CORROSION - TRAVAUX PRATIQUES

Semestre Printemps 2016

Corrosion et protection des matériaux

EPFL- Groupe Tribologie et Chimie d'Interface

1. Objectifs

Les TP de corrosion servent à illustrer pratiquement et approfondir les notions théoriques acquises pendant le cours. Ils permettent à l'étudiant de se familiariser avec les techniques expérimentales électrochimiques les plus communes dans le domaine la corrosion et avec l'utilisation d'équipements électrochimiques modernes. Les développements des capacités de rédaction de rapports, d'analyse critique des manipulations et des résultats ainsi que de l'attitude au travail en équipe constituent d'autres acquis proposés par ces TP.

2. Sécurité

Les TP se déroulent dans le laboratoire de chimie dédié (CHB0398) dans lequel il faut respecter les consignes suivantes (propres à la faculté SB):

- les étudiants porteront une blouse de laboratoire et des lunettes de protection tout au long de leur présence dans le local. Du matériel en prêt sera à disposition.

- aucun objet, à l'exception du matériel pour écrire ou des ordinateurs portables, ne sera entreposé dans le local. Des armoires seront à disposition à l'extérieur pour entreposer sacs, vêtements et autres objets personnels.

- les étudiants seront tenus à effectuer des manipulations propres dans le respect de la sécurité des personnes et l'intégrité du matériel mis à disposition.

- l'accès aux ordinateurs du laboratoire se fera uniquement via le login sur le compte Gaspar des étudiants. La connections des ces ordinateurs à des supports informatiques de n'importe quelle nature tels que par exemple des clés USB ou de disques durs externes est expressément interdite.

Le non respect de ces consignes peut entrainer l'expulsion immédiate de l'étudiant du laboratoire.

3. Organisation des sessions de laboratoire

Les essais se font par groupes de deux ou trois étudiants. Ces groupes se constituent au début du semestre et restent les mêmes jusqu'à la fin.

Au début du semestre, chaque étudiant reçoit l'ensemble des énoncés des travaux pratiques ainsi que l'horaire des dates prévues pour chaque essai. Pour des raisons de disponibilité de l'équipement, ces dates ne peuvent pas être changées.

Avant de commencer une manipulation les étudiants sont censés avoir étudié l'énoncé et assimilé la théorie qui y est associée (voir par exemple D. Landolt, Corrosion et chimie de surfaces des métaux, PPUR 2004).

Chaque essai effectué fait l'objet d'un ***rapport écrit*** (en principe dactylographié) qui sera ***remis à l'assistant responsable dans un délai de 2 semaines après avoir effectué le TP.***

A la fin de chaque séance, les étudiants remettent en place le matériel et laissent leur poste de travail propre selon les instructions de l'assistant. Toutes les défectuosités du matériel sont à signaler à l'assistant responsable pour qu'il puisse les réparer ou les remplacer dans les plus brefs délais.

4. Rapports

Chaque rapport contient les chapitres suivants

- ✓ *Pose du problème*
- ✓ *Partie théorique*
- ✓ *Partie expérimentale* ***(ne pas recopier le protocole s.v.p !!!)***
- ✓ *Résultats*
- ✓ *Discussion*
- ✓ *Conclusions*

L'importance relative des différents chapitres varie selon les essais. La partie théorique se limite à l'essentiel (1-2 pages). La partie expérimentale décrit les manipulations effectuées de façon précise et complète:

- ✓ *Prétraitement des électrodes*
- ✓ *Schéma de montage*
- ✓ *Préparation des solutions*
- ✓ *Procédures de mesure y compris paramètres de mesures (vitesse de balayage du potentiel, vitesse de rotation du disque tournant, température, ...)*

Le chapitre consacré aux résultats contient l'ensemble de ceux-ci sous forme de tableaux et/ou de graphiques. La partie discussion des résultats donne une évaluation de la fiabilité et reproductibilité des résultats, et elle donne une interprétation théorique des résultats obtenus.

Les conclusions restent brèves ne dépassant pas 1/5 page.

5. Matériel

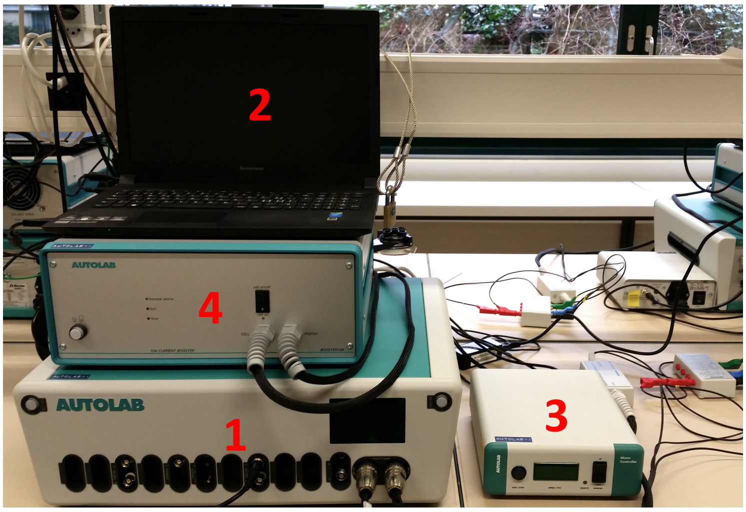
Le matériel mis à disposition consiste en:

- Un potentiostat Autolab PGSTAT302N contrôlé par PC.

- Une cellule électrochimie 400mL avec électrode de référence, contre-électrode et électrode de travail (le métal étudié) avec support.

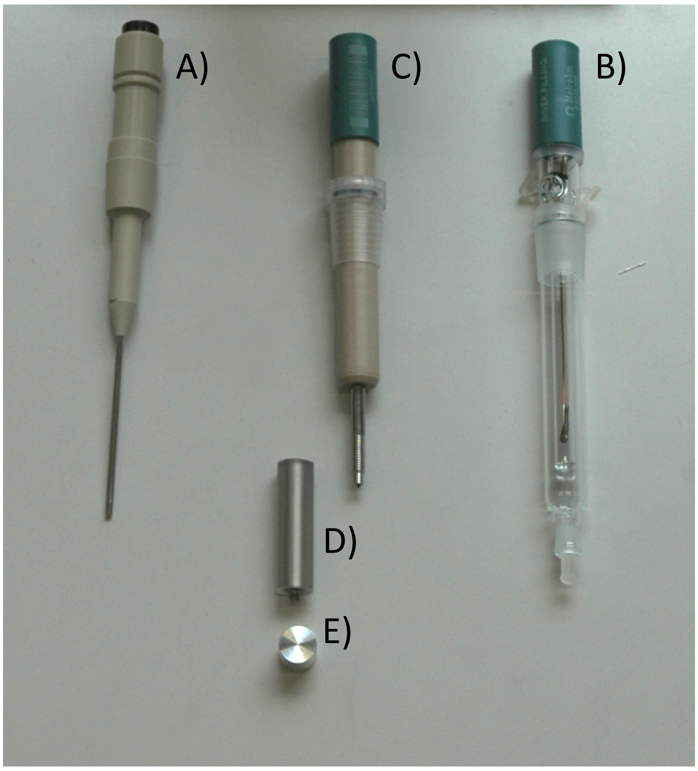
- pour le TP2 "Corrosion à l'oxygène": un dispositif électrode disque tournant avec l'électronique de contrôle.

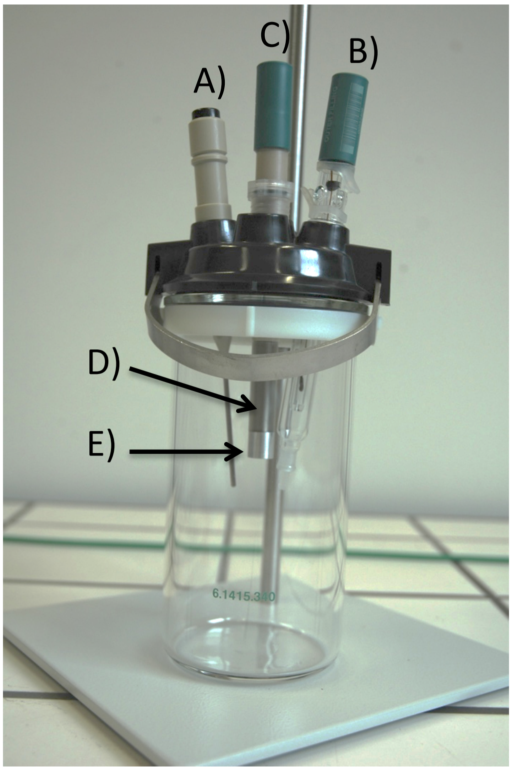
Matériel électronique



1) Potentiostat, 2) PC, 3) Electronique de contrôle pour disque tournant, 4) Booster 10A (non utilisé).

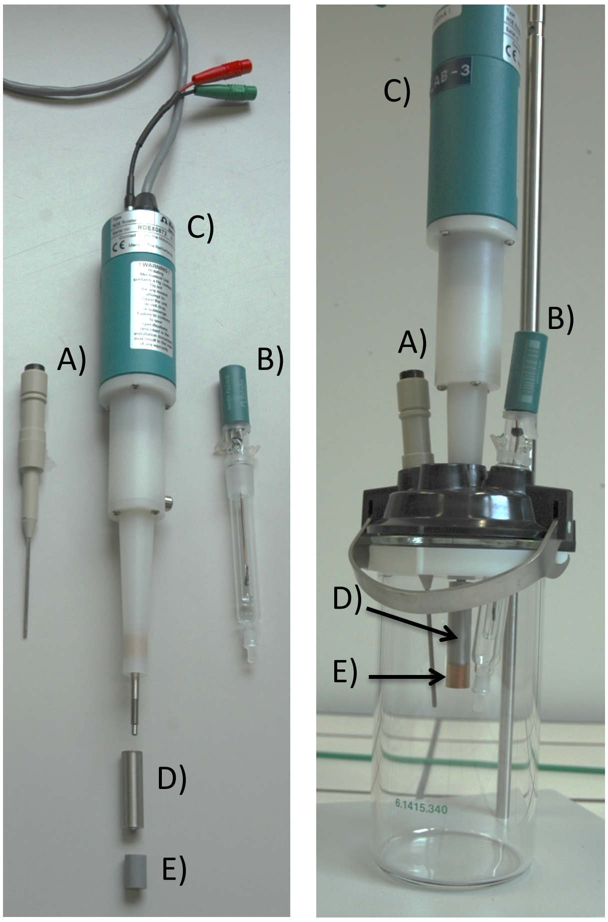
Cellule: Montage Standard (TP1, TP3, TP4)





A) Contre électrodes en platine
B) Electrode de référence Ag/AgCl
C) Corps de l'électrode de travaille
D) Connecteur
E) Électrode de travaille (Mg ou Al ou Fe)

Cellule: Montage RDE (TP2)



A) Contre électrodes en platine
B) Electrode de référence Ag/AgCl
C) Corps de l'électrode de travail à disque tournante
D) Connecteur
E) Électrode de travail (Fe)

6. Principes de fonctionnement du potentiostat Autolab PGSTAT302N

General considerations on the use of the Autolab potentiostat/galvanostat systems

This chapter provides general information on the use of the Autolab potentiostat/galvanostat. The informaiton provided in this chapter applies to all instrument, unless otherwise specified. It is highly recommended to review this information before using the Autolab potentiostat/galvanostat.

Electrode connections

The Autolab instruments are supplied with cell cables providing connections for **three** or **four** electrodes, depending on the type of instrument. The electrode connections are provided through 4 mm male banana connectors.

These electrode connections are labeled as follows:

- **Working (or indicator electrode):** WE (red)
- **Sense electrode:** S (red)
- **Reference electrode:** RE (blue)
- **Counter electrode:** CE (black)

Four electrode connections

Instruments with four electrode connectors can be connected to the electrochemical cell in three different ways:

NOTE

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.

Operating principles of the Autolab PGSTAT

The Autolab instrument combined with the software is a computer-controlled electrochemical measurement system. It consists of a data-acquisition system and a potentiostat/galvanostat. The basic working principle is schematically represented in *Figure 860*.

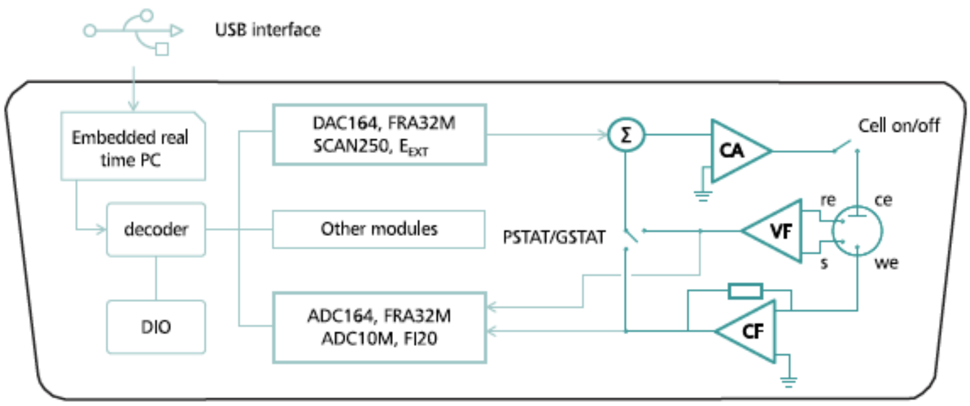


Figure 860 Schematic reprensentation of the Autolab potentiostat/ galvanostat

The Autolab system is fitted with the following common **digital** control components:

- **USB interface:** the inteface between the Autolab and the host computer.
- **Embedded PC with real-time operating system:** a dedicated controller embedded into the instrument, which is responsible for timing and intefacing the host application and the instrument controls.
- **Decoder and DIO:** a data decoder and digital input/output interface.

The digital components are interfaced through the Autolab modules to the **analog** potentiostat/galvanostat circuit. The latter consists of the following components:

- **Summation point (Σ):** a circuit used to add the control signals required to generate the waveform used in electrochemical measurements.
- **Control amplifier (CA):** a circuit used to amplify the output of the summation point.
- **Voltage follower (VF):** a circuit used to measure the potential.
- **Current follower (CF):** a circuit used to measure the current.

The arrangement of these analog circuits with respect to the electrochemical cell are represented in *Figure 861* for a four electrode Autolab system and in *Figure 862* for a three electrode Autolab system.

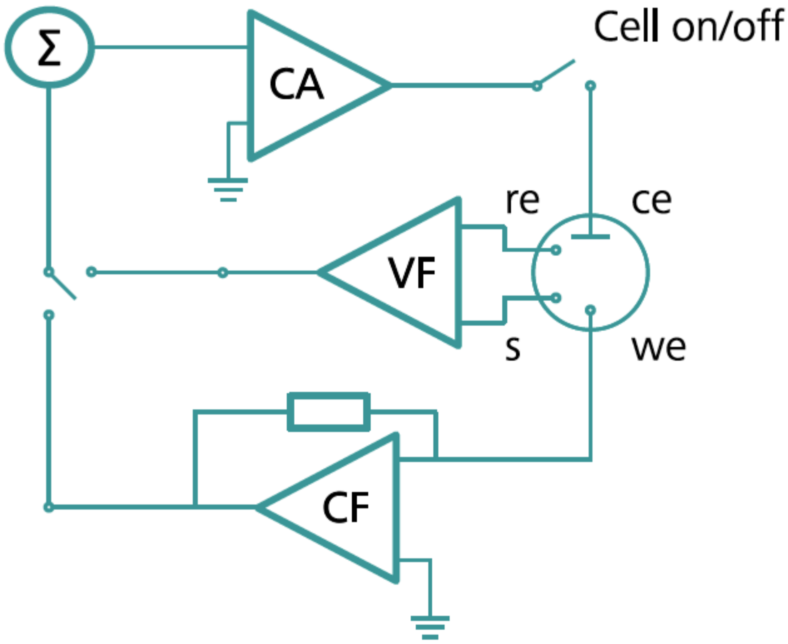


Figure 861 Schematic representation of the analog circuits of the Autolab in a four electrode system

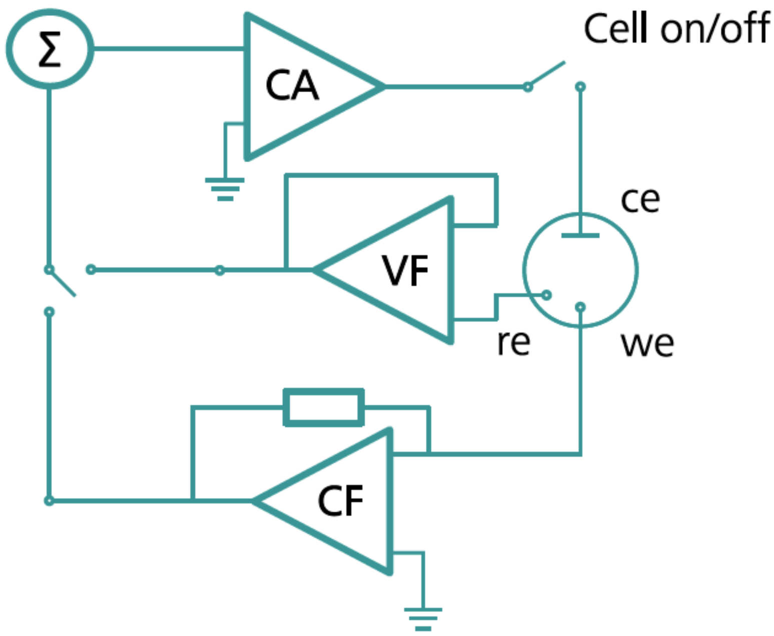


Figure 862 Schematic representation of the analog circuits of the Autolab in a three electrode system

The summation point (Σ) is an **adder** circuit that feeds the input of the control amplifier (**CA**). Each of the inputs of the summation point is divided by a hardware-defined value *(see Figure 863, page 669)*.

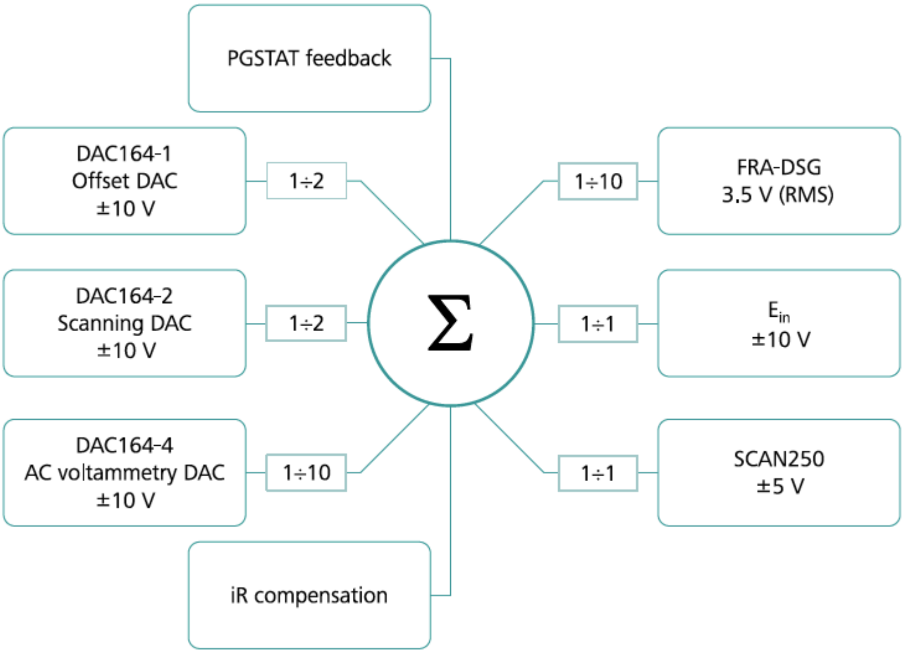


Figure 863 Schematic representation of the summation point of the Autolab

It is connected to the output of the several key modules of the Autolab:

- **DAC164 (or on-board DAC):** the digital-to-analog converters of the Autolab. Depending on the type of instrument, the following DAC inputs are available:
  - ***Offset DAC:*** used to generate an offset. This signal is divided by **2**.
  - ***Scanning DAC:*** used to generate steps and scans. This signal is divided by **2**.
  - ***AC voltammetry DAC:*** used for AC voltammetry only. This signal is divided by **10**.
- **FRA32M DSG or FRA2 DSG:** the digital waveform generator of the *optional* **FRA32M** or **FRA2** module *(see Chapter 15.3.2.13, page 887)*. This signal is divided by **10**.
- **SCAN250 or SCANGEN output:** the analog scan output of the *optional* linear **SCAN250** or **SCANGEN** module *(see Chapter 15.3.2.19, page 938)*. This signal is divided by **1**.
- **E_{in}:** the external input provided through the monitor cable. This signal is divided by **1**.
- **PGSTAT feedback:** the feedback from the voltage follower (**VF**), in potentiostatic mode or the feedback from the current follower (**CF**), in galvanostatic mode.
- **iR compensation feedback:** the feedback from the iR compensation circuit, when in use in potentiostatic mode.

CAUTION

Some of the summation point inputs are not available on all Autolab instruments.

The control amplifier 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 (S) or the potential difference between the reference electrode (RE) and the working electrode (WE) at the user defined value, in potentiostatic mode, or the user required current between the counter electrode (CE) and the working electrode (WE) in galvanostatic mode.

The output of the control amplifier can be manually or remotely disconnected from the electrochemical cell through a cell ON/OFF switch. The voltage follower (**VF**) is used to measure the potential difference between the reference electrode and the sense and the current follower (**CF**). The current follower has several current ranges providing different current-to-voltage conversion factors.

The output of the current follower (**CF**) and the voltage follower (**VF**) are fed back to the analog-to-digital converter modules of the Autolab:

- **ADC164 (or on-board ADC):** general purpose analog-to-digital converter of the Autolab instrument.
- **FRA32M ADCs or FRA2 ADCs:** two synchronized analog-to-digital converters located on the *optional* **FRA32M** or **FRA2** module used for impedance spectroscopy measurements *(see Chapter 15.3.2.13, page 887)*.
- **ADC10M or ADC750:** two synchronized analog-to-digital converters located on the *optional* **ADC10M** or **ADC750** module for ultra-fast sampling *(see Chapter 15.3.2.1, page 786)*.
- **FI20 (or on-board integrator):** an *optional* filter and integrator module (**FI20**) or on-board integrator which can be used to convert the current to charge and filter the current signal *(see Chapter 15.3.2.11, page 861)*.

Furthermore, the output of the voltage follower (VF) or the current follower (**CF**) is fed back to the summation point to close the feedback loop in potentiostatic or galvanostatic mode, respectively.

The **ADC164 (or on-board ADC)** provides the possibility of measuring analog signals. The input sensitivity is software-controlled, with ranges of ±10 V (gain 1), ±1 V (gain 10) and ±0.1 V (gain 100). The resolution of the measurement is 1 in 65536 (16 bits). Analog signals can be measured with a rate of up to 60 kHz. The ADC164 is used to measure the output of the voltage follower (**VF**) and current follower (**CF**) of the potentiostat/ galvanostat.

The **DAC164 (or on-board)** generates analog output signals. The output is software-controlled within a range of ±10 V. The resolution of the DAC164 is 1 in 65536 (300 µV). In the Autolab PGSTAT two channels of the DAC (*Scanning DAC* and *Offset DAC*) are used to control the analog input signal of the potentiostat/galvanostat. The µAutolab type II and µAutolab type III only uses a *Scanning DAC* to control the analog input. The values of the DACs are added up in the potentiostat and divided by 2. This results in an output of ±10 V with a resolution of 150 µV.

In practice this means that the potential range available with the Autolab PGSTAT during an electrochemical experiment is ±5 V with respect to the offset potential generated by the *Offset DAC*. The available potential range is therefore -10 V to 10 V with the Autolab PGSTAT and -5 V to 5 V with the µAutolab type II and µAutolab type III.

The AC voltammetry DAC, if present, is hardwired to the summation point and it is divided by 10. This input is used for measurements involving a small amplitude modulation (like AC voltammetry).

N Series Autolab front panel

The front panel of the N Series Autolab provides a number of connections, controls and indicators *(see Figure 871, page 691)*.

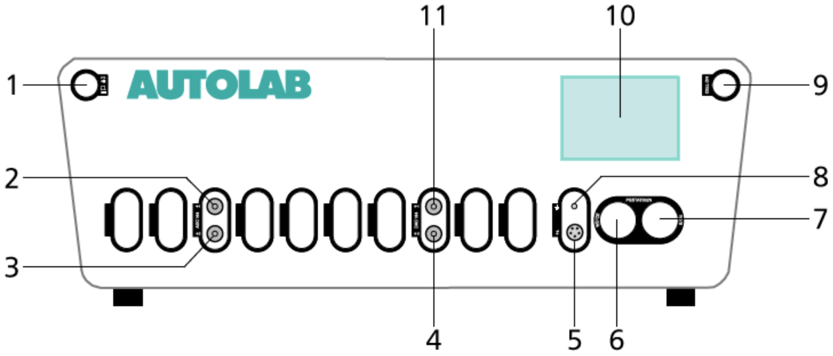


Figure 871 Overview of the front panel of the N Series Autolab

1 On/Off button
For switching the Autolab on or off.

2 ADC164 →1
Analog input for recording external signals (ADC164 →1).

3 ADC164 →2
Analog input for recording external signals (ADC164 →2).

4 DAC164 ←2
Analog output for controlling external signals (DAC164 ←2).

5 Monitor cable connector ⇄
For connecting the monitor cable.

6 CE/WE connector
For connecting the Autolab cell cable, providing connections to the counter electrode (CE), working electrode (WE) and ground.

7 RE/S connector
For connecting the Autolab differential amplifier, providing connections to the reference electrode (RE) and sense electrode (S).

8 Ground connector
Additional ground connector for connecting external devices to the Autolab ground.

9 Cell ON button
For enabling and disabling the cell.

10 Display
Display indicating real-time information on the measured current and potential and instrumental settings.

11 DAC164 ←1
Analog output for controlling external signals (DAC164 ←1).

The display (item 10 in *Figure 871*) is used to provide information about the Autolab to the user. *Figure 872* shows a detail of this display.

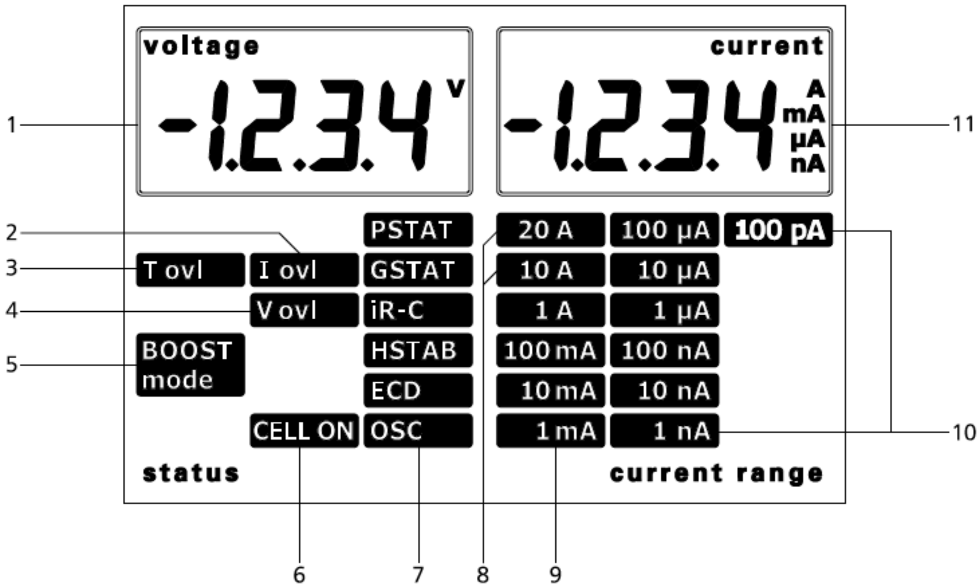


Figure 872 Overview of the display of the Autolab

1 Voltage indicator
Displays the measured voltage.

2 I ovl indicator
Indicates that a current overload is detected when lit.

3 T ovl
Indicates that a temperature overload is detected when lit.

4 V ovl
Indicates that a voltage overload is detected when lit.

5 BOOST mode
Indicates that a connected Booster is active when lit.

6 CELL ON
Indicates that the cell is on when lit.

7 Operation mode indicators
Indicate the operation settings of the Autolab. From top to bottom:

PSTAT indicates that the Autolab is operating in potentiostatic mode when lit.

GSTAT indicates that the Autolab is operating in galvanostatic mode when lit.

iR-C indicates that the ohmic drop compensation is on when lit

HSTAB indicates that the Autolab is operating in high stability mode when lit.

ECD indicated that the ECD module is on when lit.

OSC indicates that oscillations are detected when lit.

8 Booster current range
Indicate that a current range provided by a Booster is active when lit.

9 Autolab current ranges
The current range indicator which is lit corresponds to the active current of the Autolab.

10 ECD current ranges
Additional current ranges provided by the ECD module. These current ranges extend the ranges of the Autolab.

11 Current indicator
Displays the measured current.