Electrocatalysis

Complete solutions for electrocatalysis and forced convection measurements

Metrohm

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Electrocatalysis and forced convection

Electrocatalysis is the catalysis of an electrode reaction. The electrocatalytic effect leads to an increase of the standard rate constant of the electrode reaction, resulting in a higher current density, or to a decrease in overpotential when other rate limiting steps are involved. The study of an electrocatalytic process requires insights in the influence of electrode properties on the mechanism and kinetics of the electrode reaction. Forced convection methods offer the advantage of reducing the contributions from mass-transport and providing a direct access to kinetic and mechanistic information. Metrohm Autolab provides a complete range of products for these demanding experiments.

Oxygen reduction reaction (ORR) – an essential electrochemical reaction

The oxygen reduction reaction (ORR) is the most important reaction in life processes such as biological respiration, in corrosion and in energy converting systems such as fuel cells. ORR in aqueous solutions occurs mainly by two pathways: the direct 4-electron reduction pathway from O_2 to H_2O, and the 2-electron reduction pathway from O_2 to hydrogen peroxide (H_2O_2). In non-aqueous aprotic solvents and/or in alkaline solutions, the 1-electron reduction pathway from O_2 to superoxide (O_2^-) can also occur.

ORR is known to suffer from very sluggish kinetics and large overpotentials are required to achieve a decent turnover rate on the electrode. For energy convertion processes, these kinetics need to be improved to reach a practical usable level in fuel cells.

Current research focuses on platinum, the best catalyst for ORR, or combinations of this metal with other materials, as well as on the use of non-noble metal catalysts.

Forced convection has been the method of choice for studying this and other reactions. Rotating disk and rotating ring-disk measurement provide valuable insights in the kinetics and mechanism involved in the reaction.

The experimental characterization of these electrocatalysts requires the cleanest possible conditions as impurities may lead to incorrect data and conclusions.

Find out how you can perform these experiments with the dedicated Metrohm Autolab products.

ECAT-compact – basic package for electrocatalysis experiments

The compact PGSTAT204, fitted with the dual-mode BA bipotentiostat module provides a convenient solution for electrochemical measurements using forced convection. The rotating ring-disk electrode (RRDE) can be remotely controlled by the instrument and the BA module offers the possibility to perform both collection-detection experiments and shielding experiments.

• Small but powerful

Despite its small footprint, the PGSTAT204 provides all the functionality required for high quality and accurate electrochemical measurements.

• Dual mode bipotentiostat

The BA module can be used to control the second working electrode in both bipotentiostat mode or scanning bipotentiostat mode.

• Accurate motor controller

High precision control of the rotation rate, from 100 to 10 000 RPM.

• Built-in analog integrator

For charge and cyclic voltammetry current integration measurements.

• Electrochemical cell

Dedicated electrochemical cell for electro-catalysis measurements.

• Waterbath control

Software interface to external waterbath for temperature regulation

• Generation collection or shielding

The rotating ring-disk electrode can be used for both generation collection or shielding experiments.

• Monitor cable

Provides connections for analog signals and control for the Autolab motor controller.

• Powerful software

Advanced electrochemical NOVA 2 control software with built-in Levich and Koutecký-Levich analysis methods.

ECAT-complete – complete package for electrocatalysis experiments

The ECAT-complete packages provides additional functionality with respect to the compact version. The additional SCAN250 module provides true linear scan cyclic voltammetry for both ring and disk. The FRA32M module, also included, adds electrochemical impedance spectroscopy to the list of electrochemical techniques supported by the instrument. The pX1000 module offers the possibility to connect a pH sensor and temperature sensor in order to monitor these important experimental parameters at all time

• Modular system

Modular Autolab PGSTAT302N can be expanded with additional functionality at any time.

• Waterbath control

Software interface to external waterbath for temperature regulation

• True linear scan capable

The SCAN250 module provides unique true analog scan functionality for accurate interfacial electrochemistry measurements.

• Generation collection or shielding

The rotating ring-disk electrode can be used for both generation collection or shielding experiments.

• pH and temperature measurement

pX1000 module provides real time monitoring of temperature and pH.

• Electrochemical impance spectroscopy

The FRA32M module extends the instrument functionality with electrochemical impedance spectroscopy.

• Electrochemical cell

Dedicated electrochemical cell for electro-catalysis measurements.

• Analog input/output

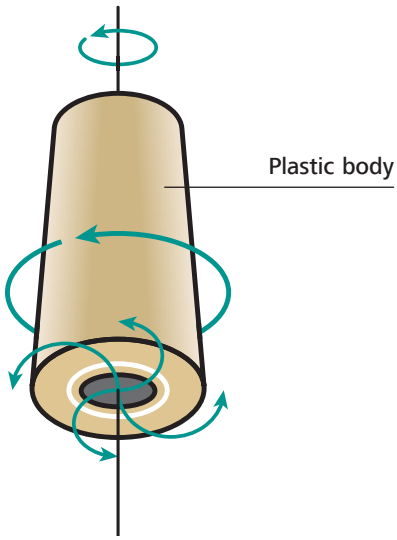
Provides connections for analog signals and control for the Autolab motor controller.

• Powerful software

Advanced electrochemical NOVA 2 control software with built-in Levich and Koutecký-Levich analysis methods.

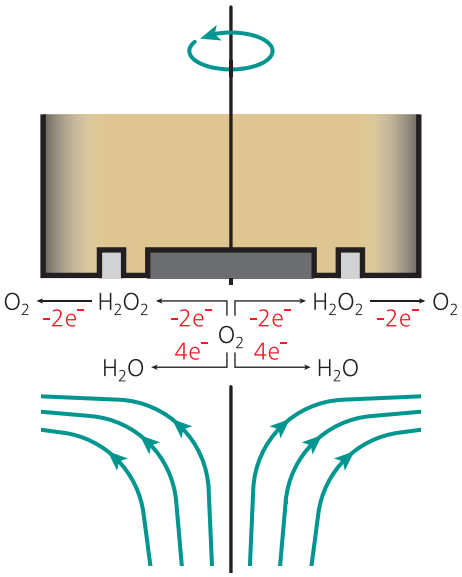
Forced convection methods and experiments

When an electrode immersed in a solution rotates, a convective drag is created. This in turn creates drag from the bulk of the solution towards the surface of the electrode. Electroactive species are therefore transported towards the surface of the electrode by convection and diffusion, with a diffusion layer thickness depending on the rotation rate of the electrode. The reaction products and intermediates or excess reactant are then expelled outwards back to the bulk of the solution. When this occurs on a rotating ring-disk electrode, an additional reaction can occur when reactants or products are transported over the ring.



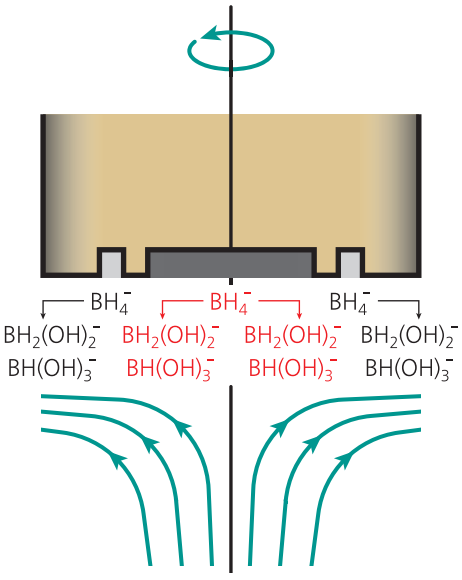
Generation/Collection experiment

In the most common use of the RRDE, products formed on the disk can be detected on the ring, provided that the ring conditions are adjusted accordingly. The oxygen reduction reaction (ORR) is a classic example of this experimental setup, where the ring is used to detect the formation of H_2O_2. This provides valuable insights in the reaction pathway.



Shielding experiment

An alternative use of the RRDE involves two consecutive measurements. In the first measurement, only the ring is polarized and the ring current is recorded. In the second measurement, the disk is also polarized at the same potential. Both electrodes then compete against one another, with the disk shielding the reaction on the ring. The oxidation of $NaBH_4$ provides a good illustration of this use of the RRDE.



RRDE Cell – measurements done right

Electrocatalysis experiments with noble metals and platinum in particular must be carried out in the cleanest possible conditions. With a total volume of 250 mL, the Autolab RRDE cell meets this requirement:

- **Easy assembly and disassembly:** the cell can be easily assembled and can be completely taken apart for cleaning.
- **The highest chemical resistance:** all parts in contact with the solution are made of materials with the best chemical resistance. These can be cleaned in the extreme conditions dictated by the experimental requirements.
- **Stable measurement environment:** when assembled, the RRDE cell provides a stable experimental environment suitable for electrochemical measurements under reproducible laminar flow conditions.
- **Thermostatic jacket:** the glass cell includes a thermostatic jacket for thermal control of the measurement conditions.
- **Two-way gas purge:** the included gas purge tube can be used to saturate the solution with a gas, typically oxygen and to blanket the solution once saturated. For fast gas saturation, the gas purge generates micro-bubbles using a small glass frit.

RRDE – ultra-low noise rotator and controller

The Autolab rotating ring-disk (RRDE) rotator uses a double, friction-less, mercury-based electrical contact for both electrodes. This ensures ultra-low noise measurements even in the most demanding experimental conditions.

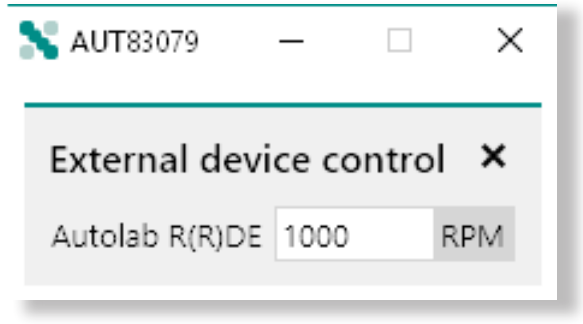
- **Full control:** the RRDE rotator can be controlled manually using the Autolab motor controller or remotely using the NOVA 2 software.
- **Perfect fit:** the RRDE rotator is designed to fit in the matching conical fittings located in the RRDE cell. This ensures stable measurements conditions regardless of rotation rate.
- **Accurate control:** the rotation rate can be controlled with a precision of a single rotation per minute (RPM) between 100 and 10 000 RPM, with an acceleration and deceleration rate of 4 000 RPM/s.
- **Compatible:** the RRDE controller can be used in combination with any Autolab potentiostat/galvanostat.

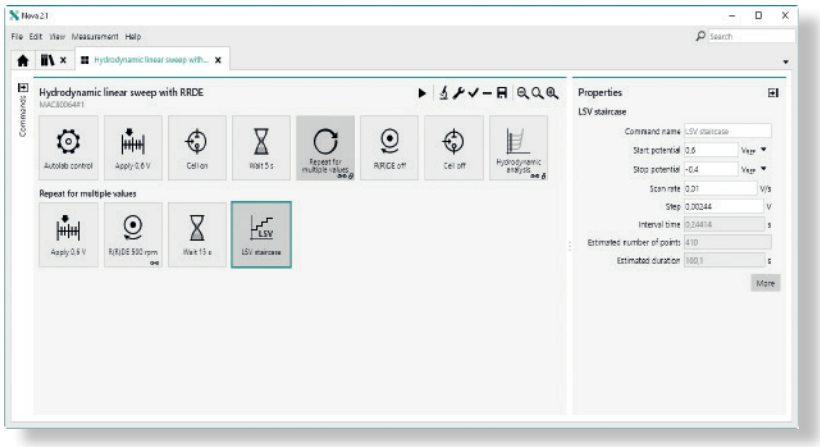
Ring disk electrodes – the key to all experiments

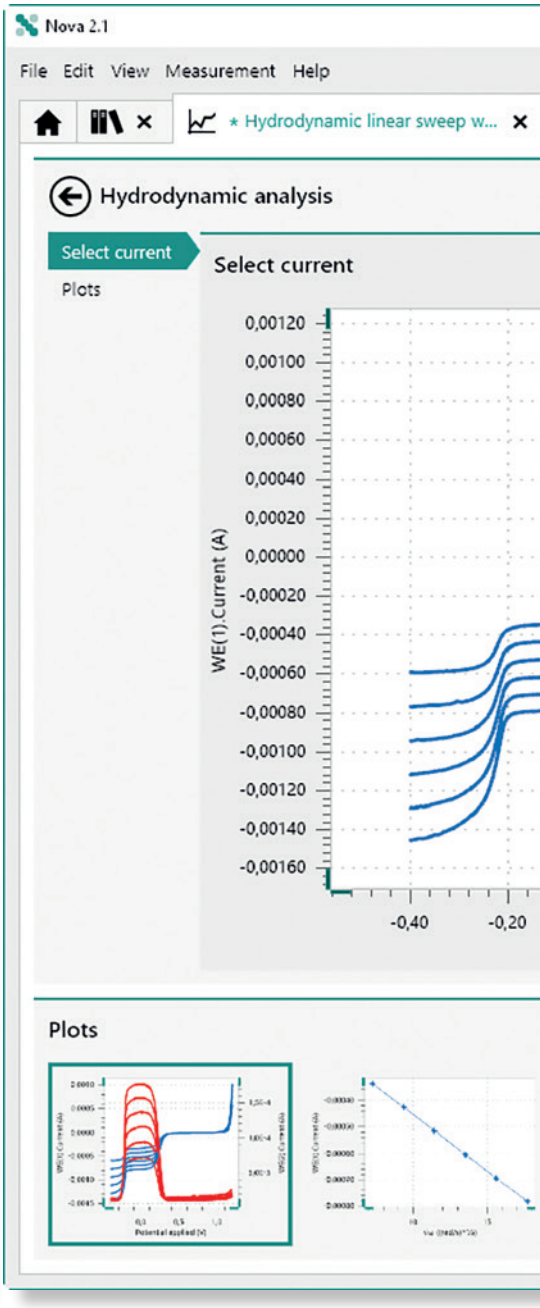
Electrocatalysis experiments can be conveniently carried out using the ring-disk electrode. Products and reaction intermediates created on the disk can be detected on the concentric ring under hydrodynamic conditions.

- **Wide rotation rate range:** the ring disk electrodes are designed to be used in the full rotation rate of the Autolab RRDE rotator, from 100 RPM to 10 000 RPM.
- **Accurate construction:** the electrodes are assembled using the most precise construction methods. A 375 µm gap between ring and disk results in a theoretical collection efficiency of 24,9%.
- **Different materials:** the electrodes are available with glassy carbon, gold, or platinum as disk material and platinum as ring material.

Autolab NOVA – Advanced electrochemistry software

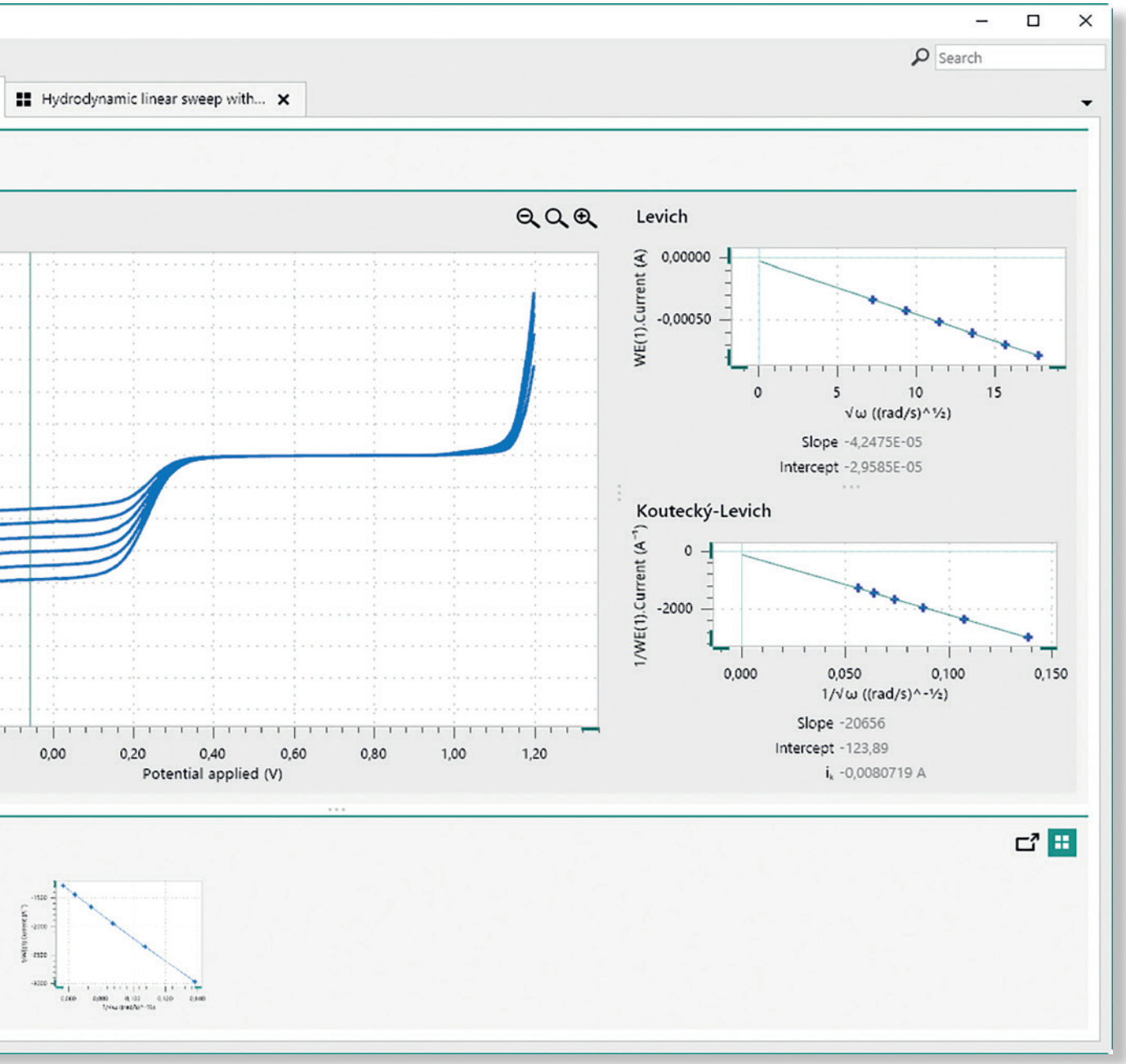






The NOVA software is used to control all Autolab potentiostat/galvanostat and accessories connected to it. It provides a simple and modern interface to all electrochemical experiments and comes with an extensive library of methods suitable for a wide range of applications.

Procedures for measurements with the rotating disk or the rotating ring-disk electrode are readily available. These methods use the remote control option of the motor controller to automatically scale up the rotation rate during the experiment, using a square root distribution.



NOVA provides answers in real-time. The detection of a reaction intermediate can be observed as the measurement proceeds.

Procedures provided for rotating ring-disk measurements include data handling and data analysis commands that perform the necessary steps to create Levich and Koutecký-Levich plots alongside the experimental data recorded with the RDE or RRDE.

These plots, provide information on the number of exchanged electrons or the kinetic constant.

This way, a single experiment provides all of the information required to provide insights on the kinetics and the reaction pathway.

Ordering information

ECAT-Compact

Autolab compact electrocatalysis package

Compact package for electrocatalysis measurements including:
• PGSTAT204 compact potentiostat/galvanostat with monitor cable
• BA dual-mode bipotentiostat module
• RRDE rotator and motor controller
• Glassy carbon disk/platinum ring electrode
• Complete RRDE electrochemical cell
• NOVA 2 advanced electrochemical software

ECAT-Complete

Autolab complete electrocatalysis package

Complete package for electrocatalysis measurements including:
• PGSTAT302N modular potentiostat/galvanostat
• BA dual-mode bipotentiostat module
• SCAN250 true linear scan generator module
• FRA32M electrochemical impedance spectroscopy module
• pX1000 pH/T measurement module
• RRDE rotator and motor controller
• Glassy carbon disc/platinum ring electrode
• Complete RRDE electrochemical cell
• NOVA 2 advanced electrochemical software
• 6.0259.100 Unitrode pH and temperature sensor

RRDE Cell

Autolab complete RRDE cell

Complete electrochemical cell for RRDE measurements including:
• 250 mL glass vessel with thermostatic jacket, thermometer, adaptors, and stoppers
• 6.0733.100 Ag/AgCl reference electrode, SGJ, Metrohm socket B
• 6.2026.010 Support stand with support rod
• PT.SHEET platinum sheet electrode, Metrohm socket B
• RRDE.CAP PTFE cell cap with 7 conical fittings
• RRDE.GAS two-way gas purge
• RRDE.CLAMP metal cell stand holder
• RRDE.ORING.SIL PTFE coated o-ring
• RRDE.RING.NYLON holding ring

Features	ECAT-compact	ECAT-complete
Potentiostat/Galvanostat	√	√
Bipotentiostat	√	√
Electrochemical impedance spectroscopy	x	√
Linear scan cyclic voltammetry	x	√
pH and temperature measurement	x	√
Built-in integrator	√	x

Specifications and features overview

Specifications	PGSTAT204	PGSTAT302N
• Maximum current	+/- 400 mA	± 2 A
• Compliance voltage	+/- 20 V	± 30 V
• Potentiostat	yes	yes
• Galvanostat	yes	yes
• Potential range	± 10 V	± 10 V
• Applied potential accuracy	± 0.2% ± 2 mV	± 0.2% ± 2 mV
• Applied potential resolution	150 µV	150 µV
• Measured potential resolution	3 µV (gain 100)	0.3 µV (gain 1 000)
• Maximum scan rate	1 000 V/s with 15 mV step	1 000 V/s with 15 mV step 250 kV/s with ADC10M/SCAN250
• Current ranges	100 mA to 10 nA (in 8 ranges)	10 nA to 1 A (in 9 ranges)
• Current accuracy	± 0.2% ± 0.2% of current range	± 0.2% ± 0.2% of current range
• Applied current resolution	0.015% of current range	0.015% of current range
• Measured current resolution - at 10 nA range	0.0003% of current range 30 fA	0.0003% of current range 30 fA
• Potentiostat bandwidth	1 MHz	1 MHz
• Potentiostat rise/fall time	< 300 ns	< 250 ns
• Input impedance of electrometer	> 100 GOhm // 8 pF	> 1 TOhm // 8 pF
• Input bias current @ 25 °C	< 1 pA	< 1 pA
• Bandwidth of electrometer	> 4 MHz	> 4 MHz
• iR-compensation - resolution	current interrupt and positive feedback 0.025%	current interrupt and positive feedback 0.025%
• Electrode connections	2, 3 or 4	2, 3 or 4
• Front panel display	n.a.	E and i
• Analog outputs (BNC)	potential and current	potential and current
• External voltage input	n.a.	yes
• Analog integrator - time constants	yes 0.01 s, 0.1 s, 1 s, and 10 s	FI20 module (optional) 0.01 s, 0.1 s, 1 s, and 10 s
• Interfacing	USB	USB
• A/D converter	16-bit with gains of 1, 10, and 100	16-bit with gains of 1, 10, 100, and 1 000
• External input/output signals	1/1	2/2
• D/A converter	16-bit, 3 channels	16-bit, 4 channels
• Digital I/O lines	12	48
• Dimensions (W×D×H)	15×26×20 cm^3	52×42×16 cm^3
• Weight	4.1 kg	18 kg
• Power requirements	75 W	300 W

Specifications (RDE and RRDE)	
• Speed control	Manual and software
• Motor speed range	100–10 000 RPM
• Manual speed setting in 1 RPM steps	100–10 000 RPM
• Acceleration/ deceleration	4 000 RPM/s
• Maximum current	500 mA
• Contact (RDE)	Sealed Hg pool
• Contact (RRDE)	Double sealed Hg pool
• Electrode tips (RDE 10 mm Ø)	3 mm active area in Ag, Au, Pt, and GC 5 mm active area in Ag, Au, Pt, GC, and empty
• Electrode tips (RRDE 11.6 mm Ø)	5 mm active area disc in Pt, Au or GC and 750 µm ring in Pt

Specifications (BA module)	
• Potential range	+/- 10 V
• Current ranges	10 mA to 10 nA, in 7 decades
• Current accuracy	+/- 0.2%
• Current resolution	0.0003% (of current range)
• Maximum current	+/- 50 mA
• Modes	Bipotentiostat and scanning bipotentiostat

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Subject to modifications
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