PEEK 4-electrode PEM Sample Holder for ProboStat™

Supplementary Material to the ProboStat™ Manual
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This is a supplement to the ProboStat™ manual, to be used together with (and not instead of) it.

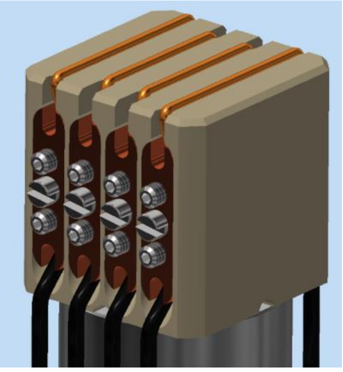
1. Introduction

1.1. PEM membrane conductivity measurements

A proton exchange membrane, also often referred to as a polymer electrolyte membrane (both abbreviated PEM) exhibits typically conductivities of 0.1 S/cm and have thicknesses of the order of 100 μm (0.1 mm, 0.01 cm). If the conductivity is measured through-plane with 2 electrodes of an area of 1 cm^2, the measured resistance is $R = d/(A\sigma) = 0.01\ \text{cm} / (1\ \text{cm}^2 \cdot 0.1\ \text{S/cm}) = 0.1\ \Omega$. This is challenging, as the spreading resistance in typical electrodes will be of significant contribution. Moreover, AC conductivity measurements (or impedance spectroscopy) are required to delineate the membrane resistance from the polarisation resistance of the electrodes. The use of two electrodes through-plane gets more difficult if the conductivity increases further, and easier and more accurate if it decreases. It may also yield information about capacitance (dielectric constant) and relaxation phenomena in the electrolyte membrane.

As an alternative, a 4-electrode measurement – either as point electrodes or more extended electrodes, like the wires we use here – eliminates the resistance of the electrodes, making the measurement more accurate, even as conductivity goes much higher. For instance, the same membrane measured as a 1 cm wide slab square between two voltage wire electrodes 1 cm apart, will yield a measurable resistance of $R = d/((t\ w)\cdot\sigma) = 1\ \text{cm} / ((1\ \text{cm} \cdot 0.01\ \text{cm}) \cdot 0.1\ \text{S/cm}) = 1000\ \Omega$ which is a much easier range to measure in, and anyway free from electrode polarisation. (In the PEEK head for ProboStat™ the actual distance between voltage wire electrodes is 0.4 cm.) However, the capacitive information of the membrane is lost (dominated by the insulating support). The measurements can and should be done at DC or low AC frequencies. It has – as said – advantages, but also its own set of potential challenges, that one should be aware of, and that we will treat here.

1.2. PEEK 4-electrode PEM sample holder



The polymer electrolyte membrane (PEM) sample holder for ProboStat™ is a PEEK head to be mounted in the top of a standard ProboStat™ sample support tube. It has a flat top surface with 4 wire electrodes onto which the polymer film is pressed down with the spring load system of the ProboStat™, for measuring the in-plane conductivity primarily of polymer electrolyte membrane films, but also other flexible and/or soft films. Since it comprises 4 wire electrodes, it is primarily intended for well conducting materials, ensuring high measurement accuracy due to the elimination of the electrode impedances. The obtained specific conductivity is in principle the same as obtained from a through-plane measurement using two electrodes, but the latter may suffer from parasitic spreading and contact resistances of the electrodes.

The PEEK holder for ProboStat™ operates in a single atmosphere, and is not intended for use to test membranes in e.g. fuel cell mode between two atmospheres.

It can operate at temperatures and conditions where the PEEK and metal parts are stable, typically long term up to around 200°C, for shorter term e.g. 250°C. As temperature goes higher, one must expect some deterioration with time, depending also on the atmosphere. In this sense, the PEEK head may be seen as a replaceable part.

The atmosphere may be any atmosphere that the ProboStat™ otherwise handles, meaning oxidising, reducing, inert, dry, and wet gases, from low vacuum to atmospheric pressure, or up to 15 bar with a steel outer tube. With a heated ProboStat™ base unit, high steam contents may also be supplied.

The PEEK head is to be used with a ProboStat™ with a 20 mm diameter support tube. This is normally a standard alumina ProboStat™ sample support tube with 20 mm outer diameter, but it can be any material as long as the inner diameter fits the base of the PEEK head.

The length of the support tube can be any, as long as the enclosing tube, spring load system, electrode contacts, and any thermocouple are at corresponding lengths. A full length ProboStat™ features a sample support tube of length 50.7 cm including socket and an enclosing tube of 60 cm. Since the temperature range of the PEEK cell is limited, a shorter sample support tube can well be used and may be preferential, e.g. a tube 20 or even 30 cm shorter than the full-length version ("-20" and "-30" systems with sample support tubes of, respectively, 30.7 or 20.7 cm length including socket.)

2. Parts

2.1. *ProboStat™ standard parts*

The system must have a ProboStat™ base unit, a 20 mm outer diameter sample support tube, a spring load system (triangular top plate and 3 spring-loaded bars), and an enclosing tube. If you are unfamiliar with these and their mounting, see the standard ProboStat™ manual.

2.2. *PEM 4-electrode sample holder parts*

The PEM 4-electrode sample holder set consists of the following parts:

PEEK head with 4 double-sided double electrode wire screw terminals.

4 (short) electrode wires with 0.5 mm diameter, typically of Pt, Au, or Cu. May be pre-mounted in the PEEK head. Extra electrode wires may be supplied separately if ordered.

4 (long) electrode contacts, typically 0.5 mm diameter of Pt, Au, or Cu, lengths according to the length of the support tube. They have female mini-contacts in one end and are either insulated with plastic, or equipped with ceramic insulating tubes.

Hex key for the wire screw terminals.

Perforated PEEK plate.

Inner thermocouple assembly TCI-P consisting of type S or type K thermocouple wires in a two-bore alumina tube, with minicontacts, and colour-coded wire insulation. It is cut to a length to fit in the inner chamber of the ProboStat™ and all the way from below into the centre hole of the PEEK head.

3. Assemble the PEEK head with electrode wires

When you ordered the PEM sample holder system, you may have specified the material of the electrode wires. The default is 0.5 mm Pt wire. These may have been pre-fixed to the head. If you need to replace them, loosen the top hex screws on both sides and fit in pre-bent short wires cut to exact length so that they fit well in the screw terminals as well as in the grooves on top of the head. Press them flat into the grooves with a flat surface.

Be sure not to unscrew the tiny hex screws too much – they are easily lost.

Tighten the hex screws gently. In a 4-wire measurement, it is *not* essential to have super good contact in each point along the wire, so again: Tighten the screws only gently.

4. Samples

The samples should be flexible films or foils, with thickness much smaller than the distance between the wire electrodes in the PEEK head. The ideal size of the sample is a rectangle which is amply longer than the distance 1.2 cm between the outer (current) electrode wires of the PEEK head and equal to or narrower than the width (length) 1.8 cm of the same current wires. For instance, a 2 x 1 cm^2 long rectangle will be fine. You must know or measure the width of it accurately. The rectangle will have to be placed accurately orthogonal to the head wires in order to achieve full accuracy.

If you want to use a sample wider than the current wires, e.g. a much larger rectangle or square or a circular disk, this is possible, but the geometrical factor of the cell is different, and can only be approximated.

5. Mounting

Have the ProboStat™ base unit ready, fixed for mounting, preferably with the mounting ring over it. If you are not an experienced user of ProboStat™ in beforehand, familiarise yourself with the ProboStat™ base unit by going through the introductory parts of its regular manual. If you have a new or relatively late ProboStat™ base unit with a Shields Bridge switch you can skip the remaining of this paragraph. *If,* however, you are using an early ProboStat™ *without* a shields bridge switch *and* want to measure directly connected to an impedance spectrometer requiring bridged (connected) shields, your shields bridge wire must be installed between feedthroughs 5, 7, 14, and 16 – see the standard manual. If you want to use a potentiostat or electrochemical interface with driven shields, the shields bridge wire must be removed. (On newer ProboStats, this function is operated by the Shields Bridge switch on the outside – it will be addressed later.)

Mount the TCI-P thermocouple on the pedestal – be sure to use the inner thermocouple minicontacts and ensure correct polarity, utilising e.g. colour coding. (First time you heat the unit, make sure that the polarity is correct by confirming that the thermocouple shows increasing temperature and not vice versa). (Fig. 1)

Mount the sample support tube by screwing it onto the thread of the pedestal, stopping normally against an O-ring at the base. The thermocouple now should protrude well above the rim of the support tube. (Fig.2)

Fig. 1. Mounting the TCI-P thermocouple on the pedestal.

Fig. 2. Sample support tube mounting.

Mount the PEEK head by inserting its round base into the support tube. It should rest against the rim of the support tube, while the thermocouple should fit from below into the hole in the PEEK (Fig. 3). The length of the thermocouple is made so that its sensing tip ends up at the top of the hole, which is just below the surface of the holder, where the film will rest. Rotate the PEEK head so that one side of the terminals faces the base unit feedthroughs 5-8 and the other side faces the feedthroughs 13-16 on the opposite side.

Fig. 3. PEEK head mounted.

Mount the four long electrode contacts, exactly as follows:

Fit the mini-contacts to the male feedthroughs 6, 8, 13, and 15, so that they contact the four wires on top of the PEEK head in this order (Fig. 4 and 5). We recommend using the stand set with mounted ring to support the electrode contacts at mounting.

Fig. 4. Fitting the mini-contacts to the feedthroughs 6 and 8.

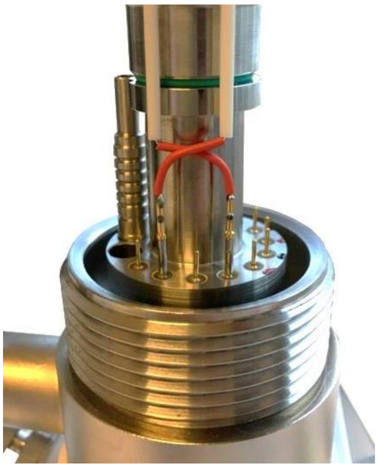


Fig. 5. Fitting the mini-contacts to the feedthroughs 13 and 15.

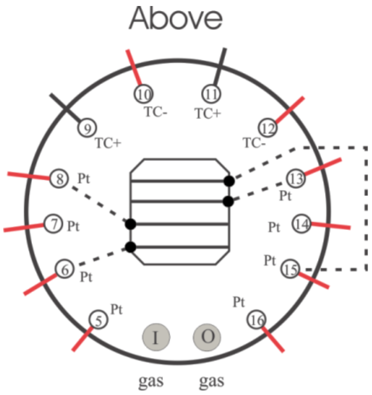


Fig. 6. Connection scheme.

This corresponds to Low current (LC), Low voltage (LV), High voltage (HV), and High current (HC) in the ProboStat™ system (and many electrochemical instruments[1]). Hence, of the 4 wires on the PEEK head the two outer are for sending current, while the two in the middle (inner) are for probing the voltage. You may confirm correct wiring and contact by a multimeter showing contact between the LC, LV, HV, and HC external terminals of the ProboStat™ and the appropriate wires on top of the PEEK head. ***NOTE***: The correct connections of the four wires means that *on one side* (and one side only), the two wires must cross each other on the way from the head to the base.

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[1] Instrument terminal naming exampels

Pin	ProboStat	Example 1	Example 2	Example 3	Example 4
15	High current	I high	Gen output	WE	Input high
13	High Voltage	V high	Hi	WS	Sense high
8	Low voltage	V low	Lo	RE	Sense low
6	Low current	I low	Current	CE	Input low

Next, the naked uninsulated (top) end shall be inserted into the lower hole of the PEEK head terminals and the small hex screws tightened with the hex key (Fig.7). Two of the wires should be connected to the PEEK head terminals on one side, and the two other on the other side, so that altogether each electrode wire has one connecting wire. (This leaves two unused terminals on each side.)

Consider to activate the electrode wires: Consider rubbing the electrode wire surfaces clean and fresh with a fine sand paper or applying an electrocatalytic paste on each. Read more about Electrode activation in a later chapter on Special considerations.

Take the measures: Measure the distance between the voltage electrodes (nominally 0.40 cm). Furthermore, decide, cut, and measure the width of a rectangle of your membrane sample. The best is to have it well narrower than the current wires (1.8 cm), and longer than the span (distance) between the current wires. Also find or measure the thickness of your membrane sample if you haven't done so already.

Mount the membrane sample. Make sure that you know the measures of everything (see above) and that it covers amply the distance between the current wires.

Consider to add a soft insulating interlayer. If the membrane is thin and stiff, it may be beneficial to apply a soft insulating gas permeable layer on top of it (between the membrane and the perforated PEEK plate), such as a fine filter paper, in order to dynamically press the membrane well into contact with each electrode wire along all of the wires' lengths.

Add the perforated PEEK plate, so that the flat side faces down and the rimmed basin faces up (Fig. 7). The rim pointing up to the spring load plate above ensures gas to spread all over the sample through the perforation. Align it with the PEEK head.

Fig. 7. Electrode contacts inserted into the the PEEK head terminals with fake membrane sample and perforated plate.

Fig. 8. Spring load system mounted (see below).

Assemble the spring load: Thread and let hang free the three spring load bars (which should have top alumina cross-bars fixed with Pt wire) through the holes of the alumina spring load top plate. Attach springs to each at the bottom. Select preferably soft springs (red belt in the NORECS spring collection ☺). If spring loads and their assembly are unfamiliar to you, please read more in the ProboStat™ standard manual.

Add the spring load over the PEEK plate and align the three holes in that with the holes in the PEEK plate, such that the three spring load bars find ways down in between the electrode connect wires (Fig. 8). With pliers around the neck of the lower spring hook, fix each spring to the collar of the pedestal of the ProboStat™ base unit.

Inspect. Check e.g. the wiring. There is a chapter on such checks in the standard ProboStat™ manual, but the main thing is that each electrode terminal on the PEEK head comes out on the right BNC centre contact, in the right order, that none of them are short-circuited to each other (except for the contact through your membrane) and that none of them are short-circuited to the chassis of the ProboStat™ base unit.

In the future, before closing, you can add more things in the ProboStat™ outer chamber, like up to two more thermocouples, gas supply tubes, etc. However, they should not be needed for normal measurements using the PEEK PEM sample holder.

Add and fasten the outer enclosing tube using the O-ring and outer flange: It is suggested to roll on the O-ring to the bottom of the outer tube before mounting it, then carefully lower the outer tube – not hooking up to springs or electrode connecting wires – and then carefully lowering the flange. Tighten the flange while holding the tube to prevent it from rotating (especially for alumina outer tubes, which have less inner diameter and where you cannot inspect if inner parts are caught up in the rotation). Note: If you are using a steel outer tube with integrated flange for high pressure, read about this and its mounting in a special section in the normal ProboStat™ manual.

6. Peripkhericals

Placement and secure fixing: Move the ProboStat™ with the sample inside the enclosing tube to the site for the measurements and fix it securely to a laboratory stand using its base unit steel bar.

Heating: If it is to be heated in a furnace, insert it and take notice of the position of the membrane sample compared to the furnace's homogeneous heat zone. If it is to be heated by a heating mantle, place the mantle over and around the outer enclosing tube. If you are using a steel outer enclosing tube (for high pressures) it must be earthed for safety against high voltages from heating elements. **Be careful and follow the process when heating for the first time:** Check that the furnace doesn't overrun because of too much power, improper PID settings, or incorrectly mounted or connected thermocouple.

Cooling the ProboStat™ base unit: A normal ProboStat™ base unit can tolerate temperatures to about 70°C, i.e. much hotter than comfortable to touch. Hence, as long as it is not warmer than you can touch, there is no need to cool it, and in fact, cooling is not beneficial (can cause condensation inside or outside). However, if it gets too hot for some reason (like very short distance to furnace, or using a steel outer tube which transports heat efficiently) you can supply cooling water to the stubs for it on the ring of the ProboStat™ base unit. Use the lower for inlet and the top for outlet. Preferably supply tempered – maybe circulated – rather than tap cold water. Read more in the standard ProboStat™ manual.

Heating the ProboStat™ base unit: If you need to measure in high steam contents, or will use other condensable gases like alcohols, you may need to let the base unit go hot, or heat it. A standard base unit should not exceed 70°C as it is limited by some connector parts. A heated base unit can tolerate up to 165°C and can be equipped with an internal heater and separate thermocouples in the base unit for control. Various designs have been sold through the years. The one sold now (2019) has the hexagonal connector box of the base unit split in two – a heated part for gas connections, and a cold part for wire connections. Read separate instructions for using heated base units.

Connect the thermocouple: The TCI-P thermocouple is connected from the bottom TCI thermocouple terminal on the base unit box via a compensation cable to a millivolt-meter or dedicated temperature readout unit or to the temperature controller for your furnace or mantle. Controlling the temperature with a thermocouple in the furnace or mantle – and using the one in the ProboStat™ just for check and readout – is safe and fast. Controlling it instead with the thermocouple in the ProboStat™ is slower (requires other PID and other parameters in the controller) and requires precautions to avoid overheating the furnace or mantle, but eventually gives you better control – you get exactly and stably the temperature you set.

Connect gas supply: If you want to control the atmosphere in the measurement chamber, connect your supply of gas to the *outlet* of the outer chamber (using a non-valve stem) and let it out through the outlet of the inner chamber. These are open quick-fits, while the two inlets are closed by default until connected with a valve stem. Hence, if you do it like this you don't need to connect and close the two remaining gas connections by separate means. Read more about gas supply in a separate section later.

Connect electrical or electrochemical measurement equipment: The PEEK PEM sample holder is made for 4-electrode measurements of in-plane conductivity of highly conducting membrane films. It is hence assumed that you have a 4-terminal device – DC (like advanced multimeters, separate current source and voltmeter, or potentiostat), AC (impedance spectrometer), or potentiostat with connected or integrated impedance spectrometer. The 4 terminals of your 4-terminal device are connected to the HC, HV, LV, and LC terminals on the ProboStat™ using BNC cables or using banana jacks via banana-to-BNC converters (supplied with many ProboStat™ systems). The ILV and ILC terminals that terminate at the feedthroughs at the pedestal are not in use with the PEEK PEM sample holder.

Set the switches on the ProboStat™ base unit correctly (see also standard manual): The switches are engaged (ON) when they point *down*.

Chassis – HCS: *Down, connected*. This connects the chassis of the base unit to the high current shield (HCS), including the base unit in the shielding system. It normally doesn't matter much since the base unit tends to be part of earth anyway through its fixation, gas lines, etc. On ProboStat™ with base unit heating, connected is *right*.

LC – HCS: *Up, disconnected.* This disconnects the LC terminal from the shielding system, meaning that the measurements are floating instead of grounded. It usually gives best performance for most measuring instruments. Only if you want grounded measurements (through a grounded LC electrode) should you switch it on (down). On ProboStat™ with base unit heating, disconnected is *left*.

Shields Bridge: If this switch exists on your ProboStat™, it must be switched ON (*down*) if you connect directly to a SI 1260 FRA or a HP 4192A or other impedance spectrometer, which explicitly needs the shields to connect together. If your ProboStat™ does not have a Shields Bridge switch it may be because it is an older version (then you may install a shields bridge wire inside it – see the standard manual) or because it is a version – like some high temperature and heated ProboStats – where the shields are permanently connected because they are not isolated from the chassis. If you are using potentiostats or electrochemical interfaces with driven shields (most of them have driven shields!) the Shields Bridge *must* be switched OFF (*up*)! If you have a ProboStat™ with permanently bridged (connected) shields (or a shields bridge wire installed inside that you don't want to take out, and you are using a device with driven shields, then connect the device to the ProboStat™ using banana jacks to banana-to-BNC converters to ensure that the shields of the instrument is not connected to the shields of the ProboStat™.

For many instruments, like DC multimeters, shields are not used, or not used in any advanced manner (not driven), and the setting of the Shields Bridge switch makes little or no difference.

On ProboStat™ with base unit heating, Shields Bridge connected is *down*, disconnected is *up*, just like on normal base units.

7. Operation and interpretation of measurements

It is beyond the scope of this manual to discuss measurements of all kinds of samples, conditions, and instrumentation, and we only make some general comments and recommendations.

7.1. *Geometry*

7.1.1. Narrow rectangle

The geometry of the standard 4-wire measurement is for a rectangle equal to or narrower than the current wires given by three factors:

The thickness t of the membrane.

The width w_c of the current path, given by the width of the rectangular membrane. This defines the current density $i = I/(w_c t)$ where I is the current.

The distance d_v between the two (inner) voltage probe wires. This defines the electric field $E = U/d_v$, where U is the voltage. This default distance is nominally $d_v = 0.4$ cm.

The measured conductance G or resistance R and the specific volume conductivity σ are then related through Ohm's law and then geometric factors as follows:

$$G = \frac{1}{R} = \frac{I}{U} = \frac{\sigma \cdot w_c \cdot t}{d_v} \qquad \text{Eq. 1}$$

or, reversely, with a bit more elaborate derivation:

$$\sigma = \frac{i}{E} = \frac{\dfrac{I}{w_c \cdot t}}{\dfrac{U}{d_v}} = \frac{\dfrac{I}{U} \cdot d_v}{w_c \cdot t} = \frac{G \cdot d_v}{w_c \cdot t} = \frac{d_v}{R \cdot w_c \cdot t} \qquad \text{Eq. 2}$$

Eq. 1 can be used to predict the measured conductance or resistance from known materials conductivity and geometry, while obviously the inverse, Eq. 2, can then be used for the calculation of conductivity from measured conductance or resistance and geometry.

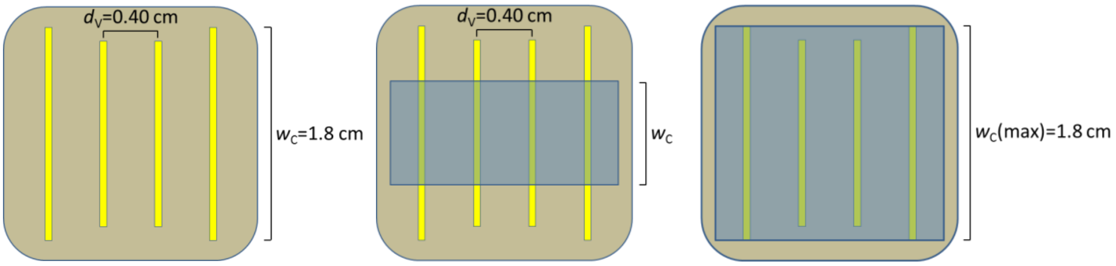

Fig.9. PEEK PEM sample holder geometries. Left: Head showing the four wire electrodes, with nominal measures. Middle: Narrow rectangular sample. Right: Rectangular sample of maximal width matching current electrodes.

7.1.2. Wider samples

For a sample wider than the current wires, the current will spread out through what is called a spreading resistance of the film, making w_c effectively larger than that given by the width of the current wires, so that only an approximate geometrical correction can be provided.

7.2. Accuracy

Usually, the *measured* conductance or resistance is very accurate. Hence, relative changes in conductivity – as plotted in an Arrhenius plot to find an activation energy – can in turn be quite accurate. But absolute values entering into conductivity and pre-exponentials of conductivity in the Arrhenius plot, will probably have the limitation in accuracy given by the geometric factors.

7.3. Parasitics

Parasitics comprise series contributions to the measured impedance (resistance) of the sample and parallel contributions to the measured admittance (conductance) of the sample. The former makes a significant contribution mainly to highly conducting samples, while the latter makes a significant contribution to samples with very low conductances. A sample with a resistance of the order of 1 kΩ will in practice not suffer any problems with parasitics, while two orders of magnitude lower or higher resistance (10 Ω and 100 kΩ, respectively) will generally start to have significant parasitic contributions.

A 4-electrode configuration eliminates the resistance in the wires, contacts, and in the electrodes, and hence eliminates most problems of series parasitics for highly conducting films.

For instance, gold foil or wire placed as sample, yields measured resistances of the order of 0.0001 Ω, only limited by the resolution of the instrument.

However, parallel parasitics cannot be avoided. This comprises in particular conduction through the PEEK block, as well as surface conduction on the PEEK surface as well as on the surfaces of the membrane sample.

We used the PEEK PEM sample holder to measure the conductance of a cast pure PBI membrane in ambient wet air using a Keithley model 6430 sub-femtoamp DC source-meter in both 2- and 4-electrode configurations, both showing resistances at room temperature of the order of 50 GΩ, i.e. 0.02 nS = 20 pS. This means that the parasitic parallel conductance of the PEEK head at RT in ambient (wet) air conservatively speaking is of the order of 0.1 nS (100 pS, 10^{-10} S).

The capacitance or dielectric constant of the thin membrane sample will be completely dominated by the parasitic parallel capacitance of the PEEK block, typically in the range of 10-100 pF.

Hence, all in all, the PEEK PEM 4-wire sample holder allows – with the appropriate instrumentation – measurements covering more than 14 orders of magnitude of resistance ($<10^{-4}$ – 10^{10} Ω) or conductance (10^{-10} – $>10^{4}$ S).

8. Special considerations and advanced topics

In this section we discuss in some detail selected special considerations and advanced topics, in a quire random order. One may also consult NORECS' web site for frequently asked questions (FAQs) and the standard ProboStat™ manual on e.g. trouble-shooting.

8.1. Gas supply

The PEEK head base is provided with grooves for gas to be able to slip through between the outer and inner chambers (outside and inside the support tube). The best way to provide a gas flow to the PEEK PEM sample holder is thus to send it in the bottom of the outer chamber, let it flow up outside the support tube, let it slip past the PEEK sample holder base and into the inner chamber, and back down and out at its bottom. Hence, one normally does not need and should not use gas supply tubes as they may create unnecessary dead-end gas volumes.

In this configuration, note that one uses both the outer gas connections as inlet and both the inner gas connections as outlet, disregarding the "In" and "Out" markings for gas connections on the ProboStat™ base unit.

One may choose which of the "In" and "Out" to use on both sides, but be aware that ProboStats by default come with valves on the inlets and not on the outlets, determining the corresponding Swagelok quick-fit stems you must use.

The best may be to split the gas line in two before entering the ProboStat™ so as to flow in through both connections to the outer chamber – this completely eliminates also the last little dead end volumes in the gas lines in the base unit. Similarly, one may use both connections to the inner chamber to take the gas out.

8.2. Electrode activation

For mainly ion conducting films, the wire electrodes may be too blocking and the resulting current too low and hence the voltage built on the voltage electrodes too small – the result will be inaccurate and noisy measurements. Moreover, if the materials tested exhibits mixed conduction (e.g. protonic and electronic), the current electrodes may selectively favour one carrier, and the resulting current, voltage built, and calculated conductivity may not reflect the true transport properties of the material. It will then be helpful to improve the kinetics of the electrodes by for instance rubbing their upper surface by very fine sandpaper, or by painting a very thin layer of an electrocatalytic paste over at least the current electrodes. This can be Ag paint, Pt black suspension, carbon nanoparticles suspension, etc. – anything that does not need a very high temperature to be cured. (For instance, Pt paints are probably not good for this purpose).

Note that one may well reorganise the wiring to an impedance spectrometer externally of the ProboStat™ so that one does a two-electrode measurement, e.g. between the two current wires. This will then contain the impedance of the electrodes, and one may monitor how large it is compared to the measured or expected bulk resistance of the film, and whether it is lowered by activating the electrodes.

8.3. Reducing noise

There are a few considerations to make and actions to take to reduce noise and get more reliable measurements – especially when dealing with high impedance samples and cases where electrodes are blocking, but also at the very lowest impedances:

Measure more slowly? Ask you instrument to integrate or average for longer times (or give you more digits or higher accuracy, which is the same thing).

Increase the voltage you apply? This increases the signal-to-noise ratio. If you are studying the bulk transport properties of a film, there is no reason to stay with the low voltages required for electrode impedance studies.

Cable length also affects measurements, keep them short if possible.

Use a metallic – e.g. steel – outer tube? This makes the cell pretty much a Faraday cage. The cell is otherwise receptive for all kinds of signals in the air including your heating system's 50 or 60 Hz (hum) current. If you are using a heating mantle, it may be beneficial to cover your outer tube with some aluminium foil during measurement, and make sure it contacts the base unit to become part of the shielding. NB: For the aluminium foil as much as the steel tube, the connection to ground earth (e.g. through the provided Earth screw terminal on the base unit) is essential to secure against high voltage crossover from the heating element in the furnace or mantle.

Ground the thermocouple? Especially when using a steel outer tube and having eliminated all external noise signals, the thermocouple may remain as an "antenna" transmitting external noise into the cell. Try to ground the negative terminal (the red-insulated Pt wire on a type S thermocouple), check that the temperature reading is not affected, and see if conductivity measurements improve.

8.4. Increasing accuracy of the geometric factor

As said, the measures of voltage electrode distance, sample thickness, sample width, and the exact orthogonal placement of the sample are limiting the absolute accuracy of the geometric factor. In addition comes how well the sample contacts the entire length of current wire along its width. Can they be improved? They can be improved by doing and measuring everything more carefully, and by calibration, but equally importantly, the accuracy can be evaluated by statistics, obtaining standard deviations and confidence intervals.

8.4.1. Statistics

The accuracy of the orthogonal placement and contact length to the current wires may be evaluated by remounting and measuring the same sample several times.

The accuracy of the thickness may be evaluated by measuring it several times or by measuring several samples of different cuts or batches.

The accuracy of the sample width should be the least problem, but may in any case be evaluated by cutting and measuring several samples.

As a suggestion, several samples cut to different widths may give both statistics of all these factors together and reveal systematic deviations, the latter expectedly reflecting variable degree of contact along the width of the current wires.

8.4.2. Calibration

Once the statistics of the other factors is under control, the effective distance between the voltage electrodes may be determined within that statistics by a standard foil of exactly known thickness, width, and conductivity.

9. Example measurements

For the following example studies, a PEEK head was mounted with 4 Pt electrode wires and connected to the ProboStat™ base unit using 4 insulated type S thermocouple Pt compensation cable wires.

9.1. Nafion® N-115 membrane

9.1.1. Sample and setup

The as-received Nafion® N-115 membrane (Alfa Aesar 0.125 mm thick) was pre-treated (activated) as reported elsewhere before test under ambient conditions [1]. One Nafion® slab 1.8 x 1.8 cm^2 was placed over the four Pt wires of the PEEK head, and measured with a Novocontrol Alpha impedance spectrometer with a ZG4 4-wire interface.

9.1.2. First 4-electrode measurement – poorly contacting, polarizing electrodes

A high oscillation voltage of 1 V (RMS) was selected to have a good signal-to-noise ratio, and AC impedance sweeps were performed in the frequency range of 1 MHz to 1 Hz. Fig. 10 shows the first Nyquist plot obtained and an equivalent circuit. The diameter of the high-frequency semicircle extrapolated in the diagram represents the bulk resistance equivalent to the polarization resistance (R_p1). The associated capacitance of approximately 70 pF is typical of bulk capacitance (here dominated by that of the PEEK parts). To obtain the bulk resistance, one may fit this semicircle, yielding approximately 1150-1250 Ω depending on whether one takes the intercept or the span of the semicircle. One may also take the point with the minimum imaginary contribution, yielding ca. 1250 Ω.

The responses at lower frequencies are attributed to effects of the electrodes. Electrode responses are in principle not expected in a 4-electrode configuration, and must be seen as an artefact of having blocking and/or capacitive current electrodes: This puts the measured current out of phase with the current passing the voltage electrodes, and yields a false imaginary response. It is these imaginary artefacts in the low frequency part of the spectrum that in turn makes it somewhat uncertain to interpret accurately the bulk resistance, and we remain with a bulk resistance of approximately 1200 Ω. The corresponding conductivity calculated according to Eq. 2 was about 0.015 S/cm = 1.5 S/m.

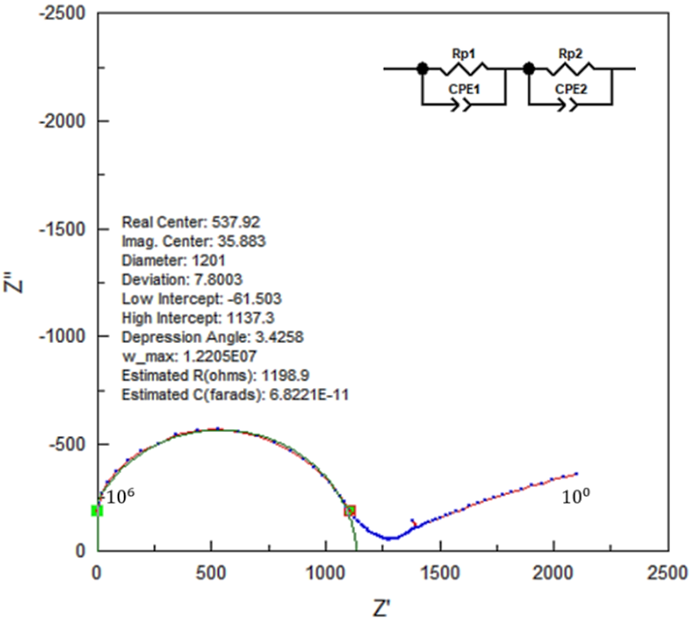

Fig.10. Nyquist plot of Nafion N-115 and its equivalent circuit in ambient atmosphere at room temperature measured by a 4-electrode configuration. The high frequency arc is attributed to the bulk response, while artefacts of the electrode responses are seen at low frequencies. The two numbers along the graph show the AC frequency range.

We attempted to measure the membrane in this state also with a 4-terminal DC instrument, but the measurements are impossible due to the polarising electrodes, and the DC voltage applied electrolysing the sample and water vapour, yielding electrochemical DC voltages that dominate over the voltages supposed to represent the ohmic drop over the voltage electrodes.

9.1.3. Two-electrode measurements

The Nafion® N-115 was measured also with a Novocontrol Alpha impedance spectrometer in a 2-electrode configuration between two and two wires at different distances (0.40, 0.80, or 1.20 cm) at two AC voltages (1 V and 0.05 V), as shown in Fig. 11, which is for the case of 0.80 cm distance. As expected, the graphs were now fully dominated by the response of the very polarising electrodes, which may be attributed to slow mass transfer such as adsorption-desorption and diffusion of oxygen on the Pt electrode as well as little contact area between the wire and the membrane. The curve for 0.05 V shows a more regular behaviour, as the electrodes then operate under more linear Butler-Volmer conditions. The intercepts at high frequencies represent the bulk resistance and were proportional to the electrode distance and in agreement with the value from the 4-point measurement.

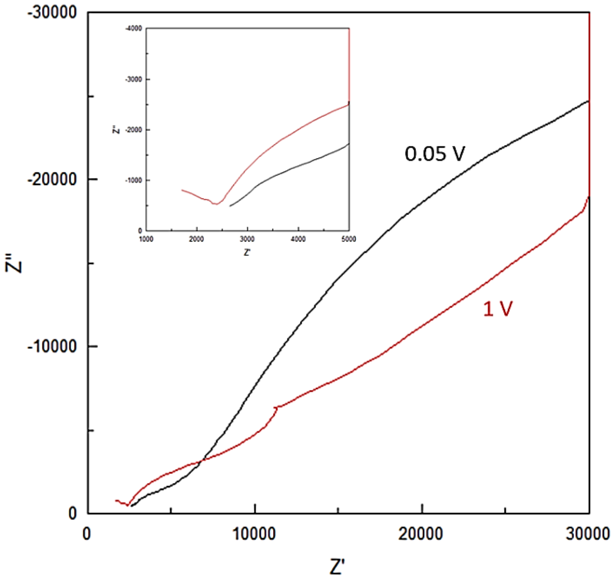

Fig. 11. Nyquist plot of Nafion N-115 measured by a 2-electrode configuration (0.80 cm distance) at 1 V and 0.05 V in ambient air at room temperature. Frequency range: 1 MHz – 1 Hz.

9.1.4. Temperature dependency

The temperature-dependence of the Nafion® N-115 membrane was investigated between RT and 160 °C in a 4-electrode configuration, over the frequency range of 1 MHz – 1 Hz at 1 V under fixed p_{H2O} = 0.026 bar. The spectra are displayed in Fig12.

The temperature was first taken to 160 °C whereafter the spectra were taken at decreasing temperatures. Firstly, we note that the room temperature spectrum shows a bulk resistance in the same order of magnitude as before (~ 910 Ω vs ~ 1200 previously). Secondly, the capacitive artefact of the electrode is much reduced, and we attribute this to a better contact grown at the highest temperature between the membrane and the Pt current wires. This gives a lower electrode polarisation, less artefacts, and possibly a better current distribution leading to the lower bulk resistance. We see finally that the determination of the bulk resistance at room temperature now can be made at a low frequency (e.g. 1-10 Hz, or even DC) while the determination previously was more challenging and required a part of higher frequencies of the spectrum, to overcome the high polarisation of the current electrodes.

At RT there were some remains of high frequency capacitive responses (semicircles), while the spectrum at 40 °C contains less of this, and this response is gone at 60°C and higher. WE attribute this to the improving electrode kinetics as temperature increases, while the bulk resistance increases.

At 60 °C and above, as bulk resistance increases and the electrode polarisation decreases, the artefactual imaginary responses gets more inductive, see the loops in the spectra. Remember that observed capacitive and inductive electrode loops or tails here have no physical meaning of their own – they just represent the fact that the current running into the current electrodes are out of phase with the current running past the voltage electrodes.

All in all, the correct bulk resistance is now easily extracted at the low frequency intercept, showing that it can be measured at e.g. 1 or 10 Hz, or simply using a 4-terminal DC instrument.

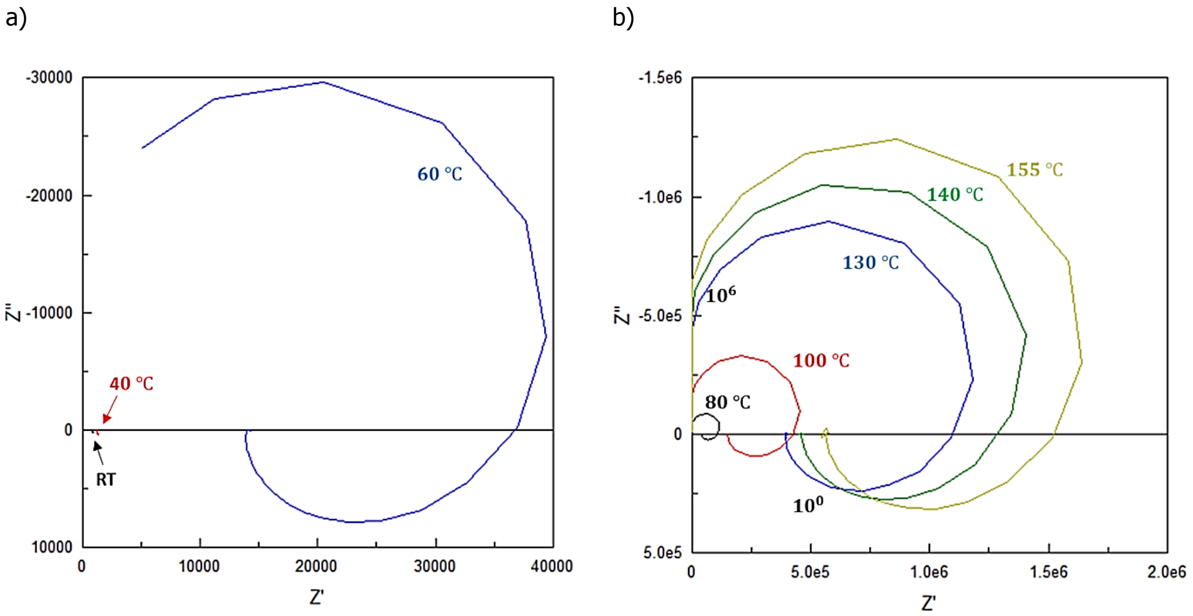

Fig.12. Nyquist plot of Nafion N-115 measured by a 4-electrode configuration at fixed partial pressure of water (pH_2O = 0.026 bar) under a) RT – 60 °C and b) 80 – 155 °C. The two numbers (in black) along the highest temperature graphs indicate the AC frequency range.

The resistance at the lowest frequency, corresponding to bulk transport, increases with temperature. The corresponding conductivities are shown in an Arrhenius plot in Fig. 13.

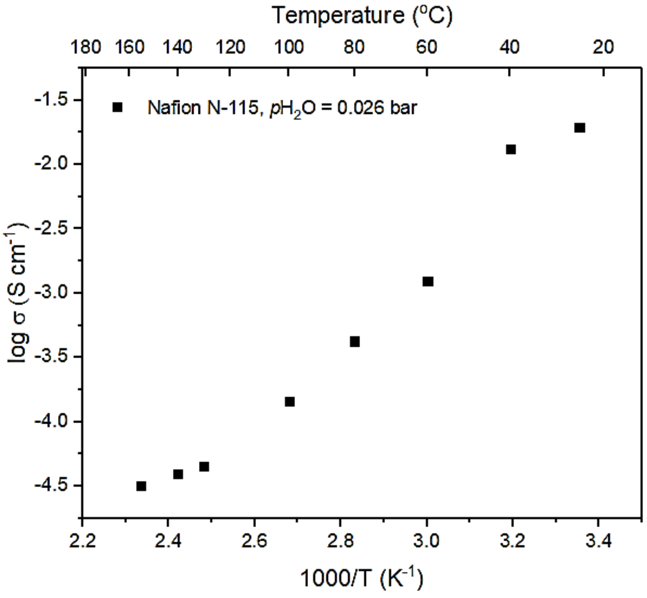

Fig.13. Log conductivity of Nafion N-115 as a function of inverse absolute temperature at constant partial pressure of water.

The conductivity decreasing with increasing temperature may be attributed to the loss of water in the membrane due to the decreasing relative humidity (RH). This lowers the mobility of the protonic charge carriers in the water channels of the membrane.

All in all, in comparison with the first measurement, we see how the high temperature has improved the electrodes, making the measurements more easy to interpret. The same may be achieved by catalytic pastes etc.

9.2. Undoped PBI membrane

We used the PEEK PEM sample holder to attempt to measure the conductance of a cast undoped PBI membrane (24 ± 2 µm thick) in ambient wet air at room temperature using a Keithley model 6430 sub-femtoamp DC source-meter in both 2- and 4-electrode configurations, both showing resistances of the order of 50 GΩ, i.e. 0.02 nS = 20 pS. This is probably affected by the parasitic parallel conductance of the PEEK head at RT in the ambient (wet) air. However, if we assign the measured values to the PBI membrane and the geometry of the film is applied, we obtain a conductivity around $2*10^{-9}$ S/cm = $2*10^{-7}$ S/m.

9.3. Gold (Au)

9.3.1. Gold wire

A gold wire of 0.5 mm diameter was placed across the four Pt wires of the PEEK head. The resistance measured using a micro-ohm-meter model 34420A 7½ Digit in 4-wire mode was 0.000496 Ω. Using a variation of Eq. 2 for wire sample,

$$\sigma = \frac{d_{\mathrm{v}}}{R \cdot \pi r^2} \qquad \text{Eq. 3}$$

where *r* is the radius of the wire (*r* = 0.25 mm), the conductivity was calculated as $4.11*10^5$ S/cm = $4.11*10^7$ S/m, in exact agreement with literature values, such as $4.11*10^7$ S/m [2]. The main errors will be the exact values of the thickness of the wire, the distance between the voltage electrodes, and the orthogonality of the placement of the wire.

9.3.2. Gold foil

A gold foil 1.8 x 1.8 cm^2 of thickness 30 ± 2 µm was placed over the four Pt wires of the PEEK head, and the resistance was measured using an Agilent model 34420A 7½ Digit micro-ohm-meter in 4-wire mode. The measured resistance was within 0.00027 – 0.00041 Ω. The variations resulted from each time the sample was assembled in the setup, and seemed somewhat sensitive to spring load force and balance. The use of various soft layers on top of the foil as well as various plates of varying flatness and surface finish was expected to have an influence on how well the foil contacted and spread the current along the length of the current wires, but had little effect. A better effect of reducing the measured resistance was achieved by wiping the surface of the Pt current wires clean with a fine sand paper, but the values were still about a factor 2 too high to agree with the conductivity of gold. We conclude that for a material as conductive as gold, the contact resistance along the current wire is determining the spreading of the current in the foil, and the use of a metal with medium conductivity and tendency of oxide layer formation, like Pt, is not ideal for this.

The gold foil was measured also with a Novocontrol Alpha impedance spectrometer with a ZG4 4-wire interface. The measurements were at moderate to low frequencies reflecting approximately the resistances achieved with the DC meter (e.g. 0.00025 Ω) while at higher frequencies they were dominated by series sample and parasitic inductance. This shows how an impedance spectrometer and AC measurements can well measure down to low resistances and give additional information about capacitive and inductive effects, but remain inferior to specialised DC equipment when it comes to very low resistances, like in many metallic samples.

Another gold foil 1.8 x 1.0 cm^2 (which corresponds to the middle case in Figure 9) of thickness 28 µm ± 2 was placed across the four Pt wires of the PEEK head. The resistance was measured with the same instrument again in 4-wire mode, showing a stable value of 0.00049 Ω. By inserting in Eq. 2, the conductivity of the gold foil was calculated to be $2.9*10^7$ S/m, which is 1.4 times lower than expected. The result confirms that the geometry of the measurement for such very highly conducting foils must somehow be optimized by improving the contact through the length of the current wires, but that the problem diminishes as the foil gets narrower.

References

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2. Serway, R.A., *Principles of Physics (2nd ed.)*. 1998: Fort Worth, Texas; London: Saunders College Pub. p. 602. ISBN 978-0-03-020457-9.