QEM 401 Operator Manual

- Q-Sense Electrochemistry Module
- Compatible with the Q-Sense E4 and Q-Sense E1 Systems

qsense®

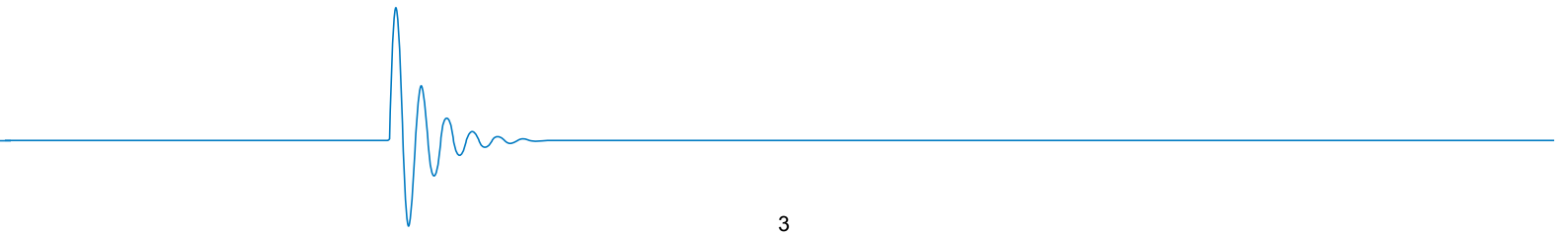
Introduction

This manual describes how to install and use the Q-Sense Electrochemistry Module, QEM 401, an add-on to Q-Sense E4 and E1 instruments, and how to make combined QCM-D and electrochemistry measurements. For a complete description of Q-Sense instrument operation, please refer to the Q-Sense E4 or E1 Operator's manuals.

NOTICE: THIS PRODUCT ENABLES THE COMBINATION OF ELECTROCHEMICAL AND QCM-D MEASUREMENTS. THE MODULE FACILITATES A COMBINED MEASUREMENT PROCEDURE, HOWEVER DEPENDING ON THE ELECTROCHEMICAL HARDWARE AND SOFTWARE, Q-SENSE DOES NOT GUARANTEE EITHER FUNCTION OR PERFORMANCE. FOR SUPPORT ON THE ELECTROCHEMICAL MEASUREMENTS PLEASE CONTACT THE SUPPLIER OF THE ELECTROCHEMICAL SETUP.

Information on the principles of the QCM-D technique, and interpretation of measurement data is not included in this operator manual.

Any comments or suggestions to changes of this manual are very welcome, please contact us at <support@q-sense.com>.



1. QEM 401 At A Glance

Below are some of the typical characteristics and opportunities with the Q-Sense Electrochemistry Module:

- Enables combined electrochemistry and QCM-D measurements.
- Quantifiable mass adsorption data from two independent techniques.
- Floating or hard ground working electrode (QCM-D sensor).
- Compatible with most potentiostats.
- Study Cyclic Voltammetry, Electrochemical Impedance Spectroscopy (EIS), Corrosion, Electro deposition, etc.
- The module doubles as a Faraday cage.
- Easy cleaning: all parts exposed to liquid can be disassembled and immersed in cleaning baths.

2. Safety

In no event shall Q-Sense ever be held responsible or liable for any direct, indirect, incidental, special or consequential damages or costs whatsoever resulting from or related to the use or misuse of the Q-Sense E4/E1 instrument or components thereof, even if Q-Sense has been advised, knows of, or should be aware of the possibility of such damages. Q-Sense emphasizes the importance of consulting experienced and qualified professionals to assure the best results when using Q-Sense E4/E1 instruments.

Safety precautions

The safety requirements listed in this manual must be followed in order to avoid personal injury and damage to the Q-Sense E4/E1 instrument.

General safety

WARNING!
RISK OF ELECTRICAL SHOCK OR FIRE HAZARD. Switches may produce electrical sparks. Do not use the Q-Sense electrochemistry module in the presence of flammable gases, fumes or liquids.

Handle carefully when removing the instrument from the transport packaging. The product must always be shipped in either the original packaging supplied by Q-Sense, or equivalent.

CAUTION!
Use only as specified in the operating instructions. Follow all instructions. Skipping steps can result in damage to the Q-Sense E4/E1 instrument and/or potentiostat.

CAUTION!
Do not use force when connecting or disconnecting connectors as damage may occur.

Do not subject the equipment to external shocks.

Do not expose any parts other than the sample volume in the electrochemistry module to water or other liquids.

When handling chemicals, refer to the safety information from the supplier and general safety regulations in your country.

Carry out appropriate decontamination if equipment is exposed to hazardous material.

Do not install substitute parts or perform any unauthorized modification to the product. Return the product to Q-Sense or other qualified and authorized personnel for service and repair to ensure that safety features are maintained. Before returning the instrument it must be free of hazardous contamination.

3. System description

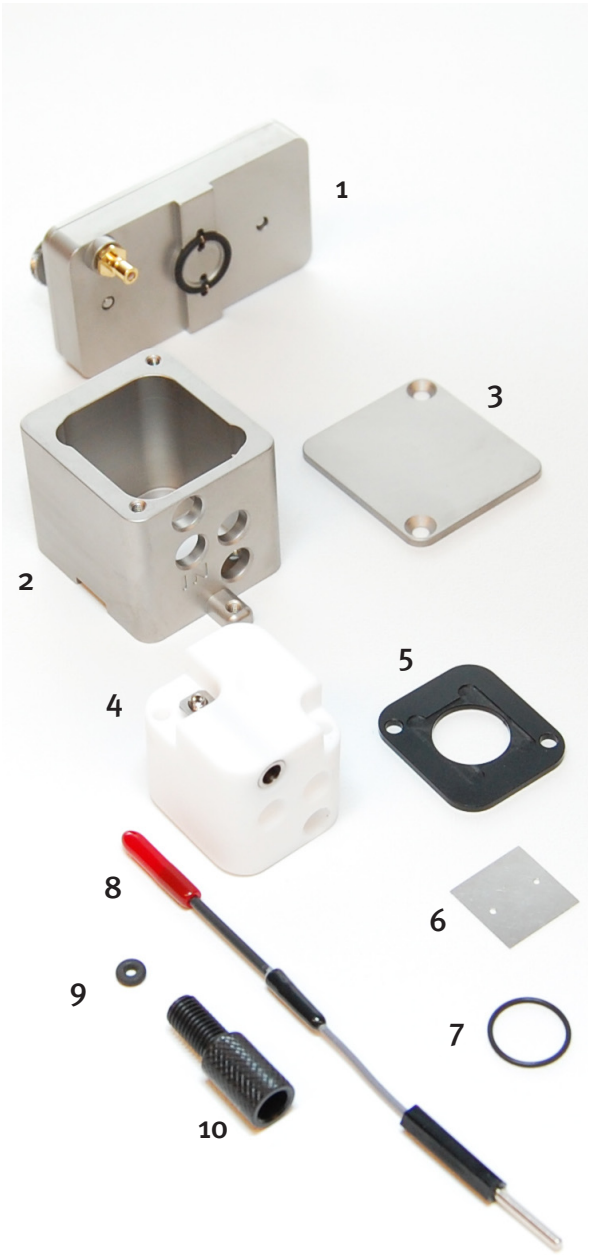
The electrochemistry module is an add-on to the Q-Sense E4/E1 instrument which enables the user to perform electrochemical measurements combined with QCM-D. The module can be used with most potentiostats or electrochemical devices.

The inner part of the module is made of Teflon® with an external stainless steel casing acting as a Faraday cage. The external cage is grounded via the SMB connector.

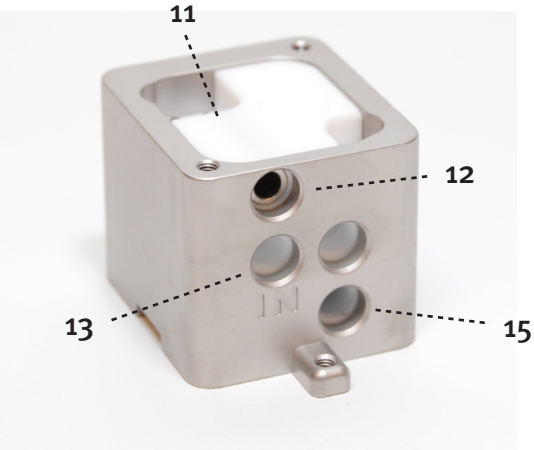
As opposed to the ordinary Q-Sense E4/E1 flow modules, the liquid is not at any point in contact with any other metal than that of the electrodes. This also allows for standard QCM-D experiments otherwise unabled by the Titanium wall present in the standard Q-Sense E4/E1 flow modules.

The module uses the same kind of liquid connectors as the ordinary Q-Sense E4/E1 flow modules (standard HPLC fittings).

The complete Q-Sense electrochemistry module consists of the following parts:



1. Module base (made of stainless steel) with SMB connection to working electrode.
2. Housing (made of stainless steel).
3. Housing lid.
4. Inner Teflon® housing, including the flow channels.
5. Counter electrode frame.
6. Counter electrode (Pt, 99.95%).
7. Sensor o-ring (Viton®).
8. Reference electrode.
9. Small o-ring for sealing of Reference electrode (Viton®).
10. Reference electrode screw.
11. Counter electrode contact screw (hidden).
12. Counter electrode connection.
13. Sample liquid inlet and outlet ports.
14. O-rings for sealing of sample ports, 2 pcs (not shown!)
15. Reference electrode connection.



Accessories supplied with QEM 401

In addition to the module itself, the following items are included:

16. Teflon® plug - for sealing of the module when no Reference electrode is mounted.
17. Screwdriver, Phillips No 1.
18. Hex wrenches, 0.9 mm (2 pcs).
19. Coaxial cable with SMB plug.
20. Adaptor: BNC male connector to SMB male connector.
21. Crocodile clip with connection for 4 mm laboratory plug.
22. Adaptor: BNC female connector with two poles (4 mm laboratory plug connectors)
23. Test lead, 50 cm long, 4mm plugs, red color.
24. Test lead, 50 cm long, 4mm plugs, yellow color.
25. Extra o-ring for sealing of Reference electrode (small).
26. Extra o-rings for sealing of sample inlet and outlet on inner Teflon® housing (small, 2 pcs).

4. Installation

Unpacking and inspection

Upon delivery, check immediately for damage to the product or packaging material. In case of damage, contact Q-Sense or your local provider before further installation.

Installing software

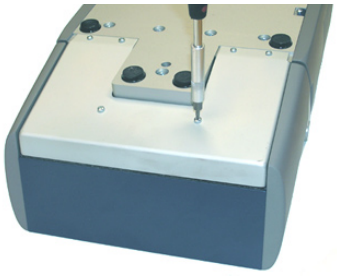
The system can be used with most electrochemical hardware and it is not locked to any maker or brand. The standard Q-Sense software Q-Soft 401 is used when performing electrochemical measurements. Electrochemistry data is not acquired by Q-Soft, but by the electrochemistry software alone. Data files needs to be combined post-measurement by the user. For operation of the electrochemistry software, see relevant manual.

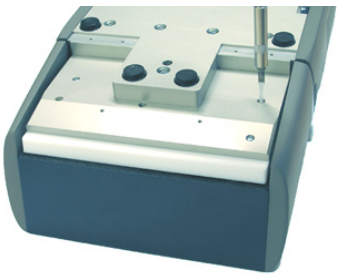
Make sure that the latest version of Q-Soft is used. New versions can be downloaded from www.q-sense.com, under the User Area. Make sure you have your customer log-in and password available.

Checking earth ground (only applicable to Q-Sense E4 instruments)

For optimal measurements with low noise, it is necessary to have the QEM 401 grounded to earth. The Q-Sense E1 chamber (QCP 101) provides this earth ground, however, on the market there are both Q-Sense E4 chamber platforms (QCP 401) with grounded and with non-grounded flow module mounting blocks. Verify that only *grounded* chambers are used with the QEM 401 electrochemistry module!

If you have an *Q-Sense E4 chamber platform*, perform the following steps to confirm that it is properly grounded:





1. Remove all modules, disconnect all cables and turn the chamber platform upside down.

2. Remove the aluminum cover plate by unscrewing 6 screws. This requires a Torx T10 screw driver.

3. Remove the cover plate. There are 5 screws going through the metal block and into the Teflon® block below. They should be made of metal. If they are white (made of Nylon), they need to be replaced. The QEM 401 module is supplied with these metal screws, if you have an Q-Sense E4 instrument. A Torx 10 screwdriver is required to install the replacement screws.

4. Unscrew the *middle* of the five nylon screws first, using a flat blade screw driver, and replace it with a metal screw (Torx T10). Then replace the other nylon screws with metal screws *one by one*. IF ALL SCREWS ARE REMOVED AT ONCE, THIS WILL LIKELY CAUSE THE E4 CHAMBER TO NOT FUNCTION PROPERLY.

5. Re-attach the cover plate and the chamber is ready for use.

Connecting the module to the Q-Sense E4/E1 chamber platform

From a QCM-D perspective, the QEM 401 electrochemistry module is handled in the same way as the standard flow module. Please refer to your Q-Sense instrument Operator Manual for how to handle tubing and liquid connectors.

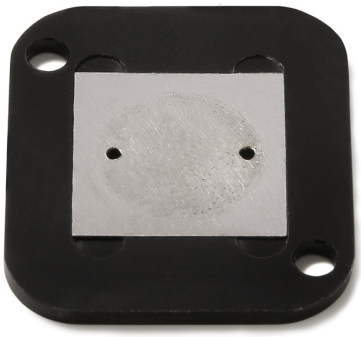
5. Handling and Assembly of Electrodes

This chapter describes how to prepare the module for experiments. Note that the cleaning agents are suggestions only; specific experimental conditions may require other cleaning agents. Numbers in parenthesis refers to System description overview.

The platinum counter electrode (CE)

Procedure to remove, clean and reinstall the counter electrode:

- Remove the top section (**2**) from the base (**1**) by loosening the two thumbscrews.
- Remove the reference electrode screw (**10**) and o-ring (**9**).
- Remove the lid (**3**) of the top section by unscrewing the two Phillips screws.
- Remove the Teflon® housing (**4**) by unscrewing the two screws in the corners (*not* the third one (**11**)). The Teflon® housing holds the counter electrode frame (**5**) with the counter electrode (**6**) in place.



When placing the platinum electrode in the frame, note the correct orientation of the flow holes.

When handling and cleaning the platinum electrode, it is recommended to use a rack, for instance the Q-Sense Sensor Cleaning Holder, to minimize contamination.

The platinum electrode can be cleaned in many ways, e.g. in sulfuric acid for 30 minutes (remember to be careful with acids, and to rinse with lots of Milli-Q water!) since platinum is such an inert metal. However, it is important to avoid physical stresses (like bending) so it stays flat. Otherwise the module may leak.

- After cleaning, place the platinum electrode into the black frame. Note the correct orientation of the flow holes ⇢.
- Ensure the 1.15x1 mm o-rings (**14**) are properly seated on the Teflon® housing (**4**).
- Lay the platinum electrode (**6**) and frame (**5**) over the center of the Teflon® housing, aligning the flow holes. Insert the two 0.9 mm hex wrenches (make sure these are as clean as the surfaces they are in contact with) into the flow holes, approximately 15 mm, to ensure the alignment of the flow holes in the electrode with those in the Teflon® housing ⇢.

- While keeping the hex wrenches in place, slide the steel housing (**2**) over the Teflon cube with the platinum electrode and frame in place, and then fully seat the Teflon® housing inside it ⇢.

- Lay the whole cube section on its side with the hex wrenches in place, and screw the two corner screws back. Do not over-tighten.

- The lower middle screw (**11**) will now be pressing a springloaded pin onto the platinum electrode (and connects it to the counter electrode plug).

The reference electrode (RE)

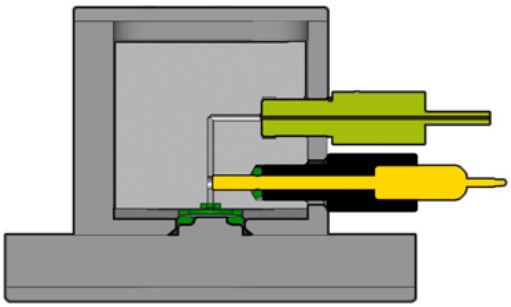
Procedure to prepare and install the reference electrode:

- Take the reference electrode (**8**) from its package and remove the protective cap (NOTE, the electrode should not be left to dry out. Store it in 3M KCl). Push the electrode through the reference electrode screw (**10**), and then the small o-ring (**9**) ⇢.

- Insert a 0.9 mm hex wrench (make sure this is cleaned properly) into the flow hole in the counter platinum electrode to provide a 1mm gap; this is to keep the outlet channel clear. Insert the reference electrode, with its screw and o-ring into the port nearest the base (**15**) until the RE reaches the 0.9 mm hex wrench, then tighten the screw finger tight ⇢.

***Above**: Cypress Systems 66-EE009 "no leak" reference electrode, formerly supplied with QEM 401. **Below**: World Precision Instruments low leakage "Dri-Ref" reference electrode.*

The reference electrode will now be in contact with the output flow from the sample volume, as shown in the graph below.



The reference electrode (yellow color in graph) mounted correctly, so that it barely protrudes into the flow channel and does not disturb the flow. The distance to the working electrode (sensor surface) is 5 mm.

The reference electrode supplied with Q-Sense electrochemistry module is a World Precision Instruments low leakage “Dri-Ref 2SH” reference electrode. **NOTE THAT THE REFERENCE ELECTRODE’S CONDITION IS CRUCIAL FOR SUCCESFUL MEASUREMENTS**. To increase the lifespan of the RE it is paramount that it is stored properly. There are two main properties that can be used as indicators of the electrodes health, namely its junction resistance and its chemical potential:

Junction resistance

A high junction resistance, Rre, can make potentiostats unstable. Most potentiostat manufacturers prefer Rre < 10 kΩ.

Rre is dominated by the resistance of the frit (the junction) at the tip of the RE and Cre comes from stray capacitances and amplifier input capacitances which are impossible to eliminate altogether. Rre and Cre acts as a first order low-pass filter with a time constant of 1/(Rre*Cre) (or a cut-off frequency fc = 1/(2*Pi*Rre*Cre)). When Rre increases, fc decreases, meaning that the feedback loop gets more and more sluggish (a change in working electrode potential takes longer and longer before it is present at the RE input), meaning that the phase between the signal the potentiostat puts out to the counter electrode, and the signal it reads from the RE, increases. When the phase goes over some particular value, the potentiostat may start to oscillate (leading to bad signals).

Also, note that if an air bubble gets attached to the frit, it will drastically increase Rre and so will the mounting of the RE if the tip (i.e. the frit) is pushed too far into the sample flow channel in the QEM 401 module, so that it touches the opposite wall of it.

Since Cre is fixed by the design of the potentiostat there are basically two different parameters that can be adjusted if this happens with the E-QCM-D setup:

1) The bandwidth of the potentiostat (i.e., how quickly it reacts on a change in signal coming from the RE input and then subsequently tries to compensate for it on the working electrode output). The bandwidth can usually be controlled by software in a couple of steps. Use as small bandwidth as possible. If an ordinary CV test is to be performed, the bandwidth can usually be set on the smallest possible value.

2) Rre. Unfortunately, it is very easy to increase Rre. The frit can become clogged when exposed to solutions containing molecules or particles that adsorb on surfaces. Such adsorbtion can drastically increases Rre. Q-Sense recommends following either of the procedures below to rejuvenate the RE:

Immersing the RE in warm or room temperatured 1 M H_2SO_4 solution for 30 minutes. *Be careful when handling acids and make sure to follow good laboratory practice*.

Q-Sense recommends storing the RE in 3M KCl between measurements.

Chemical potential

If you detect a significant shift in the reference electrode’s potential (>200 mV compared to normal) this probably means that the sealing of the filling solution under the black cap has leaked and the junction where the Ag wire is soldered to the gold pin is wet. No fixing in this case is recommended. The electrode must be re-built by the manufacturer or replaced for a new one.

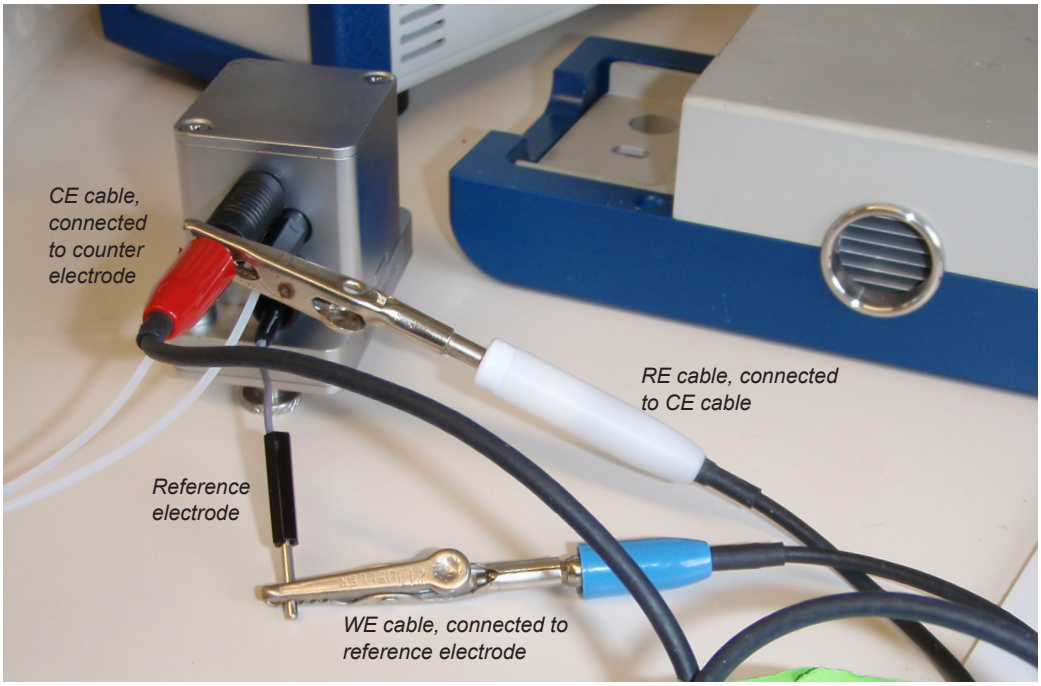
How to measure the Reference electrode resistance

To ensure good quality E-QCM-D data, it is recommended to measure the reference electrode resistance right before the E-QCM-D experimental setup, and confirm that it is below 10 kΩ.

1. Connect the working electrode cable from the potentistat to the reference electrode on the cell.

2. Connect both the reference and the counter cables from the potentiostat to the counter electrode on the cell.

3. In the potentiostat software, there should be a function to acquire the value of this resistance. Depending on the potentiostat brand, it can be named in different ways. The RE resistance are sometimes called Ru (uncompensated resistance), and, for instance, in Gamry the function is called “Get Ru”.



Checking the reference electrode resistance before a measurement.

The working electrode (WE)

The working electrode of the module is the QCM-D sensor surface itself. For cleaning of sensor surfaces, please consult Q-Sense cleaning protocols, found on the User Area at www.q-sense.com.

6. Operation

From a QCM-D perspective there are few differences when running an electrochemical measurement compared to a normal QCM-D measurement. The same software is used and set up as preferred by the user.

Preparing the module for an experiment

1. Install the counter electrode and reference electrode according to section 5 “Handling and Assembly of Electrodes”.
2. Place the sensor o-ring (**7**) on the counter electrode.
3. Insert the sensor surface, according to the picture, on the sensor o-ring. *Make sure it lays flat, and is in contact only with the o-ring*! Note the direction of the anchor shaped electrode, as described by the cut-out in the aluminum.

Note the sensor orientation.

Liquid setup

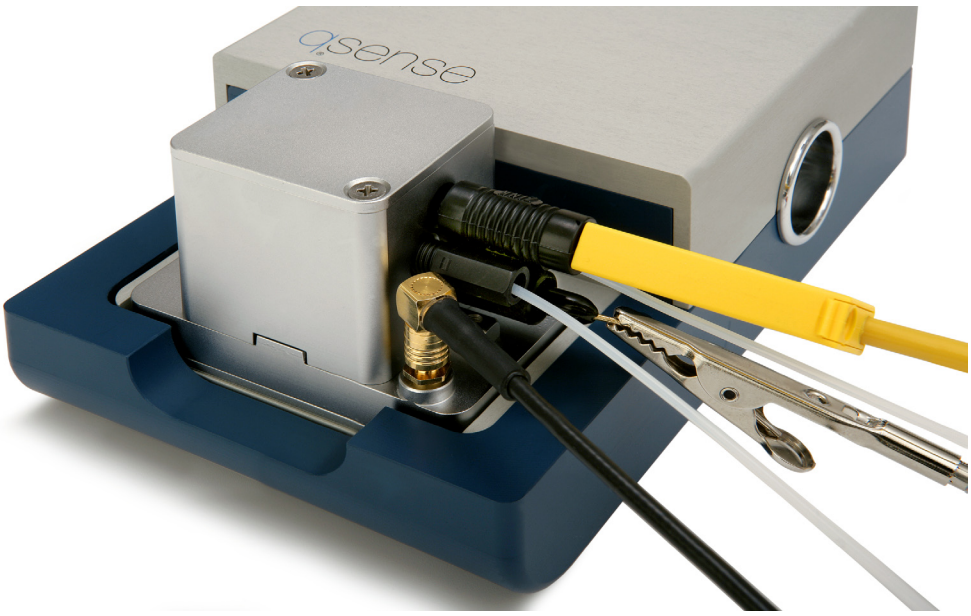
The liquid set up for the QEM 401 is analogous to the normal Q-Sense E4/E1 flow modules.

4. Note that the reference electrode is positioned in the sample outlet channel: thus make sure the input tubing is connected to the flow port (**13**) denoted “IN”.

Connecting the cell to the potentiostat

5. Connect one end of the SMB cable to the SMB gold connector on the EC Cell, then connect the other end to the SMB/BNC adaptor. Connect the adaptor to the BNC Banana Binding Poles to allow interfacing with the potentiostat.
6. Connect the reference cable from the potentiostat to the reference electrode tip using an alligator clip.
7. Plug the counter electrode cable into the jack (**12**) above the flow ports.

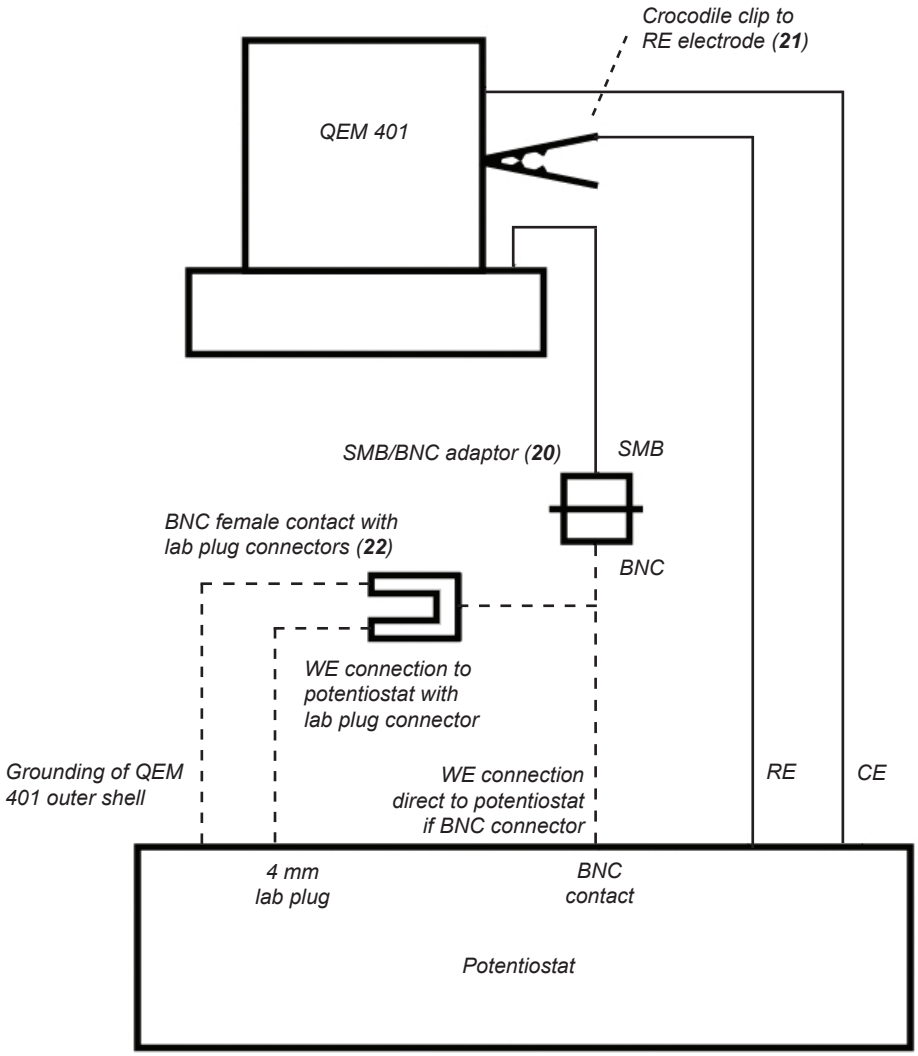
For operation of the QCM-D instrument and the software, please refer to the Q-Sense E4/E1 Operator’s manual.



Connected cell:
Working electrode (gold contact); counter electrode (yellow plug); reference electrode (alligator clip); tubings.

Wiring diagram of experiment setup

The diagram below shows how cables and connectors are set up with accessories supplied by Q-Sense. Numbers in paranthesis refers to System description overview (chapter 3).



1. How to clean the module

If you want to clean the Teflon® part inline then remove the Reference electrode screw and replace it with the Teflon® plug supplied with the module. Clean the cell according to Q-Sense Cleaning protocols, found on the User Area at www.q-sense.com (10 ml Hellmanex 2% followed by plenty, > 50 ml, of milli-Q water).

Alternatively, you can clean the Teflon® part separately, while the module is disassembled. Then soak the whole Teflon® part (including the stainless steal contact plug for the counter electrode) and sonicate it in Hellmanex and then rinse in plenty of milli-Q water. Note that the contact plug is not acid proof so strong acids cannot be used in this configuration.

2. System performance

QCM-D signals

Noise levels of *f* & *D* signals should not differ from those acquired from measurements performed with standard flow modules.

Open circuit potential

It is recommended to take a note of the open circuit potential (OCP) before starting the potentiostat measurement to keep track of the electrodes' performance. The OCP can usually be measured directly from the potentiostat.

If the QEM 401 module is equipped with the platinum CE and the World Precision Instruments low leakage "Dri-Ref 2SH" RE (as provided by Q-Sense), and filled with 3M KCl, the absolute value of the potential should be in the interval 200-400 mV, and should be stable to a few millivolt. If the OCP is outside this value (or the value it usually is for your system) or if it is unstable it is an indication that something is wrong with the set-up.

Sensor stability

If a strong positive polarization of the working electrode is maintained over a longer time without any electro couple present, the working electrode might oxidize completely causing the experiment to fail (the electrode layer peels off). This will be noticed in the QCM-D data by a massive positive frequency shift followed by a loss of signal.

Troubleshooting

Symptom	Possible cause	Solution
Unstable OCP	Contaminated RE	See RE cleaning instructions
	Contaminated CE	See CE cleaning instructions
	Contaminated WE	See sensor cleaning instructions
	Contaminated solution	
	Chemical reactions taking place	
QCM-D sensor (WE) peals off	Too high applied voltage	Reduce maximum and minimum voltage settings on potentiostat.
	Too high RE resistance	Make sure RE is not pushed in too far or not far enough into the Teflon®. If it is too far pushed in, the RE could be sealed against the opposing wall, or if it is not pushed in far enough there is risk for an air bubble on the RE junction. The RE junction may also be contaminated. See RE cleaning instructions.
CV is shifted or unstable	Contamination	See solutions for unstable OCP
	The RE has shifted potential	If cleaning the RE does not help, the RE is probably damaged and has to be replaced.
Noisy QCM-D signals	The potentiostat cables act as antennas and lead in noise to the sensors.	Make sure to use good quality cables and that they are well connected to the potentiostat and the module. Use as short cables as possible. Try moving the cables around to see if there is an arrangement that minimizes the noise in the QCM-D signals.

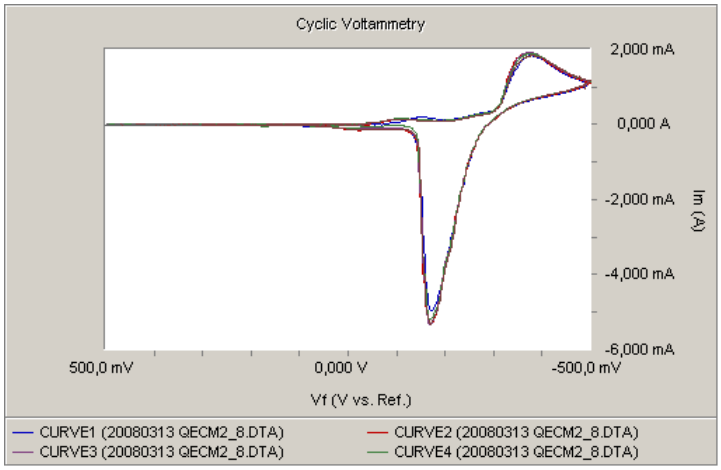
Test of general EC performance

As a general test it is suggested to perform a cyclic voltammetry measurement on the redox couple $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ (experimental specifics described elsewhere). This system only takes place in the solution and does not bind to the QCM-D sensor surface at all, and could be a way to discriminate between contributions from the QCM-D part of the setup and the EC part.

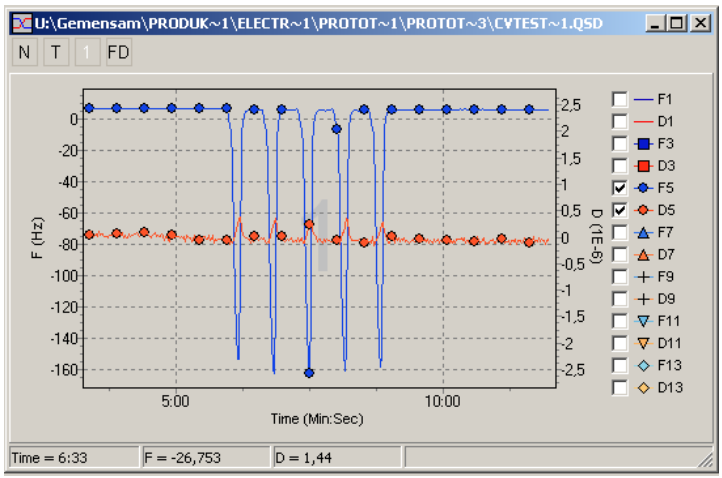
Test of combination performance: E-QCM-D data

To test the simultaneous performance of Electrochemistry and QCM-D, the following simple system could be used: plating of copper from $Cu^{2+}SO_4^{2-}$ solution.

The graphs show the results obtained when 10 mM $CuSO_4$ in 0.1 M H_2SO_4 was injected into the EQCM-D module containing a standard Au sensor (QSX 301) and QSoft was initialized. After stabilization, five cycles of cyclic voltammetry (CV) were performed starting at 0 V and cycling back and forth from -0.5 V to +0.5 V at 50 mV/s, starting at +0.3V.



Corresponding *f* & *D* signals:



3. Technical Specifications

General:	
QCM-D sensor surfaces compatible	All Q-Sense 14 mm QSX sensor crystals can be used
Flow measurements enabled	Yes
Cleaning	All parts may be disassembled for separate cleaning, except the module base contacting the chamber platform
Cell specifications:	
Internal volume	~ 100 µl above sensor; ~25 µl from inlet to sensor
Materials exposed to liquid	Teflon® (tubing and flow channels), Platinum (counter electrode), Viton® (o-rings), Polyurethane-based polymer (reference electrode)
Distance from RE to WE	4 mm (5 mm from center of RE)
Distance from CE to WE	0.8 mm
Electrodes:	
Working electrode	The QCM-D sensor itself
Counter electrode	Platinum disk
Reference electrode	World Precision Instruments low leakage “Dri-Ref 2SH”