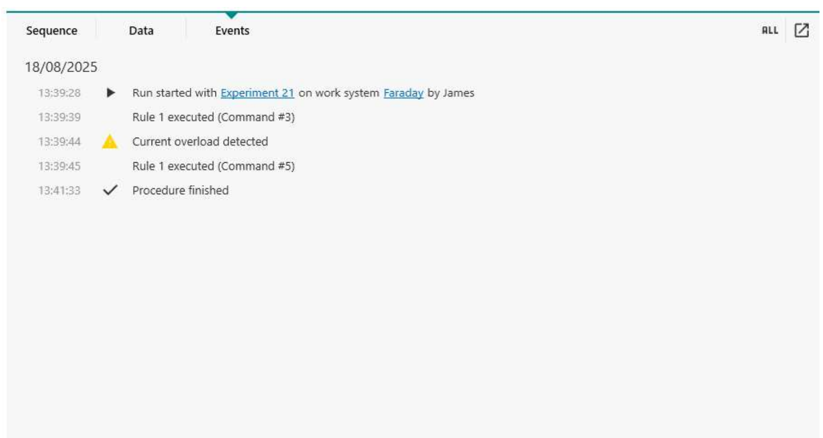


Figure 80 Events view of an INTELLO run

12 Command tiles

This section describes the command tiles of INTELLO and how they are used.

12.1 Chrono methods command tile

The general use of the **Chrono methods** command is to perform any of the following: chronoamperometry, chronopotentiometry, or chronocoulometery. Chronoamperometry is performed by placing the Chrono methods command in the sequence where the mode is set to **potentiostatic** by a preceding **Apply settings** command tile. Similarly, chronocoulometry is performed in potentiostatic mode by observing and plotting the WE.Charge signal. Chronopotentiometry is performed by using the Chrono methods command in a sequence where the mode is set to **galvanostatic**.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Potential / Current**: Input for the potential or current set point. This field will be adjusted automatically depending on the **Mode** setting of the nearest preceding Apply settings command tile.
- **Duration**: The duration of the measurement.
- **Sampling interval**: The time between two consecutive sampled points.

Estimated number of points: Here the number of data points that will be acquired is displayed (read only) according to the actual parameter values. If any of the parameters are altered during the measurement, this estimate will not be accurate.

12.2 CV linear scan command tile

The general use of the **CV linear scan** command is to execute the cyclic voltammetry electrochemical technique. With this CV command, the potential is swept with a linear ramp (in contrast to the CV staircase command, which uses a stepped ramp). This command can be used only in potentiostic mode; galvanostatic CV linear scan is not possible. The mode is set by a preceding **Apply settings** command tile.

Parameters

Display name: this name is displayed on the command tile, a user-defined name may be input here.

Parameters relating to the applied waveform refer to potential with the unit of V or subunits (mV). The potential may be specified with respect to the *reference potential*, V_{REF} or the *Open Circuit Potential (OCP)*, V_{OCP}. When V_{OCP} is used, OCP measurement is required before the CV linear scan command.

- **Start at**: The start value must be between the two vertex values. To start outside the boundaries of the vertices please use the *Pre-scan from the last applied value* toggle and place an **Apply** command tile before the **CV linear scan** command tile.
- **First vertex**: The value of the first vertex.
- **Second vertex**: The value of the second vertex.
- **Stop at**: The waveform stops at this value. The stop value is not restricted by the boundaries of the vertices.

The scan direction is defined by the value of the **First vertex** parameter with respect to the **Start at** value. When the first vertex is greater than the Start value, the scan will proceed in the forward direction; when the first vertex is lower than the start value, the scan will proceed in the reverse direction.

- **Number of cycles**: A cycle is defined as crossing both vertices. Only integer numbers may be entered in this field.
- **Add an extra half cycle at the end**: When this toggle is enabled an additional half cycle is added to the end of the waveform. An extra half cycle is equal to one additional vertex crossing before proceeding to the stop value.
- **Pre-scan from the last applied value**: When this toggle is enabled the potential will be scanned from the last applied set point of the preceding command tile in the sequence to the **Start at** value, using the **Scan rate** defined in the CV staircase command. This segment of the CV data will be labeled *Cycle 0* in the data table.

The **CV waveform plot** is displayed with the command properties. This plot is updated according to the inputted parameters and helps to visualize the applied waveform.

- **Scan rate**: Rate at which the potential will be scanned. The scan rate is always positive, regardless of the scan direction.
- **Potential interval**: The potential difference between two consecutive sampled points. Since the potential is ramped linearly, and not stepwise, this parameter does not have any influence on the applied potential profile. The potential interval is always positive, regardless of the scan direction.
- **Sampling interval**: The time between consecutive sampled points.

The **Scan rate**, **Potential interval**, and **Sampling interval** are interrelated parameters, it is only possible to define two out of the three of them. When two of these parameters are input, the third is calculated automatically.

- **Estimated number of points per cycle**: The number of data points per CV cycle is displayed (read only) according to the actual parameter values. If parameters are altered during the measurement, this estimate may not be accurate.

12.3 CV staircase command tile

The general use of the **CV staircase** command is to execute the staircase cyclic voltammetry electrochemical technique in either potentiostatic or galvanostatic mode. The mode is set by a preceding **Apply settings** command tile.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.

The parameters that describe the applied waveform will be presented differently, depending on the mode:

- **Potentiostatic CV staircase**: parameters relating to the applied waveform refer to potential with the unit of V or subunits (mV). The potential may be specified with respect to the *reference potential*, V_{REF} or the *Open Circuit Potential (OCP)*, V_{OCP}. When V_{OCP} is used, OCP measurement is required before the CV staircase command.
- **Galvanostatic CV staircase**: parameters relating to the applied waveform refer to current with the unit of A or subunits (mA or µA).

- **Start at**: The start value must be between the two vertex values. To start outside the boundaries of the vertices please use the *Pre-scan from the last applied value* toggle and place an **Apply** command tile before the **CV staircase** command tile.

- **First vertex**: The value of the first vertex.
- **Second vertex**: The value of the second vertex.
- **Stop at**: The waveform stops at this value. The stop value is not restricted by the boundaries of the vertices.

The scan direction is defined by the value of the **First vertex** parameter with respect to the **Start at** value. When the first vertex is greater than the Start value, the scan will proceed in the forward direction; when the first vertex is lower than the start value, the scan will proceed in the reverse direction. The scan always proceeds from the Start at value to the first vertex.

- **Number of cycles**: A cycle is defined as crossing both vertices. Only integer numbers may be entered in this field.
- **Add an extra half cycle at the end**: When this toggle is enabled an additional half cycle is added to the end of the waveform. An extra half cycle is equal to one additional vertex crossing before proceeding to the stop value.
- **Pre-scan from the last applied value**: When this toggle is enabled the potential (or current, in the case of galvanostatic CV) will be scanned from the last applied set point of the preceding command tile in the sequence, to the **Start at** value, using the **Scan rate** defined in the CV staircase command. This segment of the CV data will be labeled *Cycle 0* in the data table.

The **CV waveform plot** is displayed with the command properties. This plot is updated according to the parameters inputted and helps to visualize the applied waveform.

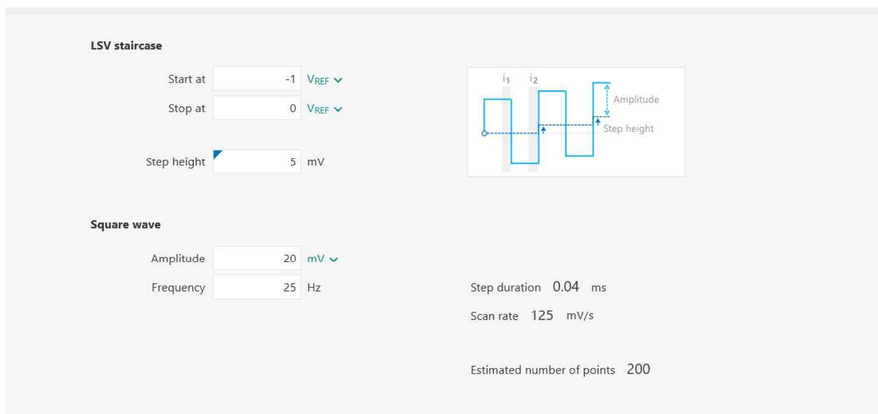
- **Scan rate**: Rate at which the applied signal (potential in potentiostatic CV, current in galvanostatic CV) will be scanned. The scan rate is always positive, regardless of the scan direction.
- **Step height**: In CV staircase, the applied signal is applied in discrete steps with a fixed step height. The step height value is always positive, regardless of the scan direction.
- **Step duration**: The time between two consecutive applied steps. In CV staircase one point is sampled per step, so the step duration is also the sampling interval. Modifying the step duration will modify the *Estimated number of point per cycle* value, which is displayed beside the step duration input field.

The **Scan rate**, **Step height**, and **Step duration** are interrelated parameters, it is only possible to define two out of the three of them. When two of these parameters are input, the third is calculated automatically.

- **Estimated number of points per cycle**: The number of data points per CV cycle is displayed (read only) according to the actual parameter values. If parameters are altered during the measurement, this estimate may not be accurate.

12.4 Square wave voltammetry (SWV)

The square wave voltammetry (**SWV**) command is used to execute a SWV measurement, a pulse voltammetric technique, in potentiostatic mode.
In SWV, a symmetrical square-wave pulse with constant height is superimposed on every step of a staircase linear sweep voltammetry (LSV).
The typical waveform (applied potential vs. time) applied to the cell is displayed in the command. Depending on the direction of the scan, the LSV steps starts with the maximum amplitude (positive) on its first half (positive scan), or with the minimum (negative) on its first half (negative scan). The plot of the waveform changes accordingly in the command view.



Parameters

- **LSV parameters**
  - **Start and Stop at**: first and last applied potential of the LSV
  - **Step height**: step potential increment of the LSV (see waveform plot)
- **Square wave**
  - **Amplitude**: amplitude of the square wave superimposed to the LSV (see waveform plot)
  - **Frequency**: frequency of the square wave superimposed to the LSV (in Hz).
  - The step duration is calculated as *1/frequency* and the scan rate as *step height x frequency*.

Signals

In SWV, the applied potential is the potential of the LSV staircase. At each step, two currents are sampled:

- **i_1**: sampled at the end of the first half of the square wave period (also known as forward current).
- **i_2**: sampled at the end of the second half of the square wave period (also known as backward current).
- **WE.Current** is defined as the differential current (**i_1 - i_2**) and is the main signal for SWV.

NB: it is possible to perform cyclic SWV by adding another SWV command after this one, with the same parameters except for Start and Stop potential (LSV parameters) which must be inverted.

12.5 Differential pulse voltammetry (DPV)

The differential pulse voltammetry (**DPV**) command is used to execute a DPV measurement, a pulse voltammetric technique, in potentiostatic mode. In DPV, a short pulse with constant height is superimposed at the end of every step of a staircase linear sweep voltammetry (LSV). The typical waveform (applied potential vs. time) applied to the cell is displayed in the command. Depending on the direction of the scan, the sign of the pulse is positive (positive scan), or negative (negative scan). The plot of the waveform changes accordingly in the command view.

Parameters

- **LSV parameters**
  - **Start and Stop at**: first and last applied potential of the LSV
  - **Step height**: step potential increment of the LSV (see waveform plot)
  - **Step duration**: duration of the LSV step (see waveform plot)

- **Pulse**
  The pulse is always added at the end of the LSV step.
  - **Height**: amplitude of the pulse superimposed to the LSV (see waveform plot)
  - **Duration**: duration of the pulse superimposed to the LSV (see waveform plot). The duration of the pulse must longer than 0.1 ms but shorter than the step duration.
  - The scan rate is calculated as *(step height)/(step duration)*.

Signals

In DPV, the applied potential is the potential of the LSV staircase (or base potential). At each step, two currents are sampled:

- $\mathbf{I_1}$: sampled at the end of applied base potential (just before the pulse, also known as base current).
- $\mathbf{I_2}$: sampled at the end of the pulse (also known as pulse current).
- **WE.Current** is defined as the differential current ($\mathbf{I_2 - I_1}$) and is the main signal for DPV.

NB: it is possible to perform cyclic DPV by adding another DPV command after this one, with the same parameters except for Start and Stop potential (LSV parameters) which must be inverted.

12.6 Export

The Export command allows for **automatic export of data tables** and in various formats by placing them next to data tables in a procedure before running it. When selecting a command in a procedure, empty data tables are accessible and display the measured and applied signals generated by this command. When nested in the selected command, next to the data table the export command will automatically generate a data file and export it after the run in a selectable format.

Parameters

- **Export folder**: specify the folder into which the data file is exported.
- **File name**: specify the name of the exported file

It is possible to create unique folder/file names by inserting metadata (such as the date, time, or a main parameter) to the name of the folder/file name : available metadata are accessible via the **{}** at the end of the text box.

The following metadata/parameters are accessible:

Table 10 Available metadata and parameters for the creation of unique folder and filenames

Metadata	Value in text-box	Format	Example*
Work System Name	${work system}	text	VIONIC
Procedure name	${procedure}	text	CV linear potentiostatic
Run number	${run_no}	text	1
Command name	${command}	text	CV linear
Command number	${command_no}	numeric	3
Command start date	${date}	yyyymmdd	20250827
Command start time	${time}	HHmm	1345
main parameter	${*label of main parameter*}	value	

If a file already exists, several options are available:

- **Make file name unique by adding a number**: the new file will have an incremental number at the end of its name (File (1).txt, File (2).txt, etc.)
- **Overwrite**: the pre-existing file is deleted and replaced by the new one
- **Append new data at the end**: the file is modified and new rows of data are added at the end of the table in the existing file.

File format: *ASCII/CSV*, *Excel* are available for all data tables, *Relaxis* and *ZView* only for impedance data

Comment lines

One or several comments lines can be added. Metadata related to this specific run can be added via the **{}** at the end of the text box. Rows can be added with the **+** button and removed with the cross. The toggle can be used to disable the export of the comments lines.

Columns tab

In this tab (top part of the command), the signals to be exported can be selected, reordered and the headers can be customized. By default, all sampled signals appearing in the data table are exported, with default headers and units and in the order displayed in the data table.

- **Select the exported columns**: check or uncheck the Export at the end of the line. Only checked parameters will be exported
- **Reorder the columns**: the rows with the different signals can be dragged and dropped to reorder the columns in the exported file

Automatic export for individual cycles, or EIS iterations

When a measurement command is placed in a repeat command, and contains an export command:

- *Individual files are generated* if the Export command is attached to the data table of the nested commands and "make file unique" is selected. A new file is exported every time the command is repeated, and the name modified with the iteration number.
- *Files are combined* into one data table if the Export command is attached to the data table of the nested commands and "Append new data" is selected. If the export command is attached to the data table of the repeat command, all repeats are combined in one file.

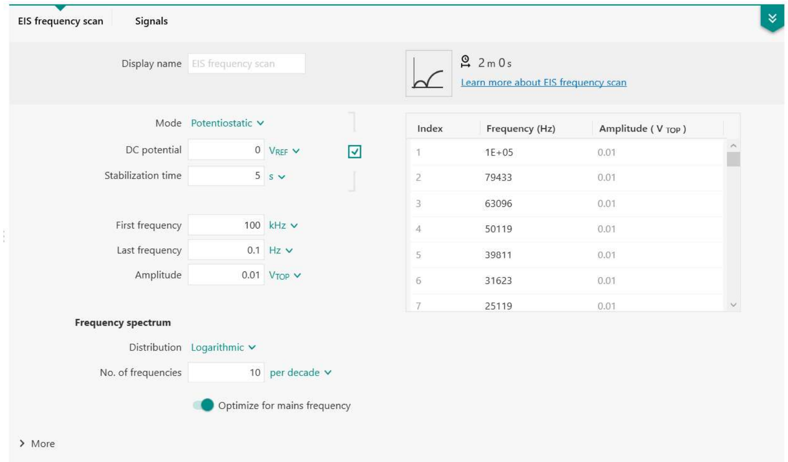
12.7 Electrochemical Impedance commands

Electrochemical impedance measurements can be performed at one single frequency *(see "EIS single frequency command tile", chapter 12.7.2, page 174)* or by scanning a range of frequencies (Electrochemical Impedance Spectroscopy, EIS *(see "EIS frequency scan command tile", chapter 12.7.1, page 170)*

12.7.1 EIS frequency scan command tile

The **EIS frequency scan** command is used to execute an electrochemical impedance spectroscopy (EIS) measurement. The command can be used in either potentiostatic or galvanostatic mode.

General parameters



- **Display name**: a user-defined name may be input here.
- **Optional mode and DC settings**: these options allow for selecting the mode (Potentiostatic or Galvanostatic), the **DC setpoint** (potential or current depending on the mode) and the **DC stabilization time.** The DC stabilization is the time during which the DC setpoint is applied without superimposed sine perturbation (AC signal). This allows the system to equilibrate before running the EIS measurement. Note that these are optional settings. They are applied only if the box is checked. If this box is not checked, the mode and DC setpoint are defined by the mode of VIONIC prior to this command (defined in an apply settings command at the beginning of the procedure and/or a prior apply command for the set point and DC stabilization time). The required duration of the DC stabilization period depends on the cell and the previous state of the cell.
- **First frequency**: The frequency of the first applied sine wave in the frequency scan. It is generally recommended to start with the highest desired frequency.
- **Last frequency**: The frequency of the last applied sine wave in the frequency scan. It is generally recommended to end with the lowest desired frequency.
- **Amplitude**: The amplitude of the applied sine wave. The units depend on the specified mode and the selection of the amplitude definition from the drop down menu. The amplitude of the sine wave can be defined based on the RMS (root mean square) value, or the TOP (peak) value. Note that the RMS amplitude of a sine wave is approximately 0.71 (specifically: ½ √2) of its top value.

When the DC setpoint is not applied, INTELLO displays the values of the setpoint, based on the previous command in the sequence (this value is greyed out, and given only for information).

Frequency spectrum parameters

- **Distribution**: The type of distribution used to calculate the frequency values that will be applied in the frequency scan. Linear and logarithmic distribution of frequencies are possible. When switched to **custom**: the frequency table on the right can be edited (values can be changed, frequencies can be added with the + sign, rows can be deleted).
- **No. of frequencies**: Input and selection to designate the number of frequencies that will be applied during the frequency scan. It is possible to designate the number of frequencies in total, or per decade.
- **Optimize for mains frequency**: When this toggle is enabled, the applied frequency values in the frequency scan will be adjusted slightly to avoid the mains frequency (50 Hz or 60 Hz), and its harmonics. Avoiding these frequencies generally results in better quality EIS measurement, as increased noise may be present at these frequencies. This is most relevant for potentiostatic EIS measurements on high impedance samples as low currents are more sensitive to distortion from mains currents.

When **Optimized for mains frequency** option is used, some of the adjusted (shifted) frequencies might overlap with the adjacent (not shifted) frequency values. If this happens, one of the overlapping frequency will be automatically removed from the frequency scan resulting a lower number of frequencies in the data table and on the plots.

A table with all frequencies scanned during the execution of the command is visible on the right of the command. It is possible to edit this table by clicking on a row or a cell or by setting the distribution to custom:

- **edit a frequency**: double-click on a frequency in the table to change it to a custom value
- **add a frequency**: either use the **+** symbol at the bottom of the table to add a row after the selection or select a row and right click to insert a row before the selection. The default value for a new row is 100 Hz.
- **delete a frequency:** select a row and right click to delete the selected row.

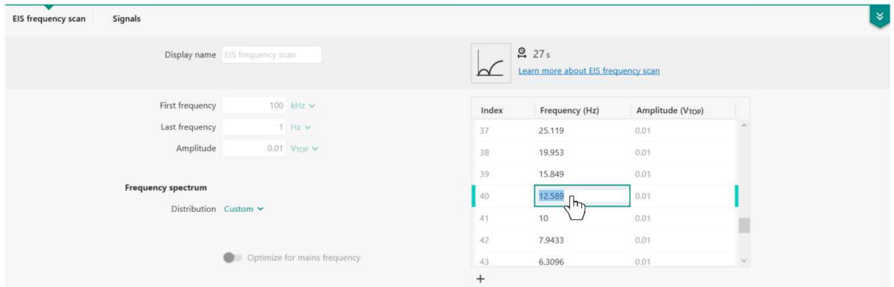


Figure 81 Custom distribution of frequencies in EIS frequency can be set by clicking on one frequency or a row.

The EIS command automatically switches the cell on, if the mode and DC setpoint are specified. In GSTAT more, the current range is selected automatically to optimized the results for the entire scan. All other settings (bandwidth, current range in PSTAT), are as specified by an Apply settings command if necessary. For example, if a procedure is set in potentiostatic mode, with automatic current range and automatic bandwidth (default settings) set at the beginning of the sequence with an Apply settings command, any EIS command in the same sequence will also have the bandwidth and current range selected automatically and optimized during its execution.

Table 11 The following default settings apply during an EIS measurement when the DC setpoint and stabilization time are specified in the EIS command and the Apply box is ticked.

Mode	**Potentiostatic**	**Galvanostatic**
Cell	Switched On	Switched On
Bandwidth	Defined by the Apply Settings command	Defined by the apply Settings command
Automatic current range	Optimized at each frequency	Based on DC setpoint + AC Amplitude, A_{TOP}

If a different behavior is required, an **Apply settings** command tile is typically placed ahead of the **EIS frequency scan** command in the procedure sequence in order to define the mode (Potentiostatic or Galvanostatic), the set point (fixed DC potential or current) upon which the sine wave will be superimposed, a stabilization time at the specified DC setpoint, the bandwidth settings and current range.

More parameters

Measurement Optimization

Optimize measurement : EIS measurement according to the user's priority, as selected on the slider: speed, quality, or a balance of both.

Optimization impacts the quality of the result, as well as the time required to carry out the frequency scan. At each frequency, the impedance measurement will take place over multiple sine wave periods. The measured data is averaged to one period to improve the signal to noise ratio and then used for the impedance calculation. When the EIS measurement is optimized for Speed, the minimum number of periods that is practical for any given frequency value will be used and the overall EIS measurement time will be short. A short measurement time is ideal when noise in the acquired signal is expected to be low (*i.e.* due to low impedance of the electrochemical cell, or due to a high applied sine wave amplitude), or when the electrochemical cell is not expected to be stable over a longer measurement time.

AC Stabilization time

Cell stabilization in EIS measurements is optional, but strongly recommended. The AC stabilization time refers to the amount of time that the sine wave will be applied to the cell before data used towards the impedance calculations will be collected. Stabilization time is beneficial as it allows the electrochemical cell to experience and respond to the sinusoidal perturbation before data is collected. The choice of stabilization time depends on the time constant of the electrochemical cell being studied. Cells that respond slowly to perturbation may benefit from a longer stabilization time.

- **Apply AC stabilization time**: When this toggle is enabled, the sine wave will be applied for the designated amount of time before data is collected for the impedance measurement. When it is disabled, data for the EIS measurement will be collected immediately upon application of the sine wave.

12.7.2 EIS single frequency command tile

The **EIS single frequency** command is used to execute an electrochemical impedance spectroscopy (EIS) measurement with a single frequency. The command can be used in either potentiostatic or galvanostatic mode.

General parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Mode**
  - **Potentiostatic**: parameters relating to the applied waveform refer to potential, with the unit of V or a subunit (mV).
  - **Galvanostatic**: parameters relating to the applied waveform refer to current, with the unit of A or a subunit (mA, µA).

- **DC potential/current**: DC setpoint applied to the cell before adding the Sine wave. This allows the cell to stabilize and reach a steady-state. A DC stabilization is recommended to ensure that the system has reached a steady state before recording impedance data. The required duration of the DC stabilization period depends on the cell and the previous state of the cell.
- **Stabilization time**: time during which the DC setpoint is applied
- **Frequency**: frequency of the applied sine wave.
- **Amplitude**: amplitude of the applied sine wave. The units depend on the specified mode and the selection of the amplitude definition from the drop down menu. The amplitude of the sine wave can be defined based on the RMS (root mean square) value, or the TOP (peak) value. Note that the RMS amplitude of a sine wave is approximately 0.71 (specifically: $\frac{1}{2}\sqrt{2}$) of its top value.

The general behavior of the command regarding current ranging, cell state, and bandwidth is identical to the EIS frequency scan command (*(see "EIS frequency scan command tile", chapter 12.7.1, page 170)*).

More parameters

Measurement Optimization

Optimization impacts the quality of the result, as well as the time required to carry out the single frequency measurement. The impedance measurement will take place over multiple sine wave periods. The measured data is averaged to one period to improve the signal to noise ratio and then used for the impedance calculation. When the EIS measurement is optimized for Speed, the minimum number of periods that is practical for the applied frequency will be used and the overall EIS measurement time will be short. A short measurement time is ideal when noise in the acquired signal is expected to be low (i.e. due to low impedance of the electrochemical cell, or due to a high applied sine wave amplitude), or when the electrochemical cell is not expected to be stable over a longer measurement time.

Optimize measurement slider: The software optimizes the EIS measurement according to the user's priority, as selected on the slider: speed, quality, or a balance of both (by default).

AC Stabilization time

Cell stabilization in EIS measurements is optional, but strongly recommended. The AC stabilization time refers to the amount of time that the sine wave will be applied to the cell before data used towards the impedance calculations will be collected. Stabilization time is beneficial as it allows the electrochemical cell to experience and respond to the sinusoidal perturbation before data is collected. The choice of stabilization time depends on the time constant of the electrochemical cell being studied. Cells that respond slowly to perturbation may benefit from a longer stabilization time.

- **Apply AC stabilization time**: When this toggle is enabled, the sine wave will be applied for the designated amount of time before data is collected for the impedance measurement. When it is disabled, data for the EIS measurement will be collected immediately upon application of the sine wave.

To avoid erroneous interpretation, *invalid data points* are, by default, not displayed in plots and tables in INTELLO. For EIS, points measured during current or potential overload are invalid, To minimize the occurrence of invalid data points during EIS measurements, it is recommended to use automatic current ranging in potentiostatic mode.

A toggle is available in tables and plots for displaying or hiding all contingent invalid data points.

12.8 Group command tile

The general use of the **Group** command is to structure a complex procedure in the Procedure Sequence Editor. Multiple command tiles can be grouped together within the procedure sequence in a container (group) with a specific **Display name**. Use of the Group command introduces convenient functionality for structuring long or complex sequences:

- Control and measurement commands can be placed inside the Group ("nested") with drag and drop, this will create a sub level of the sequence.
- When a Group is relocated in the procedure sequence, all nested commands are relocated with the Group.
- When a Group is deleted from the procedure sequence, all nested command tiles are deleted as well.
- When a Group command tile is selected in the procedure sequence, the **Ungroup** button will appear. This button removes the Group command and places the nested commands in the sequence at the position where the Group tile was formerly located. The original order of the nested commands from the group is preserved.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be inputted here.

12.9 LSV linear scan command tile

The general use of the **LSV linear scan** command is to execute the linear sweep voltammetry electrochemical technique. With this LSV command, the potential is swept with a linear ramp (in contrast to the LSV staircase command, which uses a stepped ramp). This command can be used only in potentiostatic mode; galvanostatic LSV is not possible. The mode is set by a preceding **Apply settings** command tile.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.

Parameters relating to the applied waveform refer to potential with the unit of V or subunits (mV). The potential may be specified with respect to the *reference potential*, V_{REF} or the *Open Circuit Potential (OCP)*, V_{OCP}. When V_{OCP} is used, an OCP measurement should be executed before the LSV linear scan command.

- **Start at**: The start value.
- **Stop at**: The stop value.
- **Scan from the last applied value**: When this toggle is enabled the **Start at** value will not be used and its input field will be disabled. Instead, the scan will start from the last applied set point. When the **Start at** value is linked (for example, to a main parameter) the toggle will be disabled and the **Start at** value will receive the input from the link.

The scan direction is defined by the **Stop at** value with respect to the **Start at** value. When the Start at value is greater than the Stop at value, the scan will proceed in the reverse direction.

- **Scan rate**: Rate at which the potential will be scanned. The scan rate is always positive, regardless of the scan direction.
- **Potential interval**: The potential difference between two consecutive sampled points. Since the potential is ramped linearly, and not stepwise, this parameter does not have any influence on the applied potential profile. The potential interval is always positive, regardless of the scan direction.
- **Sampling interval**: The time between consecutive sampled points.

The **Scan rate**, **Potential interval**, and **Sampling interval** are interrelated parameters, it is only possible to define two out of the three of them. When two of these parameters are input, the third is calculated automatically.

- **Estimated number of points**: The number of data points is displayed (read only) according to the actual parameter values. If parameters are altered during the measurement, this estimate may not be accurate.

12.10 LSV staircase command tile

The general use of the **LSV staircase** command is to execute the staircase linear sweep voltammetry electrochemical technique in either potentiostatic or galvanostatic mode. The mode is set by a preceding **Apply settings** command tile.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.

The parameters that describe the applied waveform will be presented differently depending on the mode:

- **Potentiostatic LSV staircase**: parameters relating to the applied waveform refer to potential with the unit of V or subunits (mV). The potential may be specified with respect to the *reference potential*, V_{REF} or the *Open Circuit Potential (OCP)*, V_{OCP}. When V_{OCP} is used, OCP measurement is required before the CV staircase command.
- **Galvanostatic LSV staircase**: parameters relating to the applied waveform refer to current with the unit of A or subunits (mA or µA).

- **Start at**: The start value.
- **Stop at**: The stop value.
- **Scan from the last applied value**: When this toggle is enabled the **Start at** value will not be used and its input field will be disabled. Instead, the scan will start from the last applied set point. When the **Start at** value is linked (for example, to a main parameter) the toggle will be disabled and the **Start at** value will receive the input from the link.

The scan direction is defined by the **Stop at** value with respect to the **Start at** value. When the Start at value is greater than the Stop at value, the scan will proceed in the reverse direction.

- **Scan rate**: Rate at which the applied signal (potential in potentiostatic LSV, current in galvanostatic LSV) will be scanned. The scan rate is always positive, regardless of the scan direction.
- **Step height**: In LSV staircase, the applied signal is applied in discrete steps with a fixed step height. The step height value is always positive, regardless of the scan direction.
- **Step duration**: The time between two consecutive applied steps. In LSV staircase one point is sampled per step, so the step duration is also the sampling interval.

The **Scan rate**, **Step height**, and **Step duration** are interrelated parameters, it is only possible to define two out of the three of them. When two of these parameters are inputted, the third is calculated automatically.

- **Estimated number of points**: The number of data points is displayed (read only) according to the actual parameter values. If parameters are altered during the measurement, this estimate may not be accurate.

12.11 Repeat command tile

The general use of the **Repeat** command is to create a section of the procedure that will be repeated in a loop. One or more command tiles can be placed inside the Repeat, this will create a sub level of the sequence.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **For n repetitions**: this repeat type is used to repeat *n* times one or several command tiles inside the Repeat command
  - **Repetitions**: The number of times that the section of the procedure sequence located within the Repeat loop will be repeated.
- **For multiple values**: this repeat type is used to repeat one or several commands with variable parameters for each iteration. The table displays the different iterations (rows) and the values of one or multiple parameters (columns) for each iteration. The plus (+) sign on the top right corner of the table allows for the addition of one parameter (column). The plus (+) sign at the bottom of the table adds a new iteration (row) to the repeat command.
  - **Label**: this name is given to the user-defined parameter
  - **Type**: the type of parameter can be selected here
  - **Unit**: the units available depend on the selected **Type** of parameter
  - **Default**: the default value for the chosen parameter. This value is attributed by default to all iterations (rows).

  Once the parameter (column) is added to the table, the values can be manually modified by the user for each iteration or generated by accessing **generate values**. The values are generated for the active column on a user-defined range (from **Start value** to **End value**) following a **linear**, **square-root** or **logarithmic** (log_{10}) distribution. For a Logarithmic distribution, the number of values can be given **in total** or **per decade** (the number of decades depends on the range between the start and the end value). The table on the right provides a preview of the values generated for each iteration.

In the Values table, parameters or iterations can be **inserted** or **deleted** by right-clicking on a column or a row.

The generated parameters can be linked to one or several parameters of commands in the sequence. Linking can be done by:

- creating a **Link to repeat command parameter** from command tiles placed inside the Repeat loop.
- clicking on the link symbol in the header of the parameter column and creating a link to a parameter already nested into the repeat command. Only parameters of the same type and unit will appear in this list.

A main parameter cannot be linked to the repeat command. The user must first unlink it from the main parameters in order to link it to the repeat command.

The **Repeat** command will be seamless when all commands in the loop are seamless. This will be indicated by a green bar below the Repeat command tile. **There are no time gaps between the iterations of a seamless Repeat loop.**

12.12 Battery Cycling

INTELLO provides a complete and flexible set of commands and automated data analysis tools to investigate the performance of battery electrode materials, electrolytes, full or half cells for battery electrodes, either to cycle cells or perform advanced analysis. The following section describes the commands available in INTELLO for battery or supercapacitor research. These commands can be combined in any order to build advanced testing procedures. Examples of more advanced uses of these commands are provided in the Autolab library with, among others, Galvanostatic Intermittent Titration Technique (GITT) or its potentiostatic counterpart Potentiostatic Intermittent Titration Technique (PITT).

12.12.1 Cycle

The **Cycle** command is specifically designed for testing batteries or supercapacitors (energy storage devices) by repeated charge and discharge cycles. This command can contain several specific commands and repeat them to cycle the device under test:

- Constant-current (CC) charge: applies a constant positive current to the cell
- CC discharge: applies a constant negative current to the cell
- Constant-voltage (CV) charge: applies a constant voltage to the cell, for example, after a CC charge command with a potential limit
- CV discharge: applies a constant voltage to the cell, for example, after a CC discharge command with a potential limit
- Rest: the cell is set off and the open circuit potential (OCP) is measured

- EIS (frequency scan and single frequency): electrochemical impedance spectroscopy can be performed anywhere during the charge or discharge.

The main parameter of this command is the number of cycles (number of times the nested sequence is repeated). When this command is added to a procedure, the **cell capacity** (theoretical or nominal) is automatically added to the **Cell properties** section of the run control: when provided, this value is used to specify (dis)charging and limit currents in CC and CV commands in C-rate instead of an absolute current in A. The C-rate is calculated as *C-Rate* (h^{-1}) *= Current (A)/Specified cell capacity (Ah)*. For example, if a capacity of 120 mAh is specified in the cell properties, a CC discharge at 0.5 C (or C/2) will apply *-120 x 0.5 = -60 mA* to the cell. For the same cell, a current limit set 0.05 C (or C/20) on a CV charge command will stop the command when the measured current reaches a value below *+120 x 0.05 = +6 mA*.

The data table of the command contains cycling information:

- **Cycle**: cycle number
- **WE.Current (A) and WE.Potential (V)**: measured current and potential during all the CC and CV commands
- **Charge and discharge capacity (Ah)**: capacity measured during the charge (any CC or CV step) and discharge (any CC or CV). This value is set to 0 at the beginning of each new cycle.
- **Σ Capacity (Ah)**: this is the total capacity of the cell over the entire set of cycles. This value is set to 0 only at the beginning of a new cycle command.
- **dQ/dV (Ah/V)**: this is the differential capacity measured as the differential of the charge or discharge capacity vs potential. This value is set to 0 only at the beginning of a new cycle command.

The data table also contains an **Analyze Battery** result table which automatically extracts and calculates the following cycling parameters:

- **Charge capacity (Ah)**: the last charge capacity value recorded per cycle
- **Discharge capacity (Ah)**: the last discharge capacity value recorded per cycle
- **Coulombic efficiency (%)**: ratio of the discharge capacity (after a full charge) and the charge capacity of the same cycle. This value is meaningful only if the cycle starts with a charging sequence (at least one CC charge command) *CE (n) (%) = (Discharge capacity)/(Charge capacity)*x*100* for the cycle *n*. By definition a cycle starts by charging the battery: if the battery must first be discharged before starting the cycling, it is recommended to add this preconditioning step outside of the Cycle command, at the beginning of the procedure, so that the coulombic efficiency calculated at each cycle uses data from the same effective cycle.

- **Relative capacity (%)**: ratio of the discharge capacity (after a full charge) of a given cycle and the Capacity specified in the cell properties.

12.12.2 Constant-Current (CC) Charge or Discharge

The Constant-Current (CC) Charge or Discharge commands can be used to apply a constant current (or C-rate) to a cell. This command is specifically designed to be used for battery testing and cycling, in a Battery Cycling repeat command.

The CC command sets VIONIC to galvanostatic mode and holds the specified current or C-Rate while recording the cell potential (voltage), cell capacity and other signals available in the signals tab. The optimal current range is automatically selected by INTELLO based on the input C-rate or current.

When this command is inserted right behind a CC charge or discharge command which contains a potential limit, the switch "Use CC cut-off potential" is automatically set on and the potential limit is held with this command. If the WE.Potential limit is not reached during the previous CC step, the last measured WE.Potential is applied in the CV command.

End conditions: it is possible to specify end-conditions for the CV step based on

- **Potential**: when the value of the potential is higher or lower (charge or discharge respectively) than the specified value, the CC step ends. This setting is used to perform Galvanostatic charge/discharge with potential limits.
- **Time**: maximum duration. If this is the only end condition, this is the total duration of the CV.

This command uses **dynamic data acquisition**. Data points are sampled and recorded whenever one of the given signals or values has changed by its sampling interval.

- **Δ Time**: data points are recorded every specified interval time. This is the only necessary sampling condition.
- **Δ WE.Potential**: data points are recorded every time the potential changes by more than the specified interval. This option allows for faster sampling when the potential of the cell changes quickly (for example, at the beginning or the end of the CC command).
- **Δ S2.Potential**: data points are recorded every time the S2.Potential changes by the specified interval.

Signals

By default, the current (*WE.Current*), the potential (*WE.Potential*), and the charge or discharge capacity (in mAh) are sampled. The *charge* and *discharge capacity* are reset to 0 at the beginning of each new cycle.
It is possible to sample the capacity of the cell continuously over all

cycles, by enabling the sampling of the *Σ Capacity* (mAh). *Σ Capacity* is calculated as the total charge measured from the beginning of the cycling (Σ Capacity = sum over all the cycles of (charge capacity) - (discharge capacity)).

If a three-electrode configuration is used (e.g. with a Swagelok cell and reference electrode), and the potential at the counter-electrode is measured with the second-sense (S2), the signal *(WE-S2).Potential* will sample the total voltage across the whole battery.

The differential capacity, *dQ/dE*, also known as dQ/dV can be calculated during a CC step:

$dQ/dE|_{n+1} = |Q_{n+1}-Q_n|/(E_{n+1}-E_n)$, where n is the index of the data point, Q_n is the charge or discharge capacity and E is the measured potential (WE.Potential) for the data point of index n.

12.12.3 Constant-Voltage Charge or Discharge

The Constant-Voltage (CV) Charge or Discharge commands can be used to apply a constant voltage (potential) to a cell. This command is specifically designed to be used for battery testing and cycling, in combination with CC (constant current) charge or discharge commands, in a Battery Cycling repeat command to hold the potential for a given time or until a current limit is reached.

The CV command sets VIONIC to potentiostatic mode and holds the specified voltage, while recording the current, cell capacity and other signals available in the signals tab.

When this command is inserted right behind a CC charge or discharge command which contains a potential limit, the switch "Use CC cut-off potential" is automatically set on and the potential limit is held with this command. If the WE.Potential limit is not reached during the previous CC step, the last measured WE.Potential is applied in the CV command.

When following a CC charge or discharge, the transition from CC (GSTAT) to CV (PSTAT) is **seamless**.

End conditions: it is possible to specify end-conditions for the CV step based on

- **Time**: maximum duration. If this is the only end condition, this is the total duration of the CV step.
- **Current**: when the absolute value of the current is lower than the specified value, the CV step ends
- **d(i)/dt**: when the absolute value of the current varies less than the specified rate (in mA/s)

This command uses **dynamic data acquisition**. Data points are sampled and recorded whenever one of the given signals or values has changed by its sampling interval.

- **Δ Time**: data points are recorded every specified interval time. This is the only necessary sampling condition.
- **Δ WE.current**: data points are recorded every time the current changes by the specified interval. This option allows for faster sampling when the current of the cell changes quickly (for example, at the beginning of the CV step).
- **Δ S2.Potential**: data points are recorded every time the potential at the second sense (S2) changes by more than the specified interval. This option allows for faster sampling when the voltage of the cell changes quickly (for example, at the beginning of the CV step).

Signals

By default, the current (*WE.Current*), the potential (*WE.Potential*), the charge or discharge capacity (in mAh) are sampled. The *charge* and *discharge capacity* are reset to 0 at the beginning of each new cycle. It is possible to sample the capacity of the cell continuously over all cycles, by enabling the sampling of the *Σ Capacity* (mAh). *Σ Capacity* is calculated as the total charge measured from the beginning of the cycling (Σ Capacity = sum over all the cycles of (charge capacity) - (discharge capacity)).

If a three-electrode configuration is used (e.g. with a Swagelok cell and reference electrode), and the potential at the counter-electrode is measured with the second-sense (S2), the signal *(WE-S2).Potential* is the total voltage across the whole battery.

Note

The differential capacity, *dQ/dE*, also known as dQ/dV is not calculated during a CV step (as the potential is constant).

12.12.4 Rest command

The Rest command switches the cell off, setting the battery or cell to the **open-circuit potential** (OCP, also known as open-circuit voltage, OCV) for the specified amount of time. During this rest, the potential is monitored and recorded. It is possible to monitor other signals such as the potential of the second sense (S2.Potential), the total voltage of the battery in a three-electrode configuration (WE-S2 Potential, if S2 is connected to the CE) or the temperature (if a thermocouple is connected to VIONIC, added to the work-system and specified in the required work-system of the procedure).

It is possible to update the value of the OCP for subsequent commands by enabling the option. When toggled on, any potential setpoint specified vs. OCP (V_{OCP}) will be applied with regard to the last WE.Potential measured during the Rest.

This command can use **dynamic data acquisition**. Data points are sampled and recorded whenever one of the given signals or values has changed by its sampling interval.

- **Δ Time**: data points are recorded every specified interval time. This is the only necessary sampling condition.
- **Δ WE.Potential**: data points are recorded every time the potential changes by the specified interval. This option allows for faster sampling when the potential of the cell changes quickly (for example, just after a charge or discharge step).
- **Δ S2.Potential**: data points are recorded every time the potential at the second sense (S2) changes by the specified interval. The S2.Potential signal must be sampled in the Rest command (signals tab) to be able to define this dynamic sampling rule.

12.12.5 Battery Analysis

The battery analysis command analyses battery cycle data to return values calculated per cycle, such as the charge or discharge capacity, coulombic efficiency, etc. This command does not have any settings or specific inputs as the calculations are based on the cell capacity (Q_{cell}) provided in the **Cell properties**, and the data recorded at each cycle. These values can also be plotted vs. the cycle number to monitor the performance of the cell with time. Each value is calculated and can be plotted at the end of each cycle.

It contains a data table with the following parameters:

Table 12 Values calculated by the battery analysis command

Value	Definition	Comments	Can be normalized (by mass or area)
Cycle	Cycle number. Incrementally increased every time the content of the Cycle is repeated	In one procedure, the cycle number is incremental from the start of the procedure and is not reset by a new cycle command.	N/A

Value	Definition	Comments	Can be normalized (by mass or area)
Charge Capacity, Q+ (Ah)	Capacity measured at the end of charge step every cycle	When several charge (CC or CV) steps, belong to the same cycle, the charge is cumulated over all the charge commands.	Yes (Ah/g or Ah/cm^2)
Discharge Capacity, Q- (Ah)	Capacity measured at the end of discharge step every cycle	When several charge (CC or CV) steps, belong to the same cycle, the discharge is cumulated over all the charge commands	Yes (Ah/g or Ah/cm^2)

Value	Definition	Comments	Can be normalized (by mass or area)
Coulombic efficiency, CE (%)	Ratio of the discharge capacity and the charge capacity of the same nth cycle. *CE_n (%) = $Q-_n$/ $Q+_n$x100* for the nth cycle	A cycle starts by definition by charging the battery: if the battery must first be discharged before starting the cycling, it is recommended to add this preconditioning step outside of the Cycle command, at the beginning of the procedure, so that the coulombic efficiency calculated at each cycle uses data from the same effective cycle.	N/A
Relative capacity (%)	Ratio of the discharge capacity of the nth cycle and the cell capacity (Q_{cell}) RC_n (%) = $Q-_n$/ Q_{cell} x*100* for the nth cycle		N/A

The battery analysis command is automatically included in any cycle command, next to the cycle data table.

The Coulombic efficiency can be used to end a cycle command when its value drops below a user-defined threshold. As the calculation takes place between two seamless cycles, the following cycle is executed completely before the cycling commands ends.

12.13 External devices

VIONIC can control external devices via its Analogue OUT (AOUT1 and AOUT2) ports or Digital Output from the DIO port, present on the back panel of the instrument. A physical description of these ports can be found in *Chapter 4.2.2*

This chapter describes how these external devices can be controlled during procedures with INTELLO.

In general, when an external device must be controlled or monitored during a procedure, it must be added to the required work system: the required work system of a procedure is defined in the procedure command tile. For more details about VIONIC as an extended work system, please refer to *Chapter 5*

12.13.1 DIO control

The DIO (Digital Input/Output) port located on the back of VIONIC serves two primary functions: sending and receiving digital (1/0 logic) signals to and from other connected devices. The following pins are used

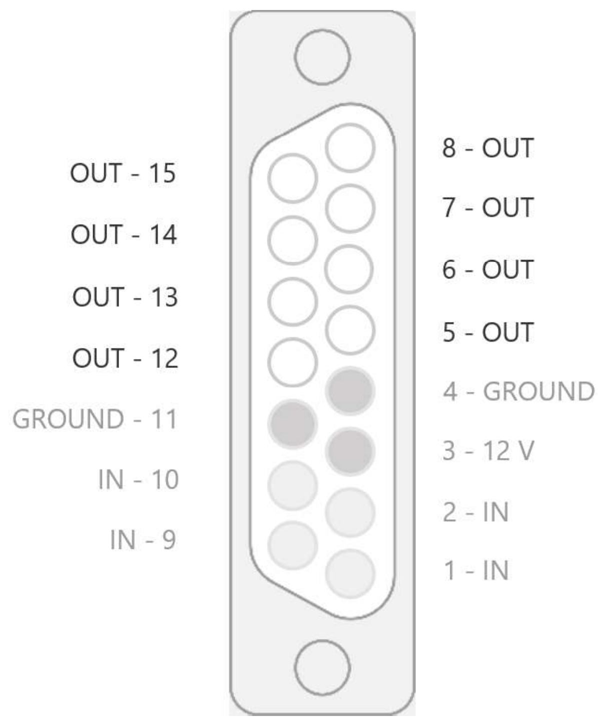


Table 13 Pin assignment of the DIO port

Pin number	Assignment
5-8, 12-15	OUT

4, 11	Digital ground
3	Isolated ground
1, 2, 9, 10	*IN (Not available yet)*

The Digital OUT pins can be used to send *TTL (Transistor-Transistor Logic) pulses*, allowing for precise synchronization of actions by sending synchronized signals to other devices. This enables seamless hyphenation between VIONIC and external devices, ensuring coordinated operations with an external device during electrochemical measurements run by VIONIC powered by INTELLO.

TTL (Transistor-Transistor Logic) pulses refer to electrical signals that transition between two logic levels: low (0, or 0 V) and high (1, or +5 V). These pulses are typically used to transmit information or synchronize actions between VIONIC digital devices. They are defined by their duration (or width, usually 10 µs to 10s of ms) and their type: rising- or falling- edge TTL:

- A falling edge occurs when the pulse transitions from a high level (1) to a low level (0)
- A rising edge happens when the pulse transitions from a low level (0) to a high level (1)

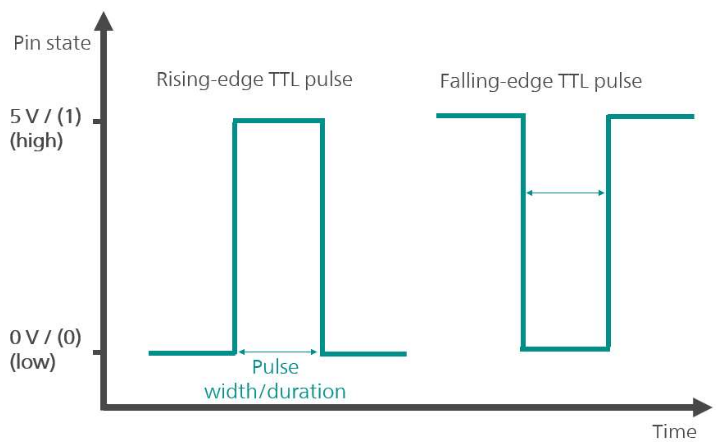


Figure 82 Rising and falling-edge TTL profile

The type of pulse (rising or falling-edge) and their width or duration depends on the instrument connected to VIONIC. Please refer to the user manual of the device to be controlled before programming these pulses in INTELLO.

Secondly, it enables the simple setting of pin levels to 0 or 1, triggering specific actions or activating external devices. Pin states refer to the logical levels assigned to individual pins of the DIO port. Changing pin states can be done either in an apply settings command or with the Set DIO command *Chapter 12.13.1.2*. The state of the pins between experiments is by default the last applied state. This can be modified by changing the end state of the DIO port in the procedure settings as shown below.

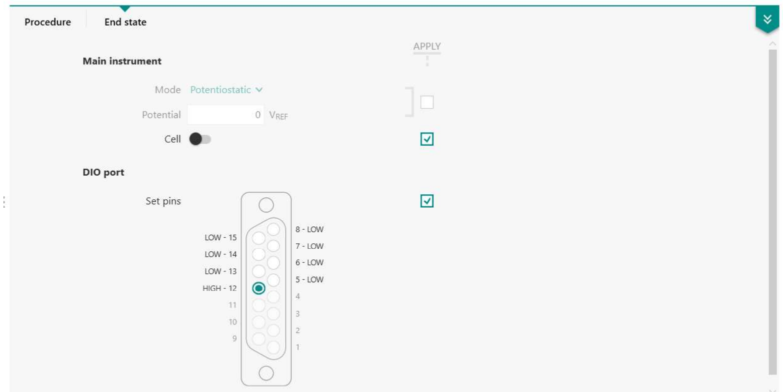


Figure 83 End state of the DIO port: with this configuration at the end of the procedure, the pin 12 remains high until the next procedure is run.

Please note that only the Digital Out pins are available with the current version of INTELLO. The input pins and the ability to execute actions upon reception of an external signal sent by another device will be available with a future version of INTELLO.

12.13.1.1 Direct DIO control of external devices

To be able to control or synchronize external devices via the DIO port of VIONIC during a procedure, the **direct DIO port control** option must be enabled (*Procedure tile > Define required works system... > Options*)

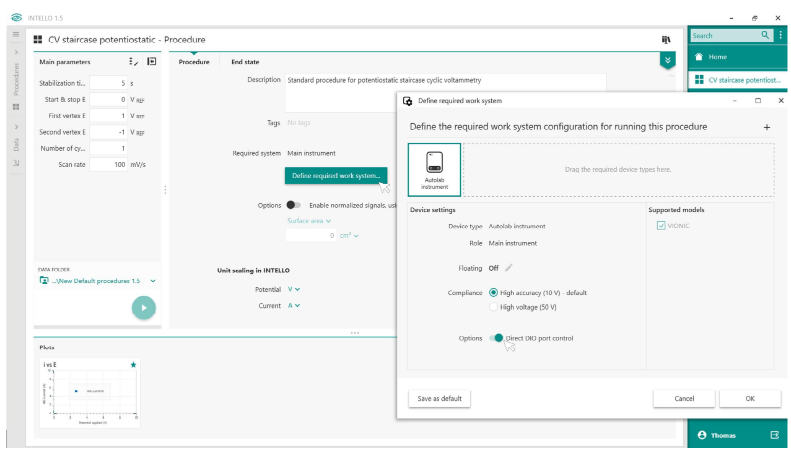


Figure 84 Enable Direct DIO port control in the Required work system of the procedure settings

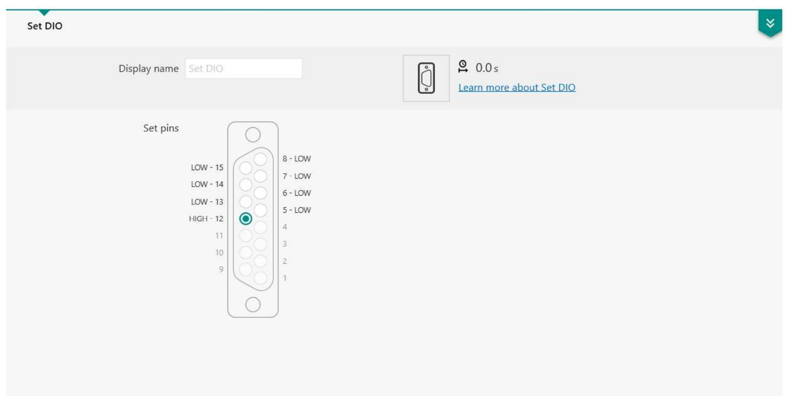
When this option is selected new command tiles are available in the list of commands as well as the synchronization option in LSV and CV staircase commands.

12.13.1.2 Set DIO command

The set DIO command defines the state of the output pins during a procedure. One or more pins can be set to high or low (1 or 0, i.e. 5 V or 0 V) by clicking on the pins. The numbers displayed correspond to the number of the pins on the port on the back panel of VIONIC.

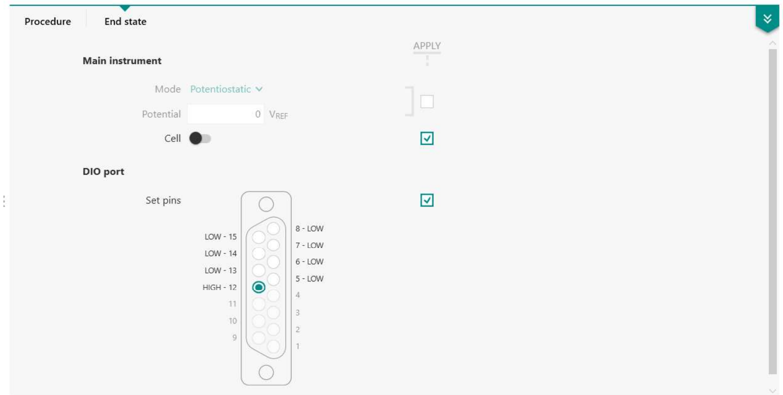
This command is used if VIONIC is used in an extended work system, connected to an external device via the DIO port on the back of VIONIC. The state of the pins will remain as set until another set DIO command with a different setting is reached or DIO pulses are sent by a dedicated command or in the synchronization options of the CV and LSV staircase commands.

In the example below, all output pins of the DIO port are set to low (default state), and only the pin 12 is set to high (1 or +5V).



Pulses programmed in this procedure will be falling-edge TTL pulses on pin 12, and rising-edge TTL pulses on all other OUT pins.

When the end of the procedure is reached, it is possible to keep the pins in a given state in between measurements, by defining the end state of the DIO port in the procedure tile (End state tab). In the following example, the pin 12 will remain high after the end of the procedure. This setting is also the one of the next running procedure unless a set DIO command is placed at the beginning the procedure, or the DIO port is edited in an apply settings command.



The set DIO command is *seamless*

12.13.1.3 DIO pulse

This command allows for sending TTL pulses on one pin from the DIO port on the back panel of VIONIC. It can be placed anywhere in a procedure where synchronization with a hyphenated instrument is required. The pin selected depends on the connection and function to be enabled and the duration of the pulse (width) depends on the requirements for the hyphenated instrument.

The direction of the pulse depends on the state of the pin defined either in the Apply settings command at the beginning of the procedure or by a Set DIO command. If the state of a pin is set to high in an apply settings or Set DIO command, subsequent pulses on the same pin will be falling edge pulses. If no default state is defined in the procedure, INTELLO will display a warning and the configuration of the pins must be set.

12.13.1.4 Synchronization (DIO pulses)

The synchronization option is available in LSV and CV (staircase) to send TTL pulses during a CV and and LSV command. It is available when the Direct DIO control is enabled in the required work system of the procedure.

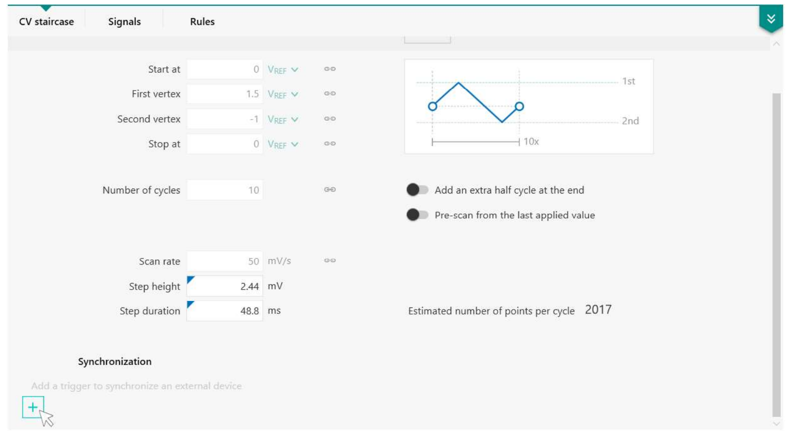


Figure 85 Add synchronization option in CV or LSV commands

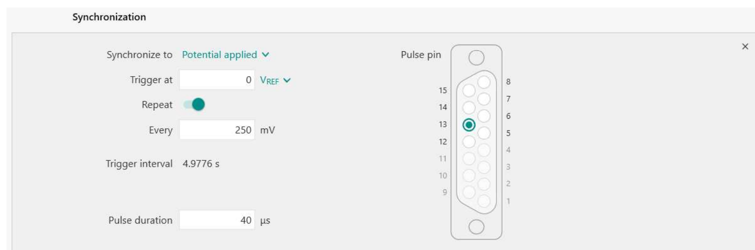


Figure 86 Synchronization settings in an LSV or CV staircase command

The following parameters can be set:

- **Synchronize to**
  - Potential applied: the interval between triggers is defined based on the applied potential during the CV or LSV, e.g. every 250 mV
  - Index: the interval between each trigger is defined by the number of sampled data points, e.g. for a CV with a sampling rate (step duration) of 48.8 ms and 2.44 mV, a trigger sent every 10 indexed points is sent every 0.488 s or 24.4 mV
  - Time: defines the time elapsed between each trigger
  - Start of cycle: this option, only available for CV allows for sending triggers as soon as a new cycle starts
- **Trigger at**: the condition at which the trigger is sent, e.g., if Trigger at 0.150 V is set, the first trigger is sent when VIONIC applies 0.150 V during the LSV or the CV.
- **Repeat every**: when enabled, triggers are sent every specified value (potential, time, index, cycle). For example, in the example above, the first trigger is sent at 0 V and one new trigger is sent every 250 mV afterwards until the end of the command.
- **Trigger interval**: estimated time elapsed between two pulses in the command. This parameter can be used to estimate the maximum integration time of an hyphenated spectrometer when pulses are sent to acquire spectra (see default procedure for hyphenated EC-Raman)

- **Pulse duration**: please refer to the user manual of the hyphenated instrument to find the recommended duration of pulses. Note that the pulse duration cannot be higher than the step duration (sampling interval) in the LSV or CV.
- **Pulse pin**: select the pin on which the TTL pulse must be sent.

The direction of the pulse depends on the state of the pin defined either in the Apply settings command at the beginning of the procedure or by a Set DIO command. If the state of a pin is set to high in an apply settings or Set DIO command, subsequent pulses on the same pin will be falling edge pulses. If no default state is defined in the procedure, INTELLO will display a warning and the configuration of the pins must be set.

12.13.2 External devices

VIONIC can control external devices via its Analogue OUT (AOUT1 and AOUT2) ports or Digital Output from the DIO port, present on the back panel of the instrument. A physical description of these ports can be found in *Chapter 4.2.2*

This chapter describes how these external devices can be controlled during procedures with INTELLO.

In general, when an external device must be controlled or monitored during a procedure, it must be added to the required work system: the required work system of a procedure is defined in the procedure command tile. For more details about VIONIC as an extended work system, please refer to *Chapter 5*

12.13.2.1 Rotator control

The Rotator control command tile is used to define the rotation rate of the RDE/RCE connected to the main instrument. The rotator must be part of required work system, as defined in the procedure settings, and defined as an external device in the work system settings.

Rotation rate: the rotation rate is given in rpm (revolution per minute).

Stabilization time: if toggled on, the rotator will rotate at the input rotation rate for the defined time before the procedure executes the following command.

When a rotator control is placed under a repeat from multiple values tile the rotation rate can be linked to a parameter (type: rotation rate, unit: rpm) from the repeat table to repeat the following command or series of command (LSV, CV, Chrono method) at different rotation rates. When a LSV is placed after the RDE command and run with different rotation rates, hydrodynamic analysis (Levich and Koutecký-Levich) is possible in NOVA by exporting the data with IN2NOVA when the procedure is finished (Use IN2NOVA and *Analyse in NOVA with Hydrodynamic Analysis*).

A procedure for Hydrodynamic Measurements (LSV) is available in the Autolab Library. This procedure can be modified with personalized settings. It allows for a simple Hydrodynamic analysis with IN2NOVA when the procedure is finished. Use IN2NOVA and *Analyse in NOVA with Hydrodynamic Analysis.*

12.14 Data analysis

Data analysis tools are available in INTELLO to meet the specific needs of electrochemical measurements. Analysis can be performed on data from plots or data table in a run.

Data analysis commands available in INTELLO appear in the Data handling section of the commands menu in procedures and runs.

Analysis commands can be dragged and dropped in a procedure, next to the data table upon which the analysis must be performed, before a measurement or after the measurement, in a run. If placed before a measurement, the input can be adjusted and the analysis will be executed as soon as the measurement command it is attached to is finished.

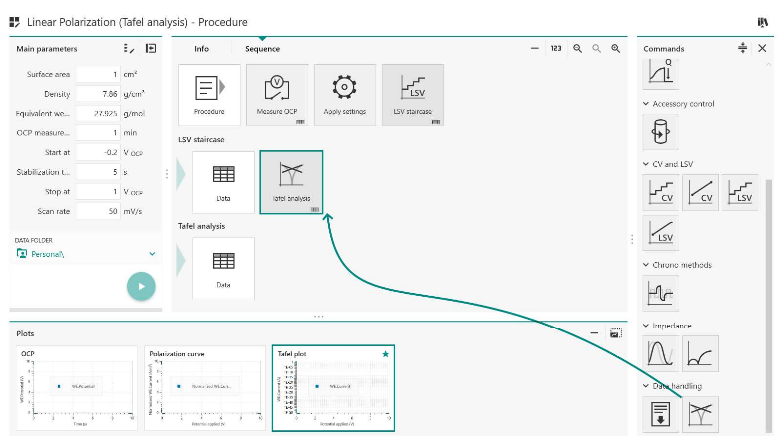


Figure 87 Drag and drop an analysis command next to the data table to be analysed

Data analysis is also accessible directly from the plot, by clicking on the *add analysis* button. Analytical tools available for this type of plot will be visible. Clicking on one of them opens the analysis command itself and calculations can be performed immediately.

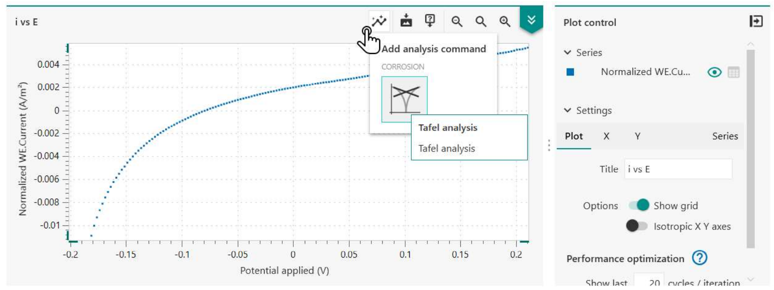


Figure 88 Add analysis command directly from a plot

The following analysis commands are available in INTELLO

- EIS data fitting *(see "EIS data fitting", chapter 12.14.2.2, page 203)*
- Electrochemical circle fit *(see "EIS circle fit", chapter 12.14.2.3, page 208)*
- Tafel analysis *(see "Tafel analysis (corrosion rate)", chapter 12.14.1.3, page 199)*
- Polarization resistance (corrosion rate) *(see "Polarization Resistance", chapter 12.14.1.4, page 200)*
- Butler-Volmer fit (corrosion rate) *(see "Tafel analysis (corrosion rate)", chapter 12.14.1.3, page 199)*
- Battery analysis *(see "Battery Analysis", chapter 12.12.5, page 185)*

12.14.1 Corrosion rate analysis

Corrosion rate (CR) is the speed at which any metal or alloy in a specific environment corrodes. It can be defined as the thickness of material loss in mm per year. One widely used approach for corrosion rate analysis is electrochemical corrosion rate analysis, which involves studying the electrochemical behavior of metals in corrosive environments. A key technique within electrochemical corrosion rate analysis is Tafel analysis, which provides valuable insights into the corrosion kinetics.

12.14.1.1 Tafel analysis

The Tafel method is a widely used electrochemical technique for corrosion rate analysis. It involves measuring the current-potential relationship (polarization curve) of a metal or alloy immersed in a corrosive solution. It is a graphical method used to extract the corrosion current and Tafel slopes from a current vs. potential plot (**polarization curve**). A polarization curve is the sum of the cathodic reaction current, I_c (hydrogen evolution or oxygen reduction, for example) and the anodic reaction current, I_a (metal dissolution).

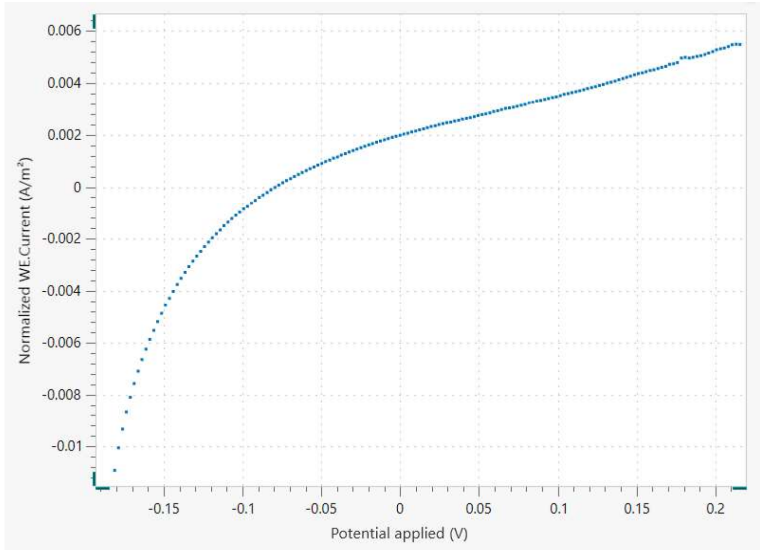


Figure 89 Polarization curve of a stainless steel electrode (1 cm²) in 0.1 M KCl recorded at 5 mV/s from -0.2 to 0.2 V vs. OCP.

The rate of the corrosion reaction is given by the exchange or corrosion current (i_{corr}) in the Butler-Vomer equation:

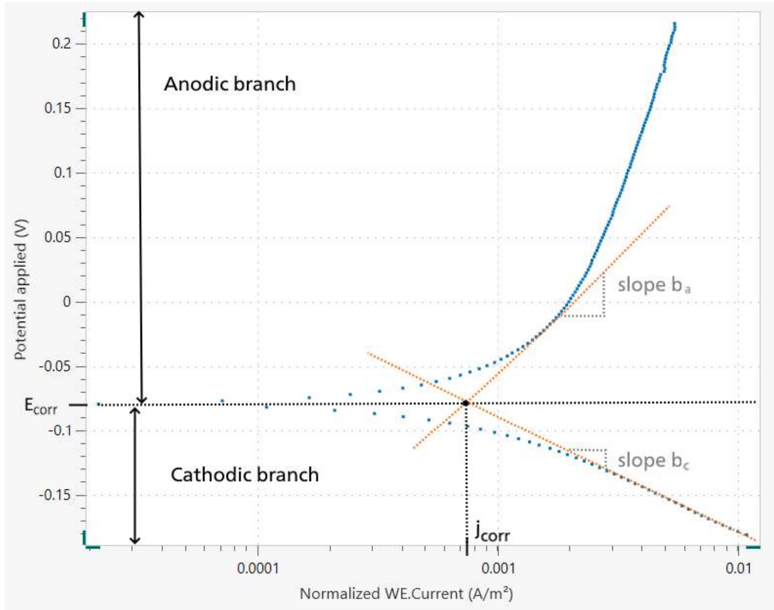
$$\boldsymbol{i} = i_a + i_c = i_{corr}\left(\exp\left(\frac{\ln(10)(\mathrm{E}-\mathrm{E_{corr}})}{b_a}\right) - \exp\left(\frac{\ln(10)(\mathrm{E}-\mathrm{E_{corr}})}{b_c}\right)\right)$$

where i_a and i_c are the anodic and cathodic current contributions, respectively, E is the applied potential, b_a (>0) and b_c (<0) are the anodic and cathodic Tafel slopes, in mV/decade. The corrosion potential, E_{corr}, is the open-circuit potential of the cell (OCP), or potential where the current is 0 on the polarization curve. At large overpotentials ($E \gg E_{corr}$, $E \ll E_{corr}$) , the Butler-Volmer equation simplifies to only the anodic or cathodic current, and the log(i) vs. E plot is linear.

$$\ln(|i|) = \ln(i_{corr}) + \frac{\ln(10)\ (\mathrm{E}-\mathrm{E_{corr}})}{b_{a/c}}$$

$$\log_{10}(i) = \log_{10}(i_{corr}) + \frac{(\mathrm{E}-\mathrm{E_{corr}})}{b_{a/c}}$$

On a Tafel plot, the intercept of the linear cathodic and anodic branch occurs ar E_{corr} and the intercept on the current axis is i_{corr}.



The slope of each branch, b_a and b_c (expressed in mV per decade of current on the log(i) scale) are indicative of the underlying mechanism for the corrosion reaction. Typical values lie between 10 to 250 mV/decade.

The corrosion rate can be directly linked to the measured corrosion current (density) by

$$\mathrm{CR} = i_{corr}\frac{\mathrm{K}\times\mathrm{EW}}{\mathrm{d}\times\mathrm{A}}$$

Where

- CR is the corrosion rate (mm/y),
- i_{corr} (A), the corrosion current determined from Tafel analysis,
- K = 3272 mm·A^{-1}·cm^{-1}· $year^{-1}$, constant to express CR in mm/year
- d (g·cm^{-3}), density of the studied material
- EW (g·mol-1), equivalent weight of the studied material
- A (cm^2), the sample surface area

12.14.1.2 Polarization curves, practical considerations

Potentiodynamic polarization curves are usually acquired using potentiostatic LSV staircase (*Chapter 12.10*) with few tens to hundreds of mV around the OCP (open-circuit potential), at low scan rates (0.1 to 5 mV/s). A typical procedure is available in the Autolab Library (*Linear polarization (Tafel analysis)*).

It is recommended to use LSV staircase over LSV linear to minimize the capacitive contribution to the polarization curve.

This procedure starts by measuring the Open-Circuit Potential (OCP), also known as corrosion potential for 5 minutes. Then the cell is switched on and Start potential is applied (-0.2 V vs. OCP) for stabilization before running an LSV staircase at 2 mV/s up to +0.2 V vs. OCP. Tafel analysis can be performed on the measured data by opening the Tafel Analysis tile in the LSV command.

These parameters must be adjusted depending on individual requirements for the material, electrolyte, temperature, etc.

12.14.1.3 Tafel analysis (corrosion rate)

Tafel analysis allows for the determination of the corrosion rate of a material by interpolating the linear portions (anodic and cathodic) of the Tafel plot. The limits of the linear parts must be selected by clicking on 4 points of the Tafel plot (E_{a1},E_{a2}, E_{c1}, E_{c2}). The limits can be modified by dragging the full portion or changing each limit individually. When the Butler-Volmer fit option is selected, the curve is fitted with the Butler-Volmer equation between E_{c1} and E_{a2}.

The Butler-Volmer fit is performed using the Levenberg–Marquardt algorithm. The number of iterations required to fit the results is provided in the results, along with the value of the Chi-square, χ^2 (goodness of the fit).

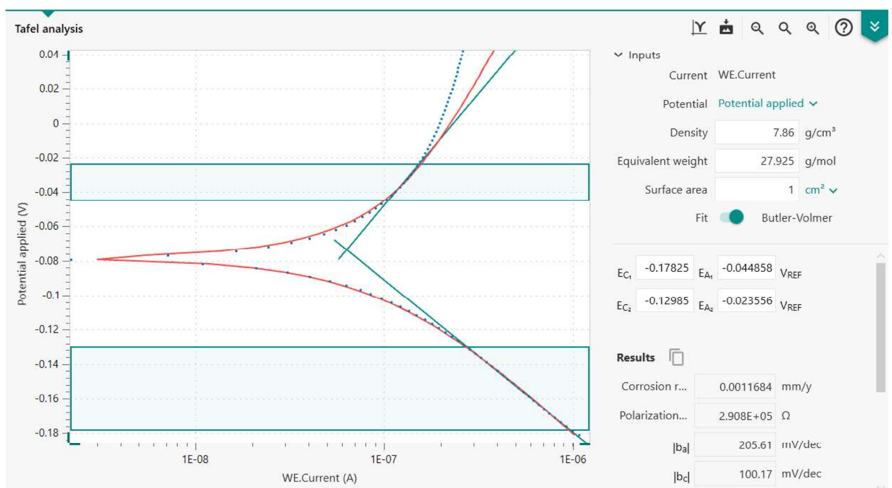


Figure 90 View of the Tafel analysis command with results. The green areas are added by selecting four points on the plot and can be moved and resized. Results are updated instantaneously. The red line is the result of the fitting with the Butler-Volmer fitting.

Cells parameters (surface area) and physical properties of the working electrode must be provided in the input section to run the analysis on the measured data. Default values are the ones of stainless steel.

Results are updated after each interaction with the plot or change in the inputs. The results can be copied to the clipboard (as a table) and pasted in any other document or report. This command also has a Tafel analysis data table (accessible from the Sequence view > Tafel analysis where all data and inputs are saved and can be exported.

The icon  on top changes the orientation of the displayed Tafel plot in the analysis command. This does not influence the results. Once the orientation has been changed it will remain the same for the INTELLO user, until this icon is clicked again (meaning this setting can be permanent for a user).

When the Tafel analysis is placed in a repeat command and the Tafel analysis has to be run on several polarization curves, a cycle selector in the Tafel analysis command allows for batch analysis of all the repeats with the same parameters. It is also possible to adjust the potential limits on each individual repeat. In the case of multiple repeats, the data table of the analysis command will display the results of each repeat in successive rows.

12.14.1.4 Polarization Resistance

The polarization resistance method is a widely used electrochemical technique for corrosion rate analysis. It involves measuring the current-potential relationship (polarization curve) of a metal or alloy immersed in a corrosive solution, usually over a small potential range (10 mV around the OCP). It is a method used to extract the polarization resistance, related to the corrosion current via the Stern-Geary equation, and therefore the corrosion rate from a **polarization curve**. A polarization curve is the sum of the cathodic reaction current, I_c(hydrogen evolution or oxygen reduction, for example) and the anodic reaction current, I_a (metal dissolution).

The rate of the corrosion reaction is given by the exchange or corrosion current (I_{corr}) in the Butler-Vomer equation:

$$\boldsymbol{i} = i_a + i_c = i_{corr}\left(\exp\left(\frac{\ln(10)(\mathrm{E}-\mathrm{E_{corr}})}{b_a}\right) - \exp\left(\frac{\ln(10)(\mathrm{E}-\mathrm{E_{corr}})}{b_c}\right)\right)$$

where the corrosion potential, E_{corr}, is the open-circuit potential of the cell (OCP), or potential where the current is 0 on the polarization curve, I_{corr} the corrosion current, and, b_a and b_c the Tafel slopes (V/dec.).

At small overpotentials ($|E\text{-}E_{corr}| \rightarrow 0$), assuming the Tafel slopes are constant, the derivative (slope) of the Butler-Volmer equation simplifies to:

$(di/dE)|_{E\rightarrow Ecorr} = I_{corr} \times 2.303 \times (|b_a|+|b_c|)/(|b_a|\times|b_c|) = 1/R_p$

With this slope being defined as the inverse of the polarization resistance R_p (Ω). The relationship between the slope of the polarization curve at small overpotentials is known as the **Stern-Geary equation**:

$1/ I_{corr} = R_p \times 2.303 \times (|b_a|+|b_c|)/(|b_a|\times|b_c|)$

Note that this equation is applicable, with the following assumptions:

- the corrosion process follows a Tafel-like process
- the Tafel slopes b_a and b_c are known for the process
- the potential range used for analysis is smaller than $0.1 \times |b_{a/c}|$ (typically less 10 mV)
- the polarization curve is linear in the potential range used for analysis
- the current is due to corrosion only: this can be achieved by minimizing the contribution of ohmic drop (iR drop correction, increased electrolyte conductivity and/or reduced electrode size) and minimizing the capacitive current (using staircase LSV with very low scan rates, e.g. 0.1 mV/s)
- a stable OCP value was reached before measuring the polarization curve

The corrosion rate can be directly linked to the measured corrosion current (density) by

$$\mathrm{CR} = i_{corr}\frac{\mathrm{K}\times\mathrm{EW}}{\mathrm{d}\times\mathrm{A}}$$

Where

- CR is the corrosion (mm/y),
- I_{corr} (A), the corrosion current determined from Stern-Geary equation,
- $K = 3272\ mm\cdot A^{-1}\cdot cm^{-1}\cdot year^{-1}$, constant to express CR in mm/year
- d ($g\cdot cm^{-3}$), density of the studied material
- EW ($g\cdot mol^{-1}$), equivalent weight of the studied material
- A (cm^2), the sample surface area

The Polarization Resistance command

The potential range used for analysis is specified by the user, either by inputting a value (in mV) or selecting a region on the plot. The limits can be modified by dragging the lines. INTELLO selects the value of the OCP based on the measured current and the selected range is always symmetrical around the OCP (E_{corr}).

Cells parameters (surface area) and physical properties of the working electrode must be provided in the input section to run the analysis on the measured data. Default values are the ones of stainless steel.

The values of the Tafel slopes $|b_a|$ and $|b_c|$ must be provided. If a Tafel analysis command (with a Butler-Volmer fit, for example) is placed in front of the Polarization resistance command the values calculated by Tafel analysis can be copied directly into the Polarization resistance command.

Results are updated after each interaction with the plot or change in the inputs. The results can be copied to the clipboard (as a table) and pasted in any other document or report. This command also has a Tafel analysis data table (accessible from the Sequence view > Tafel analysis where all data and inputs are saved and can be exported.

Note

When the Polarization Resistance command is placed in a repeat command and several polarization curves were measured, a cycle selector in the command allows for **batch analysis of all the repeats** with the same parameters. It is also possible to adjust the potential limits on each individual repeat. In the case of multiple repeats, the data table of the analysis command will display the results of each repeat in successive rows.

12.14.2 EIS data analysis

INTELLO provides manual and automated tools to analyse EIS data measured with VIONIC.

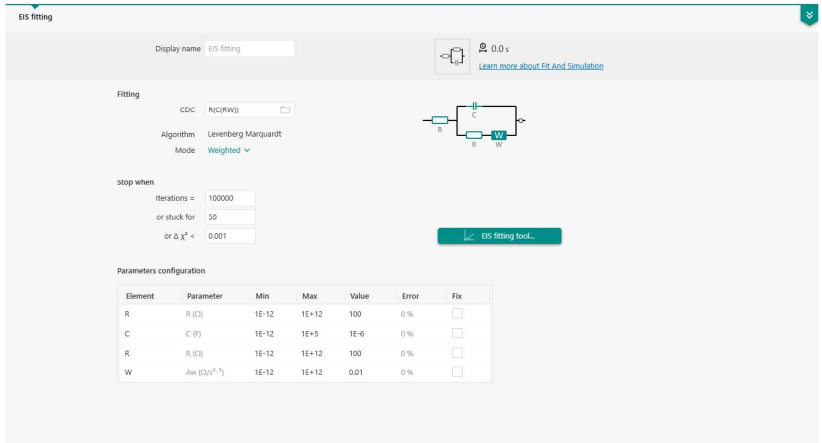
- Electrochemical circle fit: a command which can be used to quickly fit a semi-circle in a Nyquist plot using a R(RQ) equivalent circuit and identify reasonable starting values for complete data fitting.
- Fit and simulation: a command which can be used to fit measured impedance data with a user-defined equivalent circuit.

12.14.2.1 EIS fitting command

The EIS fitting command enables fitting EIS data recorded in INTELLO with a user-defined model (provided as an equivalent circuit). The tool allows for building equivalent circuits, choosing parameters for the fitting process, visualizing fitted results (Nyquist and Bode plot), and obtaining individual parameter values for each element of the equivalent circuit.

The command can be nested into an EIS frequency scan command in a procedure, so that the fitting can be automatically run as soon as the EIS frequency scan command has finished its execution and the complete EIS data is available

In this command view, it is necessary to provide a model, as a CDC, or from the library, which can be visualized as an equivalent circuit. The settings for the fitting, the stop conditions, and parameters configuration can be adjusted to optimize the speed of the fitting and increasing the chances of convergence.



For complete details about the configuration, the conditions and the algorithm, please refer to the dedicated chapter *(see "EIS data fitting", chapter 12.14.2.2, page 203)*.

12.14.2.2 EIS data fitting

The EIS fitting command enables fitting EIS data recorded in INTELLO with a user-defined model (provided as an equivalent circuit). The tool allows for building equivalent circuits, choosing parameters for the fitting process, visualizing fitted results (Nyquist and Bode plot), and obtaining individual parameter values for each element of the equivalent circuit.

EIS data

The EIS data measured in INTELLO is displayed on the left part of the tool, in a Nyquist (isotropic) and Bode plot. The complete data collected in one EIS frequency scan command is displayed by default. If the experimental data contains data points that must be excluded for the fitting (noise, glitches), or complete data point ranges at either end of the frequency scale the following options can be used:

- Clicking on a data point in the main EIS Data plot (selected as green) and then clicking on the (-) symbol will **exclude the selected data point**. This can be repeated as many times as necessary
- The **frequency range selector** allows for excluding complete ranges from the data set. The values displayed on each end of the selector are the new minimum and maximum values for the frequency range
- In either case, excluded data points are grayed-out.
- Both actions can be reversed at any point. The data collected by INTELLO is not affected.

Equivalent circuit

The equivalent circuit section provides tools to:

- **Build and edit an equivalent circuit**
  - Adding elements (complete list and definitions available in a dedicated table below), (RC), (RQ), or complete circuits from the library can be done by clicking on the **+** button
  - Adding an element at the beginning, end or between two parallel junctions can be done by clicking on the visible empty circle
  - When elements are present, adding elements in series, before, after, in a parallel of an element can be done by hovering over the element and selecting one of the three **+** options.
  - Replacing an element is done by right-clicking the element to be replaced.
  - Deleting an element is done via a right click or by selecting an element and pressing the Delete key.

- **Automatic numbering**: each element can be automatically numbered by clicking on the *n* icon. Custom names can also be typed in the parameters table.
- **Export circuit as an image** saves the circuit as a .png file.
- **Save the circuit to the library** with the library icon. When saved to the library the following parameters are saved: circuit and CDC as well as for each element its numbering and/or names along with starting values and minimum/maximum provided in the parameters table.
- **Export circuit** as a file (.icf). The file contains information about the circuit and CDC as well as, for each element, its numbering and/or names along with starting values and minimum/maximum provided in the parameters table. This can be used to share custom circuits between different users. Circuits can be imported in another circuit library at any point with the "import from file" function in the circuit browser *(see "Circuit Browser", chapter 12.14.2.4, page 209)*.

Elements, parameters and definitions

Table 14 Definition and description of the available elements, where $\omega = 2\pi f$ is the angular frequency (f in Hz) and j the imaginary number ($j^2 = -1$)

Element	CDC code	Impedance	Parameters (unit)
Resistor (R)	R	$Z_r = R$	R (Ω)
Capacitor (C)	C	$Z_c = -j/(\omega C)$	C (F)
Inductor (L)	L	$Z_L = j\omega L$	L (H)
Constant Phase Element (CPE)	Q	$Z_Q = (Q(j\omega)^N)^{-1}$	Q (F/s^{1-N}) N (-)
Warburg	W	$Z_W = A_W(1/\sqrt{\omega} - j/\sqrt{\omega})$	A_w ($\Omega/s^{0.5}$)

Short Warburg	S	$Z_S = A_S/(j\omega)^{0.5}\cdot\coth(B(j\omega)^{0.5})$	A_S ($\Omega/s^{0.5}$) B ($s^{0.5}$)
Open Warburg	O	$Z_O = A_O/(j\omega)^{0.5}\cdot\tanh((j\omega B)^{0.5})$	A_O ($\Omega/s^{0.5}$) B ($s^{0.5}$)
Gerisher	G	$Z_G = 1/(Y_0\cdot(K_a+j\omega)^{0.5})$	Y_0 ($F/s^{0.5}$) K_a ($s^{0.5}$)
Bisquert	B	See J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, A. Compte, *Electrochemistry Communications* 1999, 1:9:429-435 and J. Bisquert; *Phys. Chem. Chem. Phys., Vol. 2* (2000), pp. 4185-4192.	

Circuit Description Code (CDC)

The equivalent circuit can also be defined by a unique Circuit Description Code (CDC), as defined by B.A. Boukamp in *Equivalent circuit, Users manual* (1989, University of Twente: Enschede, The Netherlands). The CDC is automatically updated when a change is made to the graphical version of the equivalent circuit and vice-versa.

Fitting

The Levenberg-Marquardt algorithm is used to fit the EIS data in INTELLO. This algorithm is used to solve non-linear least squares problems. Several options are available to optimize the fitting process:

- **Mode (weighted or unweighted)** defines whether a weight factor should be used during the calculation. If the weighted mode is used, each point is multiplied by a weight factor equal to the inverse of the square of the impedance modulus. If unweighted is selected, the weight factor is the same for each point (the inverse of the square root of the average of the impedance modulus). The weighted mode gives more importance to data points with lower impedance values, which are often more reliable and less affected by noise (usually at higher frequency).
- **Stop when**: defines criteria for stopping the fitting process
  - Iterations: the number of consecutive calculations used during the fitting calculation without reaching convergence
  - Stuck for: maximum number of iterations without improvement, defining a second stop condition for the fitting calculation. This number defines the number of iterations that are allowed during which the χ^2 value does not improve.
  - $\Delta\chi^2$ <: defines a convergence criterion. The algorithm stops if the variation in the value of χ^2 from one iterations to another is lower than the provided value.

- **Results**
  - **Fit ID**: every time the algorithm is run, a new result is created with results and fitting conditions, equivalent circuit and results. It is possible to execute several fittings in a row and navigate between the different results (black arrows at the bottom). By default the last result is saved to the data table. To send another result to the data table, the results have to be manually validated (green checkmark).
  - **Iterations**: number of iterations required for the algorithm to reach convergence or one of the stop conditions
  - **Convergence**: Yes or No. Convergence indicates that after the given number of iterations, the algorithm has found a set of parameters for which the difference between the experimental data and the model has reached an minimum. Convergence alone does not guarantee that the quality of the fit is good.
    No convergence however, means the algorithm couldn't find a satisfactory fit, or reach a minimum. This could be due to poor initial estimates, an overly complex model, or overly noisy data (see recommendations below).
  - **χ^2**: or Chi-squared is a statistical measure of the goodness of the fit between the model and the data. While there is no absolute value below which a fit can be considered as good, the value can be used to compare the quality of the fit to different models, or with different conditions (when navigating between results for example). In general the lower the value, the better the quality of the fit.

Factors Affecting Convergence

- Initial parameter estimates: good starting values for the parameters can significantly improve the chances of convergence. For part of the model that can be fitted by a semi-circle, these values can be estimated with the circle-fit tool.
- Limited range per parameter: restricting the range of values allowed to be explored by the algorithm is defined in the minimum and maximum columns of the parameters table. The default values are on purpose very large to ensure ease of use. When the order of magnitude of the expected results are known, it can help to restrict the range to a few orders of magnitudes only, or lower.
- Model complexity: simpler models are more likely to converge than highly complex ones, which may require more iterations and better initial estimates. For example, using CPEs instead of capacitors increases the complexity of the model. To simplify the model, it can be helpful to initially fix the N parameter of the CPE to 1, fit the data, release the N parameter and fit again. In the second iteration, the complexity is higher but the initial values are close to the experimental values.

- Number of iterations: the maximum number of iterations must be high enough with complex circuits. The default value in INTELLO is 10000 which is enough for most cases.
- Data quality: good-quality and noise-free data improves the likelihood of convergence

Parameters

The parameter table contains all elements and their respective parameters used to fit the data

- Element: the name of the element, with its number or custom name if edited. When clicking on one element in the table, it is also highlighted in the circuit editor.
- Parameter: each element is associated to at least one parameter varied during the fitting process. The name of the parameters and their units are displayed.
- Value: before any fitting, all values in black are used as starting values for the algorithm, and the simulation. These values can be edited. The simulated curve is automatically calculated based on these values and displayed as a green line in the Nyquist and Bode plot. After the first fitting iteration, the values are the results of the fitting (blue). Any further fitting iteration uses these values as starting values. When one of these values is fixed, it is indicated in black.
- Error: the value in % is determined by examining small variations around the fitted or calculated value near convergence. For instance, if the optimal value for a resistor is 100 Ohms, the value is adjusted up and down until the goodness of fit starts to decline. If values of 98 and 102 Ohms yield a similar goodness of fit, but 97 and 103 Ohms result in a poorer fit, the error is calculated as (2/100)×100=2%. Large error estimates (ca 1000% or more) often indicate an incorrect model, typically one with more elements or parameters than the data can support. In such cases, the 'extra' element does not significantly affect the goodness of fit.

Circle fit

The circle fit tool, is accessible as an option on top of the EIS data section. It is used to fit a limited portion of the data with a simple R(RQ) circuit. The resulting circuit and fitted values can be copied to the equivalent circuit and be used as starting values when fitting the whole frequency range. To use it: first select the frequency range to be fitted with the R(RQ) circuit, then click on the circle fit icon. The results are displayed. If there are no elements in the equivalent circuit window, the whole circuit and values can be added, upon which other elements can be added. If there is already a circuit in the circuit editor, only the (RQ) part is added in series, to the right, of the whole equivalent circuit. More details are available in a following section *(see "EIS circle fit", chapter 12.14.2.3, page 208)*

Results and navigation between results

After a first fitting iteration, it is possible that another iteration be required, with a different circuit, fixed parameters, different minima/maxima etc. Clicking on the Fit button will resume the fitting with these new conditions. A new result is created, with its own ID (customizable). This can be repeated as many times as necessary. It is possible to navigate between the different results with the previous/next buttons appearing at the bottom. The following behaviors must be noted:

- The data saved in the data table of the command, is by default the last result of a series
- Navigating between results does not automatically send the results of an earlier fit to the data table
- To validate and save a specific result into the data table, the "accept this result" green checkmark must be clicked. The next results are discarded
- It is possible to rerun a fit from any intermediate result: the previous results are kept, but the next results are discarded and replaced by the new fitting.

12.14.2.3 EIS circle fit

The circle fit tool, is accessible as an option on top of the EIS data section. It is used to fit a limited portion of the data with a R(RQ) circuit and obtain quickly starting values when building a circuit containing (RQ) parts.

How to use the circle fit tool?

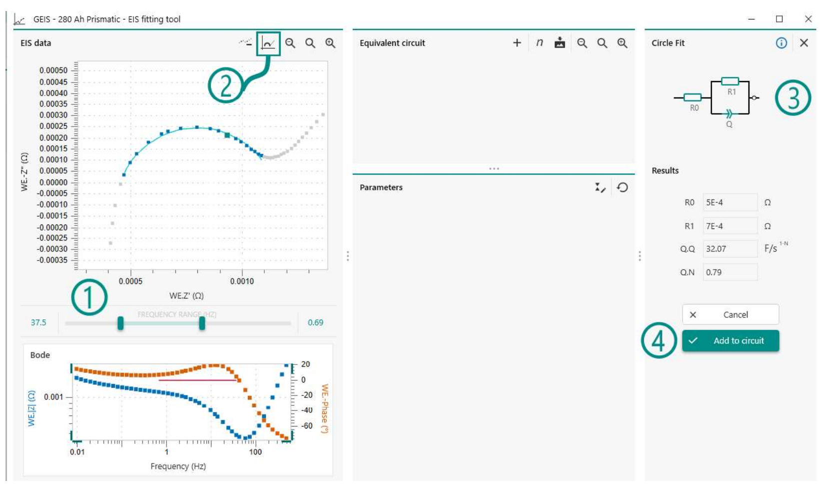


Figure 91 Overview of the circle fit tool used to obtain initial values and partially fit EIS data with a R(RQ) circuit.

- Identify a region in the data (Nyquist plot) where a semi-circle is visible, or a part that you want to fit with a R(RQ) circuit.
- Use the **frequency range selector (1)** to select one portion of the spectrum.

- Click on the **Circle fit icon (2)**.
- The selected data is fitted with an **R(RQ) equivalent circuit**, the resulting curve is displayed in the Nyquist plot (bright green line) and the values of each element and parameter are visible in the right pane (3).
- The results can be added to the equivalent circuit for further fitting (4). From here, 3 scenarios are possible:
  - If the equivalent circuit editor is empty, the complete R(RQ) circuit is added, with the values calculated from the tool used as starting values for the fitting. The frequency range can be modified again and additional elements added to the circuit in the circuit editor to account for frequency ranges excluded from the initial circle fit. A subsequent circle fit can also be performed by repeating the same steps with a different frequency range, if another semi-circle is visible in the Nyquist plot.
  - If there is already one or more element in the circuit editor, the (RQ) part of the circle fit is added, to the right, in series of the whole circuit.
  - Cancelling: the circle fit results are discarded, and the main view of the fitting and simulation tool is displayed.

12.14.2.4 Circuit Browser

The circuit browser is a library of equivalent circuits for the EIS Fit and Sim tool in INTELLO. It contains by default a list of commonly used equivalent circuits provided with INTELLO by Metrohm Autolab.

The browser can be reached from the CDC string box in the tool or command view (folder icon) allowing the possibility to insert an entire circuit in to the circuit editor. It can also be accessed by clicking on the add option in the circuit editor under "circuit".

The list of provided circuits can be edited either by:

- Saving Circuits from the circuit editor: when custom circuits are saved to the library the following parameters are saved - circuit and CDC as well as for each element its numbering and/or names along with starting values and minimum/maximum provided in the parameters table.
- Importing from an .icf file: allowing users to share useful circuits between one another.
- Removing a circuit from the list: using the - on the top right part of the browser.

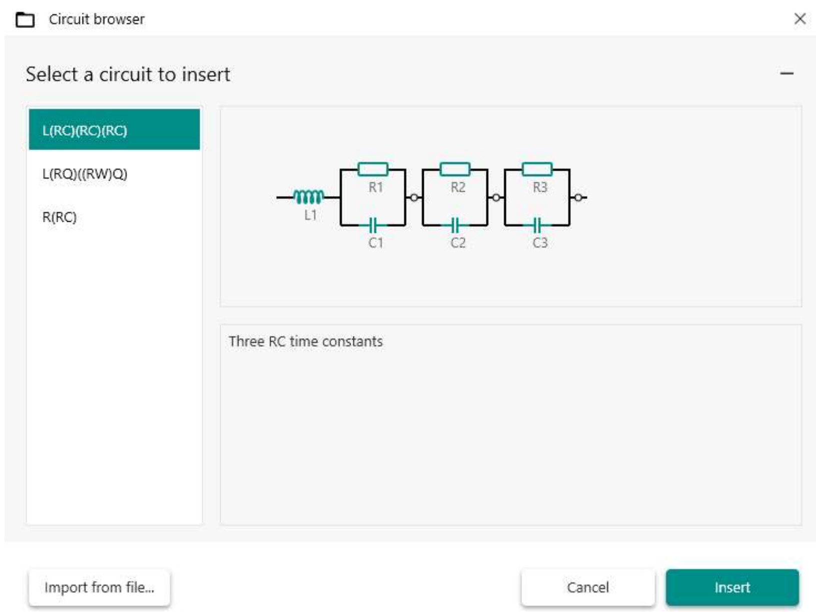


Figure 92 Circuits are saved in the circuit library together with the CDC, and optionally, a circuit description. Circuits can be browsed and inserted into the fit and simulation tool using the circuit browser.

12.15 Wait command tile

The general use of the **Wait** command is to have the procedure wait in the last applied state for a defined amount of time. The instrument will continue applying the last defined set point (i.e. potential or current) and states such as cell on or off will remain unchanged by the Wait command. Signals are not collected while the procedure is waiting.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Duration**: The duration of the wait time.

12.16 Measurement - general

12.16.1 Apply settings command tile

The general use of the **Apply settings** command is to specify settings related to the work system. It is recommended to have one Apply settings command tile at the beginning of any procedure. Additional Apply settings command tiles may be placed at any point in the procedure sequence to modify one or more of the settings.

The parameters of this command are accompanied by a check box. A selected check box indicates that this parameter must be applied when the command is executed. When the check box is not selected, the parameter will be left unchanged from the previous value. The parameter settings of the Apply settings command are inherited from either (i) a preceding Apply settings command tile, (ii) the last setting of another measurement command tile, or (iii) a setting applied with manual control, depending on which is most recent.

Main instrument settings

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Mode**: defines the mode as potentiostatic or galvanostatic.
- **Potential / Current**: input for the potential or current set point. This field will be automatically adjusted for input in potential or current, depending on the **Mode** setting.
- **Cell**: when the toggle is enabled, the cell will be switched on when the command is executed.

Note: It is necessary to define the set point when the mode is changed. When relevant, this is indicated by a merge symbol placed beside the input fields when the mode is changed.

General settings

- **Add stabilization time**: When the toggle is enabled, the defined stabilization time will be added after the settings are applied.
- **Rotator**: when a rotator is added to the required work system, its rotation rate can be set here

More settings

In general, these parameters do not require adjustment. When left on the default or automatic settings, these parameters will be optimized by the instrument to give the best quality measurement taking into consideration the measurement commands and parameters used within the procedure.

Control loop settings

- **Bandwidth selection**: when the toggle for Automatic bandwidth selection is enabled, the most appropriate bandwidth for each measurement command will be selected automatically. When the toggle is disabled, a bandwidth setting can be selected using the slider. The speed of the selected bandwidth is displayed.
- **Oscillation protection**: when the toggle is enabled, if oscillation occurs the cell will be switched off (no current will flow through the cell) automatically and the procedure will be aborted. Oscillation protection is enabled by default.
- **Bandwidth selection**: when toggled on for automatic bandwidth selection, the most appropriate bandwidth for each measurement command is selected automatically. When the toggle is disabled, a bandwidth setting can be selected using the slider. The speed of the selected bandwidth is displayed.
- **Oscillation protection**: when toggled on, if oscillation occurs the cell is switched off automatically (no current flows through the cell) and the procedure will be aborted. Oscillation protection is enabled by default.
- **iR drop compensation**: ohmic (iR) drop compensation is used to adjust the applied potential based on the resistance input in the subsequent field and the measured current during the procedure. The iR compensation settings are only available when VIONIC is in potentiostatic mode. When enabled, the current range is set to manual. The maximum compensated resistance supported by the selected current range is displayed. The complete list is available by clicking on the help icon or in the user manual of INTELLO.
  - **Manual compensation**: if the uncompensated resistance of the cell (R_u) is known, it can be input here with the percentage of it that must be compensated: the calculated value for the compensated resistance (R_c) is displayed. It is recommended not to compensate for more than 85% of the total R_u to avoid oscillations.
  - **Automatic compensation**: when this command is preceded by a Measure iR drop command tile (see *Chapter 12.16.6.3*), the result of the measurement is used as an input and compensated from the execution of the Apply Settings command if toggled on.

When the iR drop compensation is activated, the *Potential Applied* signal is the iR-compensated potential (E-iR) and the *WE.Potential* signal is the measured potential between the RE and WE.

Measurement settings

- **Current range selection toggle**: when the toggle for automatic current range selection is enabled, the most appropriate current range will be selected automatically. This is done dynamically, therefore several current ranges may be used in the same measurement command. With automatic current ranging enabled, the initial current range can be selected with the slider. It is recommended to select a value near the expected initial current in the electrochemical cell to facilitate rapid optimization.
  When the toggle is disabled, a fixed current sensor can be selected using the slider. The appearance of the slider will change to give a visual indication of the quality of the current measurement with the selected current range:
  - **Red**: the current in this region is too high for the selected current range. Overload will occur and the current signal collected will be cut off and a warning will be indicated in the events log.
  - **Green**: the selected current sensor will give the best accuracy and sensitivity for current measured in this region.
  - **Grey**: it is possible to measure currents in this region with the selected sensor, but the accuracy and sensitivity of the measurement is not optimal.

In galvanostatic mode, automatic current range selection can be used only with battery cycling commands (CC, CV) and EIS commands. With other commands (LSV, CV staircase, chrono methods), it is necessary to select the most appropriate current range for the measurement using the slider.

The **Apply settings** command is not seamless. Execution of this command requires a minimum of 27 ms to be executed.

12.16.2 Apply command tile

The general use of the **Apply** command is to apply a set point to the electrochemical cell. The applied set point is specified as a potential or a current, depending on the mode setting of the work system (i.e. potentiostatic or galvanostatic).

Note that the Apply command does not modify the cell on / cell off status. In a normal procedure sequence, the Apply command tile precedes the **Cell on** command tile so that the cell is turned on in controlled conditions, or the Apply command may be placed in the sequence where the cell is already on to simply change the set point.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.

- **Potential / Current**: Input for the potential or current set point. This field will be automatically adjusted for input in potential or current, depending on the **Mode**.
- **Add stabilization time**: When the toggle is enabled, the defined stabilization time will be added after the settings are applied.

Note: The **Apply** command is not seamless. Execution of this command requires a minimum of 20 ms to be executed.

12.16.3 Switch cell

The general use of the **switch cell** command is to put the electrochemical cell into the *on* or *off* state. With the cell on the current is able to flow between the working electrode (WE) and counter electrode (CE); the cell*off* prevents the current to flow between the WE and CE.

It is recommended that the cell is switched on in a controlled electrochemical state with the set point (current of potential) already defined. An **Apply settings** or **Apply** command should be placed in the procedure sequence preceding a cell on command.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Cell**: the cell will be switched on when the command is executed. The Cell switch command can also be used to turn the *cell off* at a desired point in the procedure sequence by disabling the Cell toggle. When the cell is off, no current flows between the working and counter electrodes.
- **Add stabilization time**: When the toggle is enabled, the defined stabilization time will be added after the cell is switched on (or off).

The **cell off** is **seamless**. It is recommended to place a Cell off command at the end of fast measurements. The **cell on** command is **not seamless**. Execution of this command requires a minimum of 27 ms to be executed.

12.16.4 Record signals command tile

The general use of the **Record signals** command is to record one or more signals over a fixed duration.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Duration**: the duration of the measurement.
- **Sampling interval**: the time between two consecutive sampled points.

12.16.5 Measure OCP command tile

The general use of the **Measure OCP** command is to measure the open circuit potential (OCP) of the electrochemical cell. Open circuit potential is the potential measured at the working electrode (WE.Potential) when no current flows in the cell (the cell is off). The Measure OCP command outputs a single **OCP value** which is either the last measured OCP value, or the result of averaged OCP values over a user-defined amount of time at the end of the determination. The OCP value may be used in subsequent commands in the procedure to set potential values relative to OCP by selecting V_{OCP} instead of V_{REF} from the unit selection menu following parameters that define potential set points.

Note: The OCP measurement command turns the cell off while OCP is being measured.

Note: During the OCP measurement, the working electrode potential is measured versus the reference electrode potential. When no reference electrode is used, the RE lead is normally connected to the counter electrode, and the reference potential is the potential at that point. For more information, please refer to the user manual section on cell connections.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.
- **Max. duration**: the maximum duration for the OCP measurement.
- **Sampling interval**: The time between two consecutive sampled points.

Options

- **Show OCP determination window**: When this toggle is enabled, an OCP monitoring pop up window is displayed during the OCP measurement.

- **Use moving average OCP**: When this toggle is enabled, the OCP value is calculated using a moving average of the WE.Potential signal over the defined time. The time for averaging is counted from the end of the measurement. For example, if the duration was 30 s and the time for averaging was 5 s, the average OCP is calculated using the WE.Potential values from t = 25 s to t = 30 s. When the moving average OCP is used, this data is also displayed in the OCP determination window and stored in the data table.
  Note: For the first portion of the measure OCP command the *moving average OCP* is calculated with a weighted moving average algorithm that gives priority to the most recent data points by giving them a higher weight coefficient. Weight coefficients are applied to the portion of the moving average OCP data from the beginning of the measure OCP command to two times the defined time for the averaging. For example, if the OCP measurement duration is 20 seconds and the time to average is 2.5 seconds, the moving average OCP data for the first 5 seconds of the measurement will be a weighted moving average, whereas the final 15 seconds will be a simple moving average.
- **Accept on dE/dt limit**: When this toggle is enabled, the OCP measurement stops if the change in OCP potential over time (dE/dt) is lower than the defined value for five consecutive points. When the dE/dt limit is used, this data is also displayed in real time in the OCP determination window and stored in the data table.
- **Switch cell on when proceeding**: This option can be used in potentiostatic mode only. When this toggle is enabled, the cell is switched on at the end of the Measure OCP command. The set point of 0 V_{OCP} will be applied prior to switching on the cell, ensuring that the system is not exposed to unexpected conditions.
  Note: The *switch cell on when proceeding* option is not available when the Measure OCP command is used in a procedure or section of the procedure configured for galvanostatic mode. For galvanostatic measurements, it is recommended to place an Apply setting command tile after the Measure OCP command to define the current set point, select the correct current range, and to switch the cell on.

12.16.6 iR drop measurement and compensation

12.16.6.1 iR drop compensation

iR or Ohmic drop is a potential drop occuring between the working electrode (WE) and the reference (RE) when a current is flowing at the WE. This potential drop is due to the uncompensated resistance (R_u) between WE and RE due to the resitivity of the electrolyte. This Ohmic drop (iR) can be compensated by VIONIC.

In order to compensate for the iR drop, it is necessary to know the value of the uncompensated resistance. It can be determined by different types of measurements, the most common and reliable being Electrochemical

Impedance Spectroscopy (EIS). At high frequency, the total impedance of an electrochemical cell is the electrolyte resistance (or uncompensated resistance, R_u). Once known, the value of R_u can be input in the Apply settings command of a procedure along with the percentage of this value that must be compensated. The resistance compensated by VIONIC is R_c (compensated resistance): $R_c = R_u \times percentage/100$.

It is recommended to compensate for up to 80-85% of the total value to avoid oscillations of the instrument.

The iR drop compensation is not available with Automatic current ranging. The list of current ranges and maximum R_c per range is provided in the following Table.

Table 15 Maximum compensated resistance per current range

Current range	Maximum R_c for iR compensation
10 A	250 mΩ
1 A	2.5 Ω
100 mA	25 Ω
10 mA	250 Ω
1 mA	2.5 kΩ
100 µA	25 kΩ
10 µA	250 kΩ
1 µA	2.5 MΩ
100 nA	25 MΩ
10 nA	250 MΩ
1 nA	n.a.

iR drop compensation cannot be active during EIS measurements: an error will be displayed on the Apply settings command tile and the procedure will not run. If a procedure contains a combination of EIS and non-EIS commands where the iR drop must be compensated, each EIS command must be preceeded by an Apply settings command with the iR compensation toggled off.

12.16.6.2 Manual iR drop compensation

When the value of the uncompensated resistance is known, it can be input directly in the Apply settings command of the procedure, in the *measurement settings* section, as shown in the figure below.

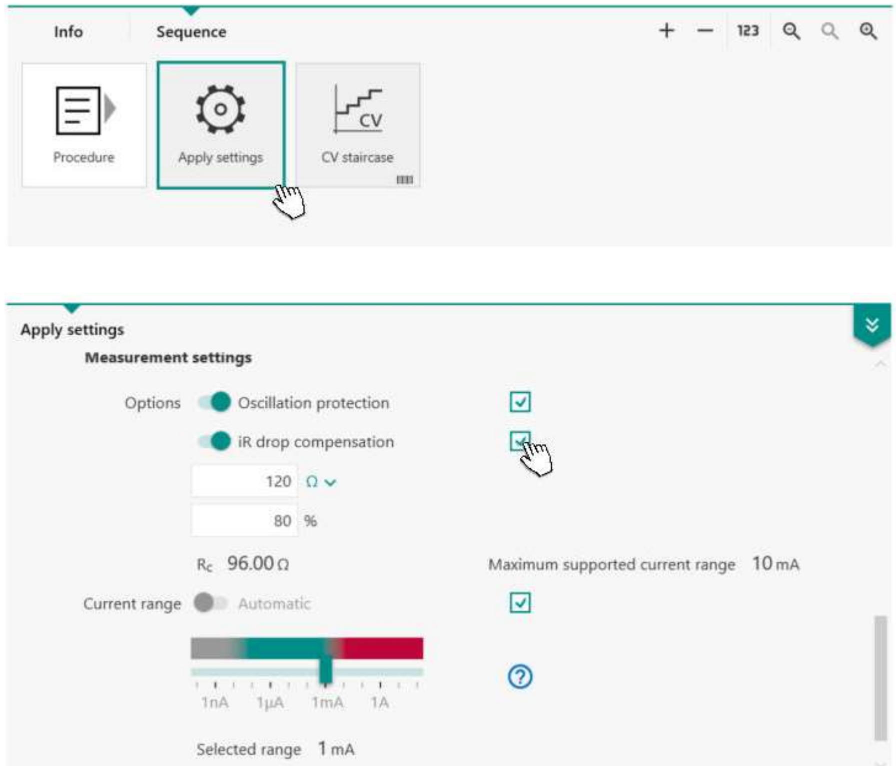


Figure 93 The iR compensation is activated in the Apply Settings command. R_u is input with the percentage of compensation. The current range is automatically set to manual.

The iR compensation is automatically turned off at the end of the procedure. It is possible to disable it manually for a section of a procedure by adding a new Apply settings command and toggle the iR drop compensation off.

12.16.6.3 iR drop measurement command

The iR drop measurement command allows the user to measure the uncompensated resistence (R_u) of the electrochemical cell (between RE and WE) in order to compensate for the ohmic drop (iR drop) in the procedure. This command uses electrochemical impedance single frequency. R_u is determined from the real part of the measured impedance (WE.Z') at a given frequency. The value measured by this command is converted into a compensated resistance (R_c) which is a percentage of the measured value used for compensation in the rest of the procedure.

This command must be followed by an Apply settings command were the compensation is turned on and the current range selected.

EIS Parameters

This command sets VIONIC in PSTAT mode, turns the cell ON, applies a specified DC potential upon which the sine is superimposed and sets the current ranging to Automatic during its execution.

- **Frequency**: the frequency of the applied sine wave. This frequency can be determined by running a separate EIS measurement beforehand: the uncompensated resistance is usually the value of the total impendance (|Z|) measured at high frequency.
- **DC potential**: DC potential on top of which the sine wave is applied. It is recommended to measure R_u at, or close to, the OCP
- **Stabilization time**: time during which the DC voltage is applied to reach a steady state
- **Amplitude**: amplitude of the applied sine wave

This command uses single frequency impedance to determine R_u. In order to determine the optimal parameters (frequency, amplitude), it is recommended to run an EIS command in a separate procedure to evaluate in which frequency range the total impedance is close to R_u. In general, R_u is the real part of the impedance at high frequency: this is usually visible as a plateau in the |Z| vs. *f* (Bode plot) at high frequency, or the intersection of the Nyquist Plot with the real (|WE.Z'|) axis.

Acceptance parameters

In order to avoid overcompensation and therefore oscillations of VIONIC, it is possible to set a range of acceptable values for R_u. The **Compensation** is the percentage of R_u used for compensation (compensated resistance, R_c) in the following procedure. It is recommended to compensate for 75 to 85 % of the uncompensated resistance.

- If the measured value of R_u is not between the specified minimum and maximum, a warning message will appear. It is possible to stop the procedure or continue with the maximum input value.
- If the measured value of R_u is within the specified range, either no message will appear and the procedure will continue or the acceptance window will appear for validation depending on the users preference and settings.

The maximum value for R_c is limited by the selected current range. The maximum value provided here cannot be higher than the maximum value supported by the selected current range in the following Apply Settings command. *(see table 15, page 217)*

An acceptance window displays the results of the single-frequency impedance measurement after the command is executed: WE.Z', WE.-Z", WE.|Z|, WE.-Phase, R_u and the R_c calculated as R_u x Compensation. In the options, the visibility of this acceptance window can be set:

- **Show iR drop measurement acceptance window**: when toggled, the acceptance window will appear regardless of the measured R_u
- **Auto-accept R_c upon timeout**: when toggled, without reaction of the user after the selected time, the value is accepted if it is within the acceptance range, or the procedure is stopped if it is out of the range.

12.16.6.4 Automatic iR drop compensation

Automatic iR drop compensation is possible by using the iR drop measurement command tile at the beginning of a procedure as shown below *(see figure 94, page 221)*.

It is recommended, for a new experiement, to first run an EIS measurement on the cell to evaluate the order of magnitude of the uncompensated resistance and the frequency range at which it can be measured. This first measurement will help find the optimal paramaters for the iR drop measurement command. This also allows for defining the **acceptance criteria** (maximum and minimum R_u): these limits increase the **safety of the automatic iR drop compensation**. If the measured value is abnormally large, it can be detected by INTELLO and he procedure can be stopped or proceed with a limited iR compensation (maximum R_c). Overcompensation can lead to oscillations of VIONIC and abnormal variations of the R_u can be a sign of issues within the electrochemical cell itself.

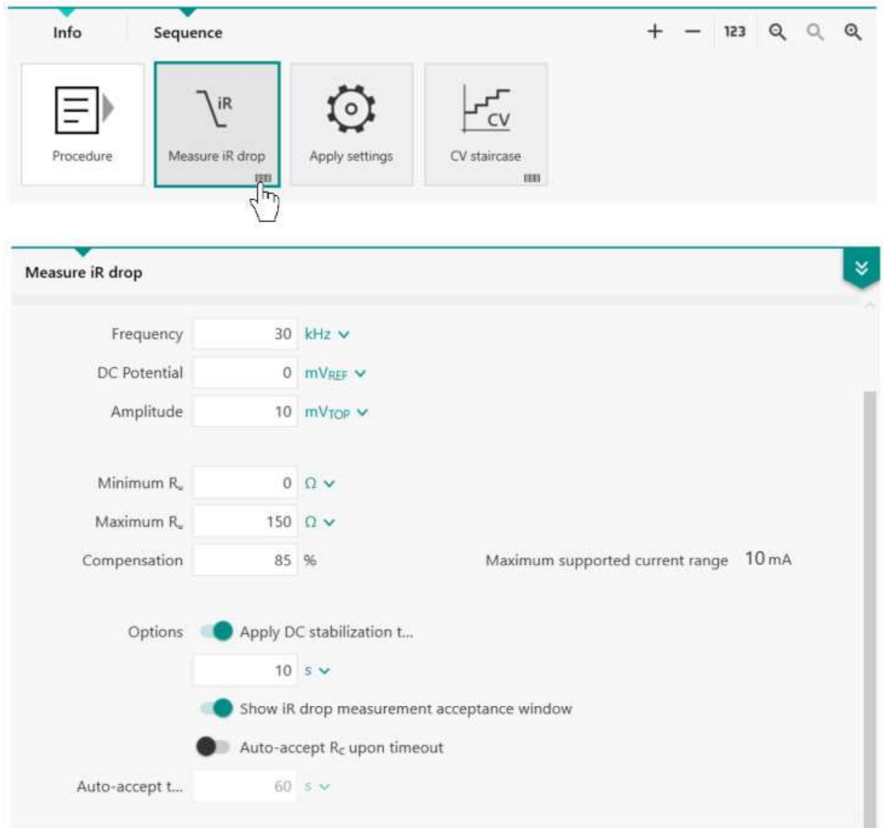


Figure 94 Typical procedure for Cyclic Voltammetry with Automatic compensation with example of settings for the measure iR drop command tile

When settings for the iR drop measurement are input, the automatic iR compensation can be set in the Apply settings command *(see figure 95, page 222)*. When preceeded by an iR drop measurement command, the iR compensation will use the value measured by the previous command. The maximum current range allowed is limited by the value of the maximum R_c as defined in the previous command.

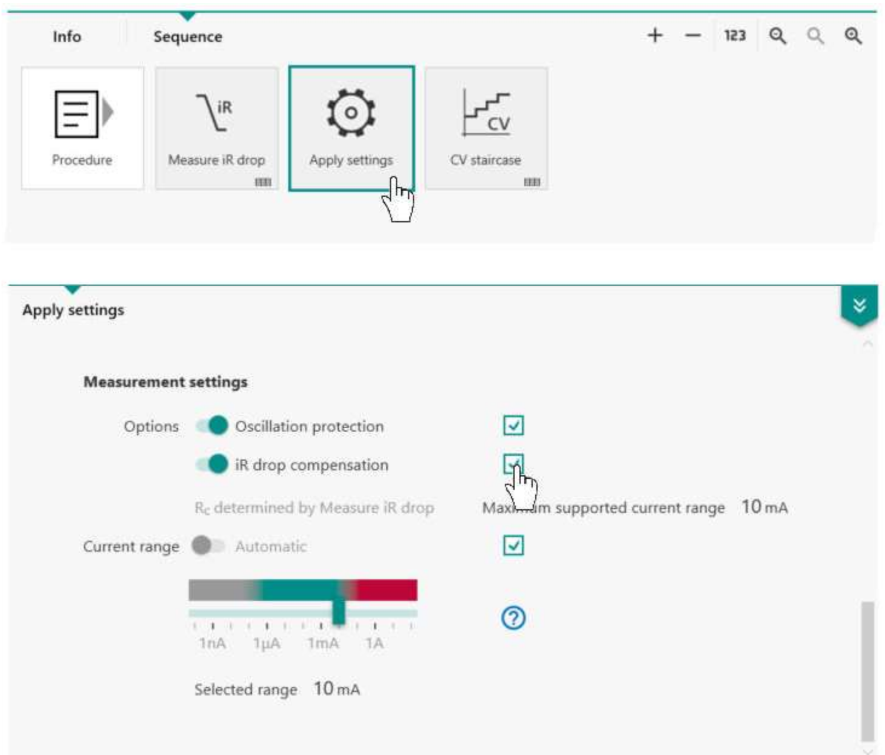


Figure 95 Automatic iR drop correction in the Apply settings command.

12.16.7 Reset charge command tile

The general use of the **Reset charge** command is to reset the charge signal (WE.Charge) to zero. Charge data can be obtained during measurements by enabling the WE.Charge signal. The charge will be calculated cumulatively though successive commands. The reset charge command can be placed anywhere in the procedure where the charge signal should be reset to zero.

Parameters

- **Display name**: this name is displayed on the command tile, a user-defined name may be input here.

Note: Reset charge is seamless. Resetting the charge to zero requires no addition time in the procedure sequence, therefore it does not insert a gap in the applied or measured signals. However, following the Reset charge command, the WE.Charge signal will lack one point because the calculation of charge requires at least two current values. Therefore, there is no WE.Charge value corresponding to the first WE.Current point following the reset.

13 VIONIC Acceptance test

A detailed description of the performance acceptance tests and the testing process of VIONIC is presented.

Before starting with the tests, VIONIC and INTELLO must be installed, VIONIC must be switched On, connected and claimed in INTELLO.

For details related to the unpacking, installation and connection of VIONIC and INTELLO, please see the dedicated **VIONIC powered by INTELLO: Unpack, install, and connect** material. For additional help, please contact your local Metrohm Autolab support office.

13.1 Test procedures in INTELLO

INTELLO is provided with a set of default procedures aiming at testing different functionalities of VIONIC:

- *Test CV* - for testing the digital staircase generator, the linearity and noise level on low current ranges
- *Test CV linear scan* - for testing the analog scan generator
- *Test current limit* - for testing the highest and lowest measured currents (± 6A)
- *Test compliance voltage* - for testing the maximum and minimum compliance voltage (± 50V)
- *Test EIS* - for testing the sine wave generator and the accuracy of the EIS measurements
- *Test floating mode* - for testing the floating mode operation, with WE grounded
- *Test EIS high frequency* - for testing the sine wave generator and the accuracy of the EIS measurements up to 10 MHz

These procedures are located in the Autolab Library, in the procedure drawer of INTELLO.

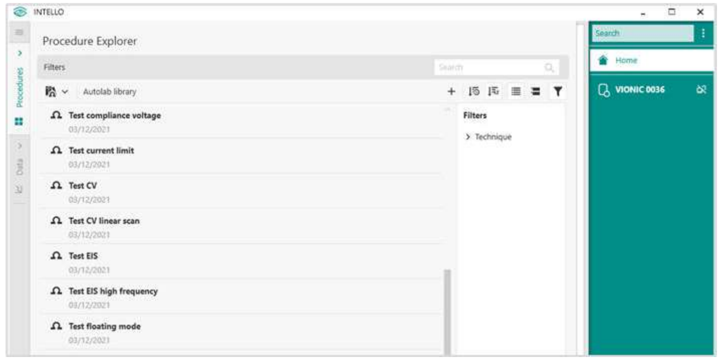


Figure 96 Acceptance Test procedures in the Autolab library in INTELLO.

The test procedures must be run on the Test Cell provided with VIONIC, following the cabling instructions provided in the description of each procedure and here, in this chapter.

The settings of the Work system (e.g., setting of the compliance voltage, floating On/Off) must be adjusted depending on the test. For the test data analysis and report generation, the latest version of NOVA must be installed.

13.2 Main steps of the Acceptance testing process

The main steps of the Acceptance testing process of VIONIC are:

1. Run the following tests on the VIONIC instrument from the Autolab library in INTELLO on the Autolab Test cell:
   ✓ *Test CV*
   ✓ *Test CV linear scan*
   ✓ *Test current limit*
   ✓ *Test compliance voltage*
   ✓ *Test EIS*
   ✓ *Test floating mode*
   ✓ *Test EIS high frequency*
2. Export all test data to the designation folder using the automatically generated filenames (exact format must be kept):
   ✓ *Test CV.csv*
   ✓ *Test CV linear scan.csv*
   ✓ *Test current limit.csv*
   ✓ *Test compliance voltage.csv*
   ✓ *Test EIS.csv*
   ✓ *Test floating mode.csv*
   ✓ *Test EIS high frequency.csv*
3. Start NOVA and load the *VIONIC acceptance test.nox* procedure.
4. Run the *VIONIC acceptance test.nox* procedure and, when prompted, specify the folder where the *.csv* files from step 2 were saved.

5. A report is generated and saved as *VIONIC Acceptance Test Report.txt* in the test folder created in step 2.

Additional details on how to connect VIONIC to the Autolab Test cell for each test procedure and how to execute each of the steps listed above are presented in the next paragraphs.

13.3 Autolab Test cell

The Autolab Test cell is included standard with each VIONIC instrument and it can be used to test the performance of the VIONIC instrument, to test new procedures and to troubleshoot possible errors by eliminating the "real electrochemical cell" from the possible sources of the problem

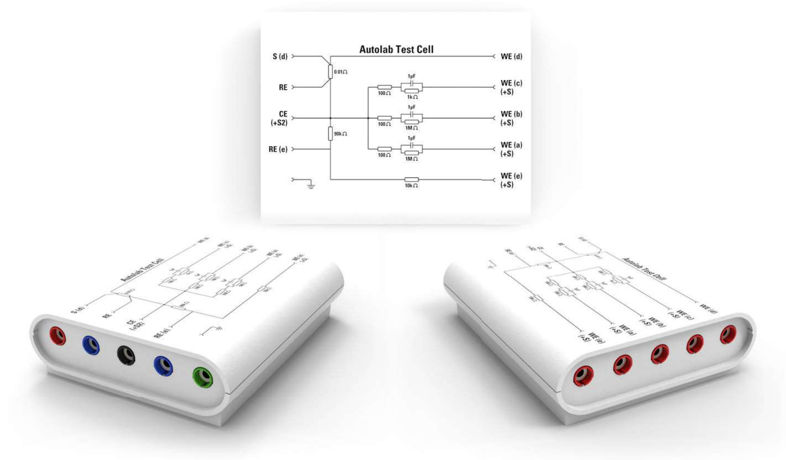


Figure 97 The Autolab Test cell: top view, left and right perspective view.

The color code of the connectors on the Autolab Test cell follows the same color convention used on the connectors of the Pure signal bridge.

The Autolab Test Cell includes 5 individual electronic circuits marked from (a) to (e). Each circuit is designed to test specific performance of VIONIC as described next, in the detailed test instructions. For testing a new procedure or troubleshooting an issue, the most relevant circuit must be usedso that the values of the resistors and capacitors will be the closest to your real electrochemical system.

The values of the Resistors and Capacitors used in Autolab Test cell as well as the circuits are printed on the box. The tolerance of the used components are presented in the table below:

Table 16 Values and tolerances of the resistances and capacitors used in the Autolab Test cell circuits

Component	Value	Tolerance
Resistance (R)	1 MΩ	0.1 %
Resistance (R)	1 kΩ	1 %
Resistance (R)	90 kΩ	1 %
Resistance (R)	10 kΩ	1 %
Resistance (R)	0.01 Ω	1 %
Resistance (R)	100 Ω	5 %
Capacitor (C)	1 µF	5 %

13.4 How to run the Acceptance test procedures

To run a test procedure, first open INTELLO and claim the VIONIC Work System to be tested.

In the *Procedures* drawer, select the *Autolab Library* and load the test procedure you would like to run to your Work system.

Check if the required parameters, settings are correct and if the connection to the Autolab Test cell are as required and then Run the test.

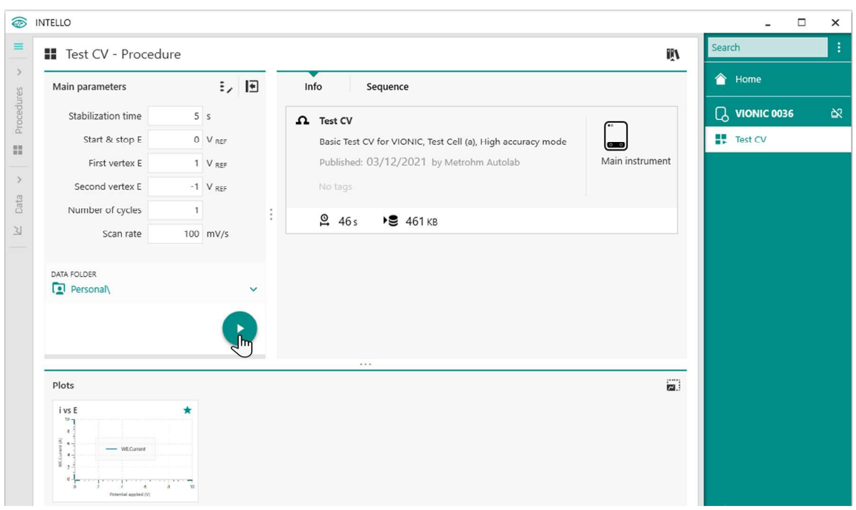
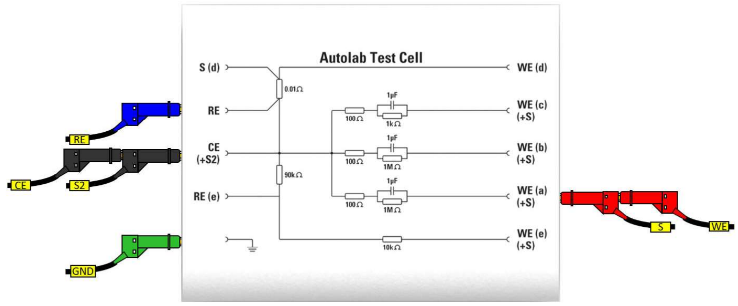


Figure 98 Starting a Test procedure (e.g., Test CV) in INTELLO

Next, the specific settings and Autolab Test cell connections will be presented for each test procedure.

13.4.1 Test CV

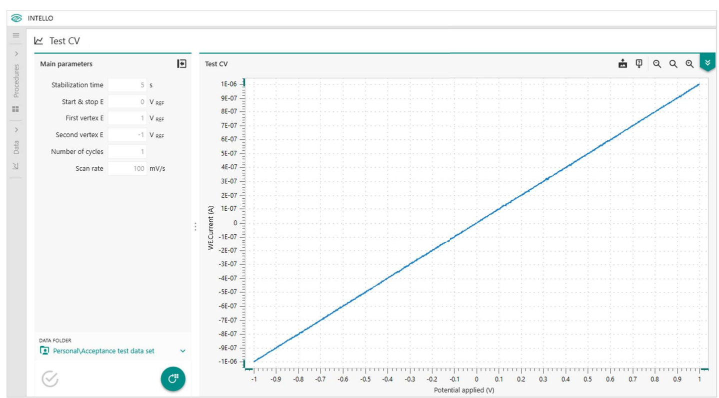
The VIONIC Work system must be in High Accuracy mode (i.e., ±10 V Compliance) and the Pure signal bridge must be connected to the Autolab Test cell (a) as shown below:



For this test, the connection of the S2 adaptive cable is optional.

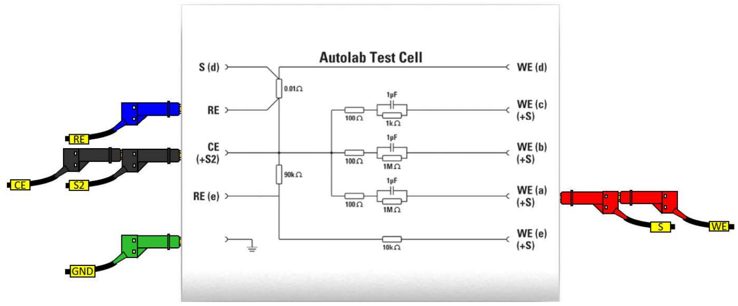
Open the *Test CV* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

The expected *Test CV* result is shown below:



13.4.2 Test CV Linear scan

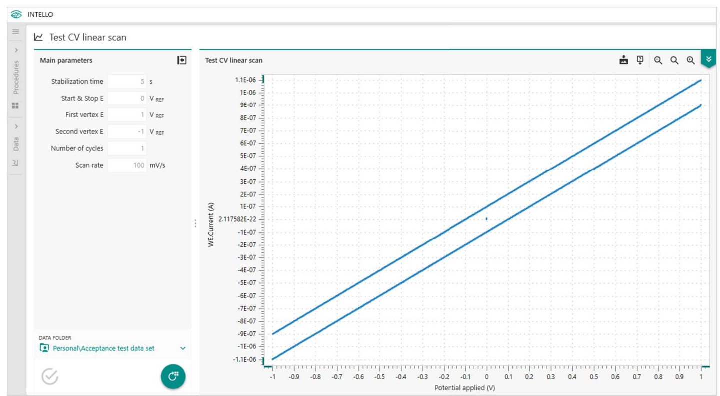
The VIONIC Work system must be in High Accuracy mode (i.e., ±10 V Compliance) and the Pure signal bridge must be connected to the Autolab Test cell (a) as shown below:



For this test, the connection of the S2 adaptive cable is optional.

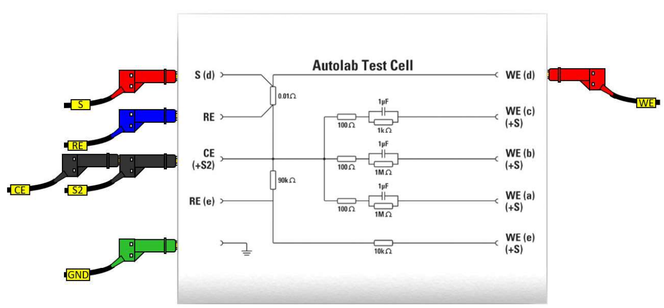
Open the *Test CV linear scan* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

The expected *Test CV linear scan* result is shown below:



13.4.3 Test current limit

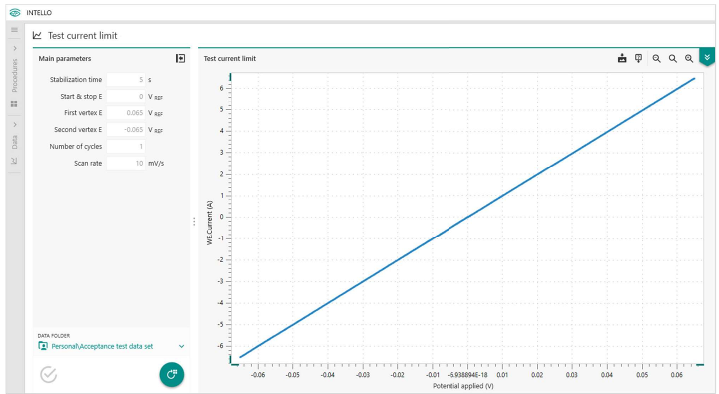
The VIONIC Work system must be in High Accuracy mode (i.e., ±10 V Compliance) and the Pure signal bridge must be connected to the Autolab Test cell (d) as shown below:



For this test, the connection of the S2 adaptive cable is optional.

Open the *Test current limit* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

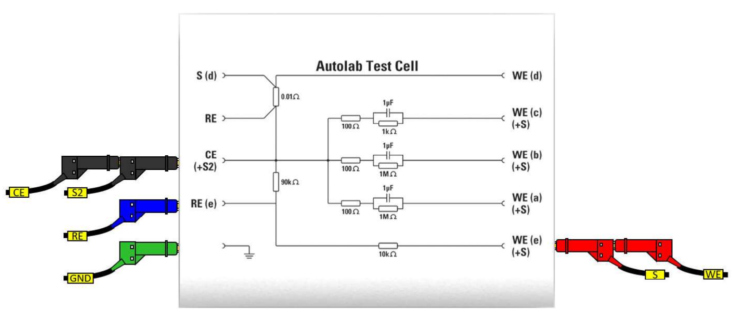
The expected *Test current limit* result is shown below:



13.4.4 Test compliance voltage

The VIONIC Work system must be in High voltage mode (i.e., ±50 V Compliance) in the Edit Work system settings window.

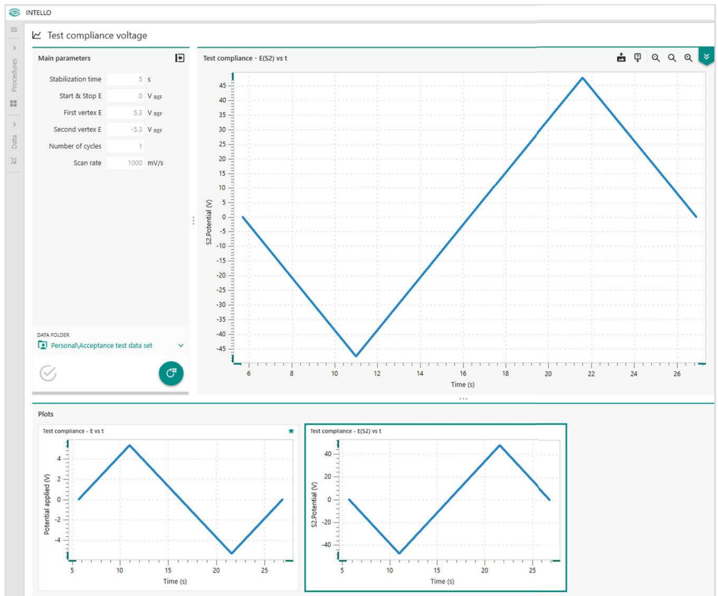
The Pure signal bridge must be connected to the Autolab Test cell (e).



For this test, the S2 adaptive cable must be used and connected to the Autolab Test cell.

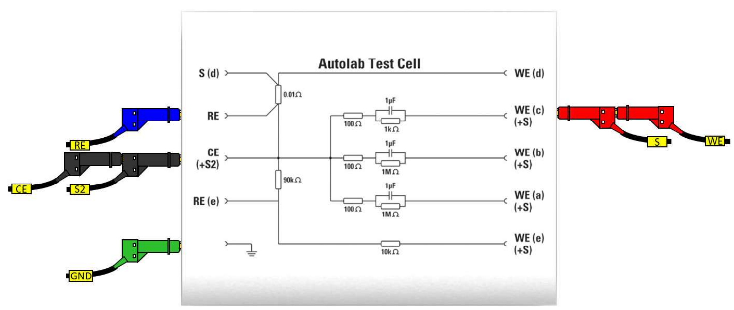
Open the *Test compliance voltage* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

The expected *Test compliance voltage* result is shown below:



13.4.5 Test EIS

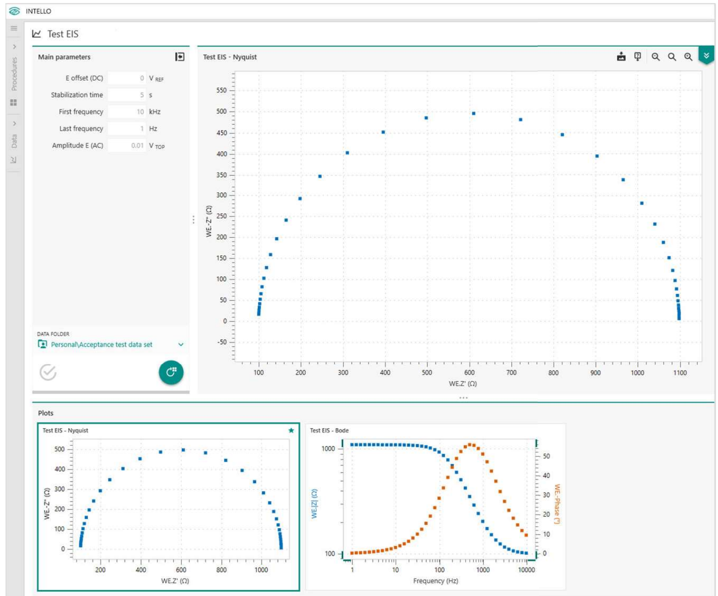
The VIONIC Work system must be in High Accuracy mode (i.e., ±10 V Compliance) and the Pure signal bridge must be connected to the Autolab Test cell (c) as shown below:



For this test, the connection of the S2 adaptive cable is optional.

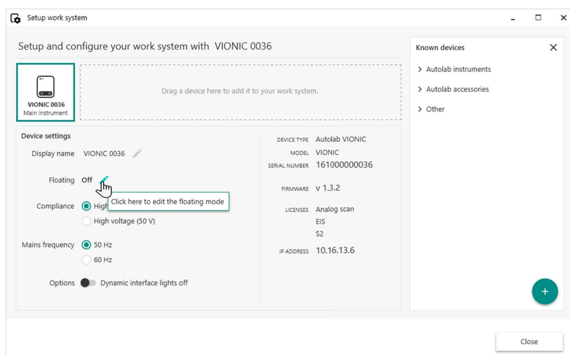
Open the *Test EIS* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

The expected *Test EIS* result is shown below:



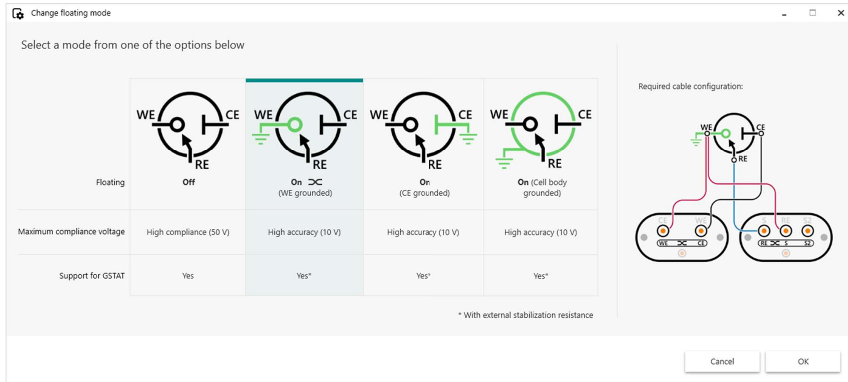
13.4.6 Test floating mode

In the Work system editor window, switch VIONIC to floating mode.



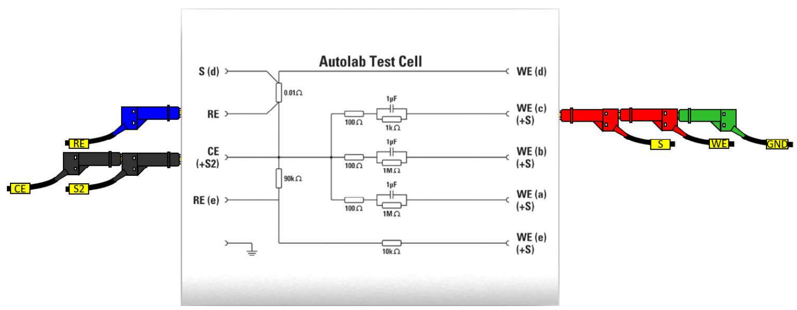
The VIONIC Work system must be set to cross-floating mode with grounded working electrode.

ℹ The required cable configuration of the adaptive cables must follow the labeling of the cross-floating mode on the buffer and splitter boxes of the Pure signal bridge.



FLOAT with the cross-floating symbol will be displayed on the Dynamic interface of VIONIC.

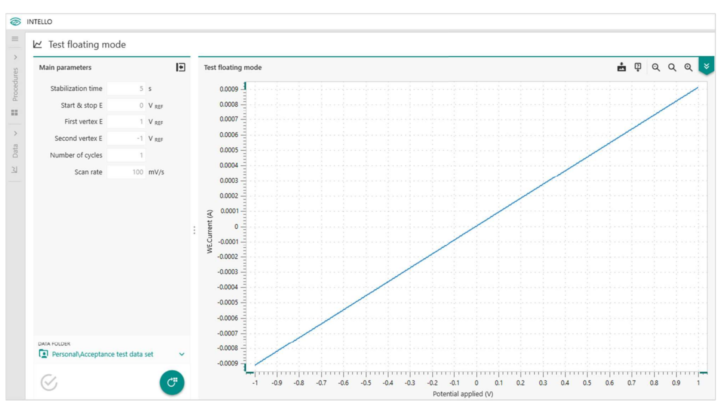
The Pure signal bridge must be connected to the Autolab Test cell (c) with the working electrode (WE) connected to the EARTH ground, as shown below:



For this test, the connection of the S2 adaptive cable is optional.

Open the *Test floating mode* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

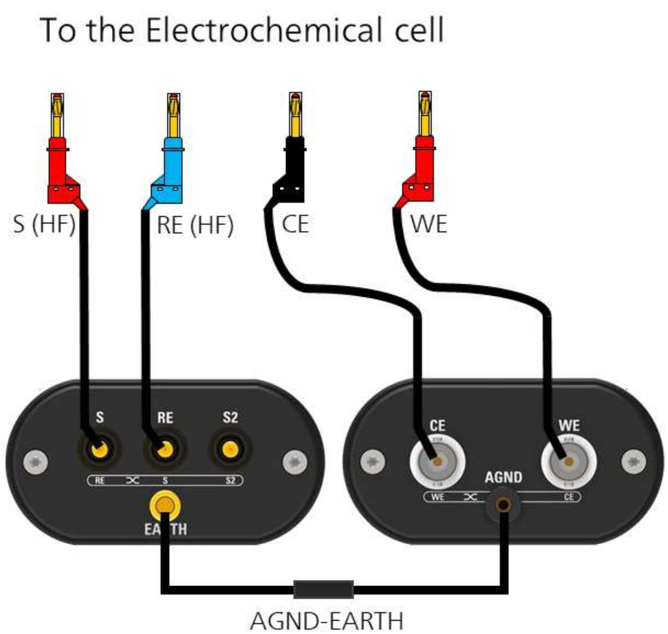
The expected *Test floating mode* result is shown below:



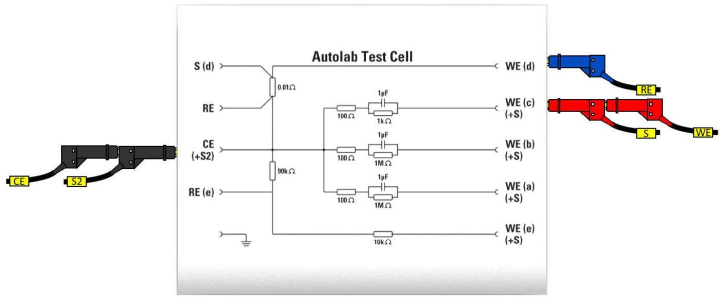
13.4.7 Test EIS high frequency

For the EIS high frequency test, the special High Frequency (HF) Adaptive cables must be used which are included standard with all VIONIC instruments.

Connect the HF Adaptive cables to the buffer and splitter box of the Pure signal bridge. The AGND-EARTH cable must be connected between the splitter and the buffer boxes of the Pure signal bridge.



The Pure signal bridge must be connected to the Autolab Test cell (c). Due to the limited length of the HF Adaptive cable, the RE Adaptive cable is connected to the connector (d) of the Autolab Test cell, as shown below:

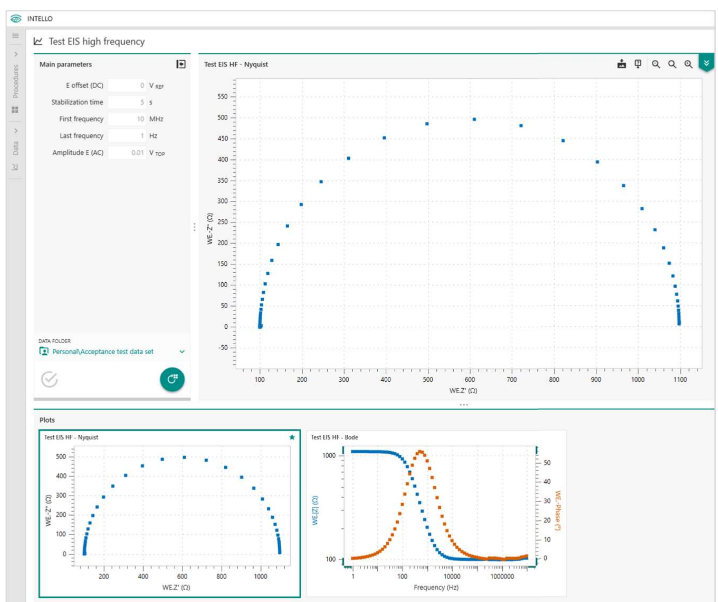


i Make sure to **turn the Floating mode Off** in the Edit Work system settings window.

i For this test, the connection of the S2 adaptive cable is not used.

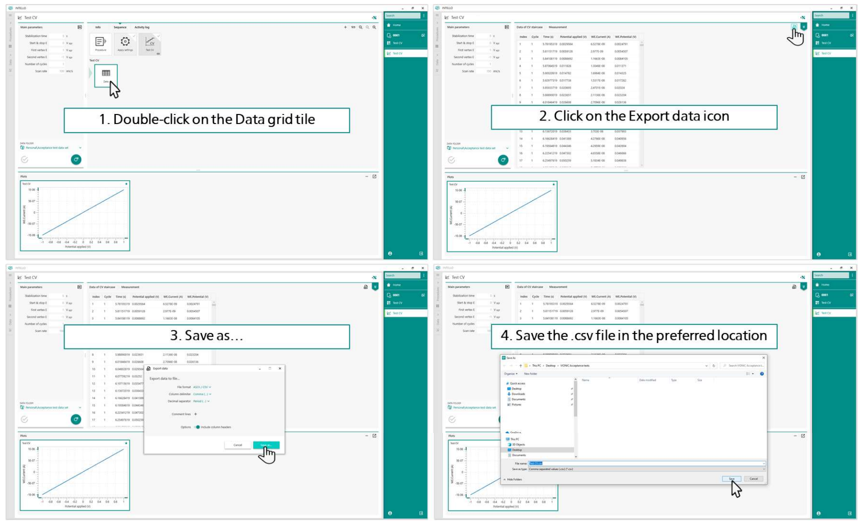
Open the *Test EIS high frequency* procedure from the Autolab library in INTELLO and run the procedure using the Main parameters which are pre-set in the respective test procedure (see also figure below).

The expected *Test EIS high frequency* result is shown below:



13.5 Export and save the Acceptance test data

Once all the Acceptance tests are run, for each test the corresponding data must be exported.



For each test run:

1. Double-click on the Data grid tile which is part of the procedure sequence
2. Click on the Export data icon
3. Save the data
4. Export and save the data with the default settings in the designated folder (user selectable)
5.

It is important that the exported *.csv* data files will have the pre-set file names, respectively:

Test CV.csv

Test CV linear scan.csv

Test current limit.cvs

Test compliance voltage.csv

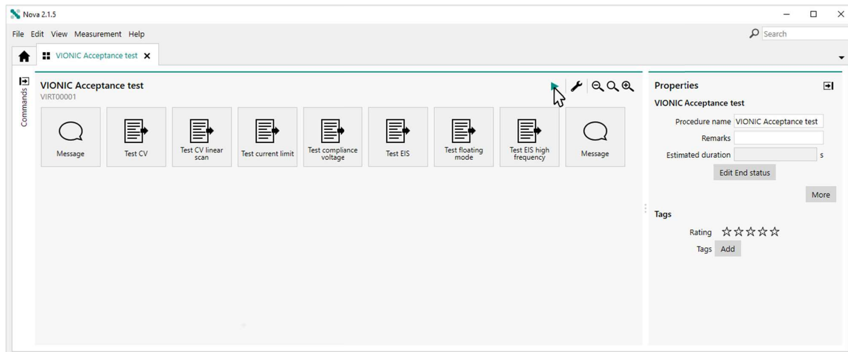
Test EIS.csv

Test floating mode.csv

Test EIS high frequency.csv

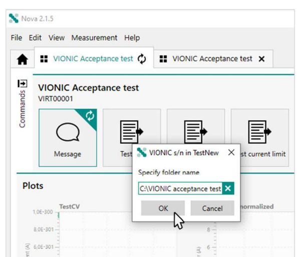
13.6 Acceptance test evaluation

For the evaluation of the VIONIC Acceptance test results and to create an VIONIC Acceptance test report, start the latest vesrsion of NOVA and open the provided *VIONIC Acceptance Test.nox* procedure.

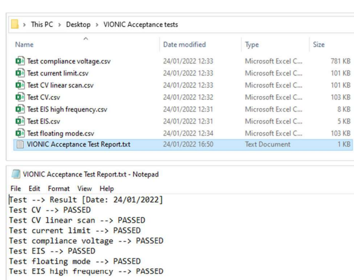


If the *VIONIC Acceptance Test.nox* is not available, please ask your local Metrohm Autolab support office.

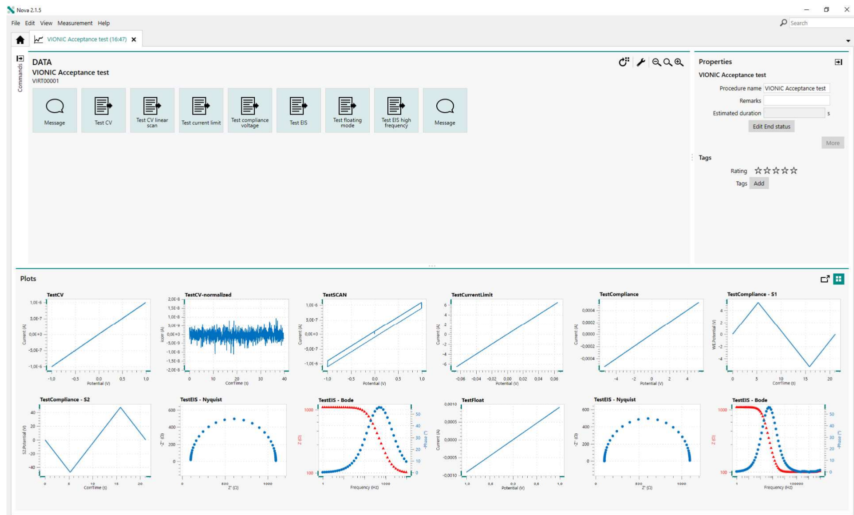
Press *Start* to run the procedure. When prompted (i.e., in a pop-up window) specify the location of the folder where the results (.csv files) are saved and then press OK.



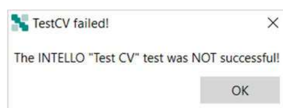
When the data evaluation is finished, a message indicates the location where the generated *VIONIC Acceptance test report* is saved.



The plots of all the tests are displayed in the plot section of the NOVA data file.



In the case of a failed test, a pop-up message appears with the information on which test failed and the corresponding test is indicated as FAILED in the generated report.



As a first step, please check the following:

✓ the VIONIC settings

✓ the parameter settings of the test procedure

✓ the connections of the Adaptive cables to the splitter and buffer box

✓ the connections of the Pure signal bridge of VIONIC to the Autolab Test cell

✓ the naming and location of the exported test files

were executed according to the instructions given in this chapter.

If all of the above are correct and one or more of the Acceptance tests still fails, please contact your local Metrohm Autolab support office.

Index

A

Acceptance test 223
Acceptance test evaluation 236
Acceptance testing steps 224
Active cells 55, 58, 120
Adaptive cables
  Pure signal bridge 24
Alphanumeric display 36
Applied AC Current resolution .. 52
Applied AC Potential Resolution 52
Apply command tile 213
Apply settings command tile ... 211

B

Back panel 20
Bandwidth
  Control loop 39
  current range 41
  EIS 43
  General definition 37
Battery Analysis 185
Battery cycling 180
Building blocks 13

C

Cell cables
  Pure signal bridge 21
Cell connections
  4-connectors mode 101
  5-connectors mode 104
Cell connections with S2 .... 72, 73
Chrono methods command tile
.... 162
Command tiles 162
Computer and network requirements 127
Connector types and ratings 7
Contact details
  Repair and service 2
Conventions
  description 1
  Scientific conventions 1
Current resolution 48
CV linear scan command tile ... 163
CV staircase command tile 164

D

Data explorer
  Procedure library 156
Differential-Pulse Voltammetry 167
DIO (set) 191
Distributed power 55, 117
Dynamic Interface
  State indication 32

E

EIS 60
EIS at High Frequencies 66
EIS Contour plot 60
EIS frequency scan command tile
.... 170
EIS on S2 64
EIS practical tips 68
EIS single frequency command tile
.... 174
Electrochemical Impedance Spectroscopy 60, 62
Eout 93
EU Declaration of Conformity
  CE declaration 11
Export
  Data export 168
Export acceptance test data 235
external devices 188, 194
external monitoring of E and i 93, 94

F

Faraday cage 122
Floating in galvanostatic mode
.... 114
Floating mode 107, 109
Front of the instrument
  Dynamic interface 18

G

Galvanostatic in floating mode
.... 114
Grounded cells 107
Group command tile 176
GSTAT FLOAT stabilization box
.... 114

H

High accuracy mode 55
High Compliance mode 55
Hydrodynamic measurements ... 86

I

INTELLO installation 127
Invalid data points 152
iout 93

L

License agreement 128
LSV linear scan command tile . 177
LSV staircase command tile 178

M

Main EIS 62
Main parameters
  General concept 150
Main specifications 6
Maximum input voltage 124
Measure OCP command tile ... 215

N

Non-floating mode 107, 108
non-Grounded cells 107
Normalized signals 153

O

Ohms law 76
Operating conditions 125
Operating principle 13
Optional accessories 83

P

Passive cells 55, 117
Potential resolution 46
Power plot
  General overview 54
Power plot VIONIC 55
Procedure
  description 149
  procedure view 149
Procedure settings 151

R

RDE in a work system 87
Record signals command tile .. 214
Release notes
INTELLO 1.0 137
INTELLO 1.1 137
Repeat command tile 179
Reset charge command tile 222
Resolution 45
Resolution specifications - overview 53
Rest (at OCP) 184
Rotating Electrodes
RDE, RCE 86
Run test procedures 226

S

Safety information
Unpacking and operation 2
Save test data 226
Scientific conventions 1
Scope of delivery 83
Second Sense and EIS 77
Second sense and the cell parameters 75
Second sense definition 69
Second Sense potential resolution 50
Spare parts availability 9
Specifications 78
Square-Wave Voltammetry 166
Switch cell 214

T

Tafel analysis 199
Temperature monitoring 90
Temperature overload 125
Test cell 225
Test compliance voltage 229
Test current limit 228
Test CV 227
Test CV linear scan 227
Test EIS 230
Test EIS high frequency 233
Test floating mode 231
Thermocouple 90
Thermocouple (TC) in a work system 90
Type of electrochemical cells 99

V

VIONIC test 223, 224

W

Wait command tile 210
Warranty 8
WEEE and disposal 9
Work system 85