Manual
ElyFlow

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1 Electrochemical test cells

One uses the three-electrode setup in order to characterize electrochemical processes. A potentiostat or galvanostat controls these kinds of measurements. (Figure 1). The three-electrode setup consists out of a working electrode, a reference electrode or sensing electrode and a counter electrode or auxiliary electrode.
Almost one century ago the Reference Electrode has been standardized. Usually one has to choose the Hydrogen electrode. More often a AgCl or HgCl electrode is used, but causes a correction of the potential with respect to pH value or temperature different to 25°C.
Unfortunately the three-electrode setup has never been standardized. Therefore, there are several – even commercial – test set ups available. But most of them have several serious mistakes.
Due to our long time experience in fuel cell and battery research as well as in corrosion tests we have constructed successfully a test setup which overcomes all these well known errors:

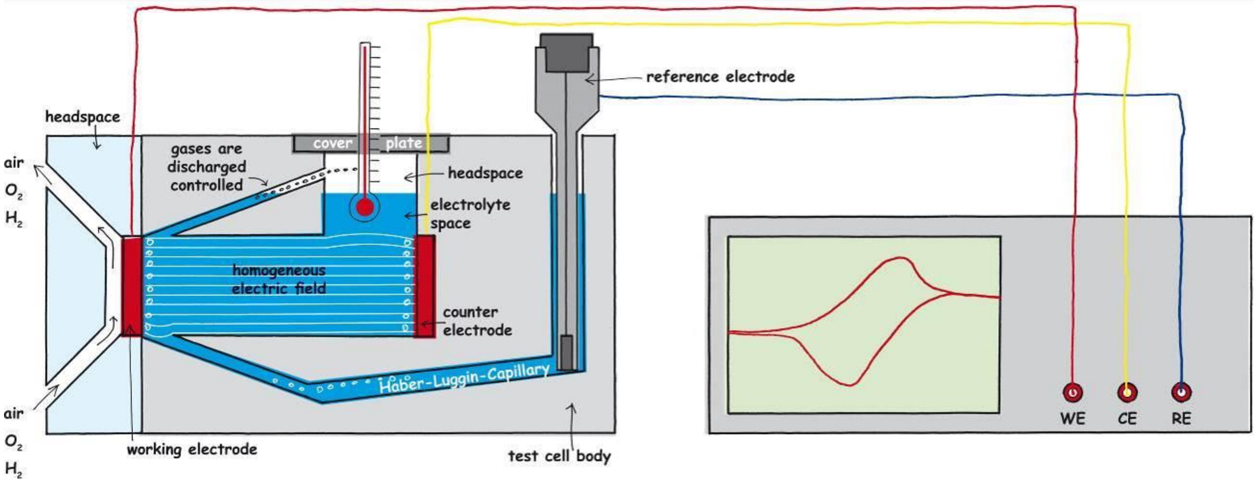

Figure 1: Sketch of an electrochemical test cell with the connected Potentiostat.

Here is a list of the most common errors:

- Reference electrode. Often one uses AgCl or HgCl reference electrodes. These kind of electrodes are pH independent, whereas your working electrode depends usually from the pH. This leads to a numerical correction of the measurement value with sometimes unknown factors. The hydrogen electrode compensates these influences.
- Field line: The field lines should be in parallel. Otherwise the equipotential lines are not in equal distance from the surface of the probe and the position of the reference electrode will have a serious influence. Only in a tube shaped set up with identical surface areas of the counter electrode and the working electrode a parallel field line distribution is guarantied.
- Haber-Luggin capillary. With the Haber-Luggin capillary one can reduce the ohmic drop of the electrolyte. In order to have similar results with different test cells the position of the capillary should be fixed and very precise. This is not manageable with the material glass. In a plastic body fabricated by CNC the precision is much better.
- Gas bubbles: If there are gas bubbles at the probe one creates local elements. Gas bubbles in the Haber-Luggin capillary may increase the impedance of the reference electrode circuit dramatically and this would lead to noisy signals of the potentiostat. Therefore, the Haber-Luggin capillary of the Gaskatel set up is filled with a solid electrolyte.

- Crevice corrosion: if the sealing of the sample is not perfect, the electrochemical reaction may take place underneath the sealing or even outside of the active area.

A proper sealing is essential. Oxygen access should only happen in a controlled matter, not because of improper sealings.

- Reaction products of the counter electrode. Often the counter electrode is the anode. That means one creates there very oxidising ions. Depending from the electrolyte this could be peroxides, perchlorate, persulfates etc. Even the smallest amount of these ions coming to the working electrode may initiate heavy corrosion processes. Therefore, we offer an additional plate to place a membrane between working and counter electrode.
- Glass as construction materials. Glass is quite durable. But usually silicates go into solution. Especially with high pH values this effect is well known. But also for light sensitive electrolytes or very poor conducting electrolytes glass is an insufficient construction material. The test cells form Gaskatel are out of PTFE. They may be cleaned in even concentrated nitric acid.

2 ElyFlow versus FlexCell

Gaskatel has launched almost 5 years ago the FlexCell electrochemical test cell. What is now the difference between ElyFlow and FlexCell, and why do we launch this new kind of electrochemical test cell?

- Active area: ElyFlow has an active area of 10cm² in comparison to the smaller FlexCell 3 cm². This would therefore be the next step when applying electrodes into a technical size.
- Electrode spacing: ElyFlow has a distance between working and counter electrode of

20 mm in comparison to the larger value of 70 mm in FlexCell. This allows you to work with less conductive electrolytes, or you may increase the current density, if you potentiostat is limited so small voltages (for example 6 V).

- Electrolyte flow: there is an electrolyte inlet with a three nozzles on each side, spreading the electrolyte flow towards the working and counter electrode. At the electrolyte outlet there is a cavity for the collection of the electrolyte flow and a controlled removement of gas bubbles coming from the electrochemical process.
- Electrolyte quantity: by pumping the electrolyte into an additional reservoir one may extend the test duration with the test cell.
- Renewing the electrolyte may be important during for example electroplating process like in galvanic industry or conversion of the electrolyte from for example phosphate to formiate or carbonate (CO_2 reduction process).

3 Detailed view

Some pictures of the cell are shown in Figure 2. They are explained more in detail in the following sections.

3.1 Counter electrode

The delivered counter electrode is a 99,98% Nickel Anode B59 from Yamamoto. You may use another standard Counter electrode 64 x 64 mm² B59 from Yamamoto (Hull Anodes) out of different materials:

- Nickel
- Carbon
- Copper
- Titanium
- Platinized Titanium

See https://yamamoto-ms.co.jp/en/product/b-59/ for further details.

The counter electrodes are connected by two gold plated 4 mm banana plugs from the back side. (see Figure 2, bottom right: cables from the right side)

3.2 Heating

Inside of the electrochemical cell there are PTC heating elements – they heat the counter electrode from the back side. The supply voltage should be in between 12 V and 24 V. The power supply should have a power of at least 100 W. Without further control the PTC heating elements will then adjust a temperature of 100° C in the PTFE test cell.
If you plan to work with different temperatures please use the Gaskatel temperature control box to adjust the power output of the power supply. The heating element PTC is shown in top left of Figure 2.

3.3 Reference electrode

The reference electrodes insert is made with a G 1/8 thread for our Hydrogen reference electrode (RHE) Mini-Hydroflex. This is shown in Bottom right (5) of Figure 2.

3.4 Haber-Luggin capillary

The Haber-Luggin capillary ensures the electrolytic contact between reference and working electrode. The following requirements belong to the capillary:

- No disturbance of the field lines (small diameter).
- Low electrolyte resistance (large diameter).
- Position very close to the working electrode.
- Insensitivity towards gas bubbles, which may block the capillary.
- From the standpoint of quality control the capillary has to be produced and positioned always in the same way.

You can see the very small opening of the Haber-Luggin capillary in Bottom left (4) of Figure 2.

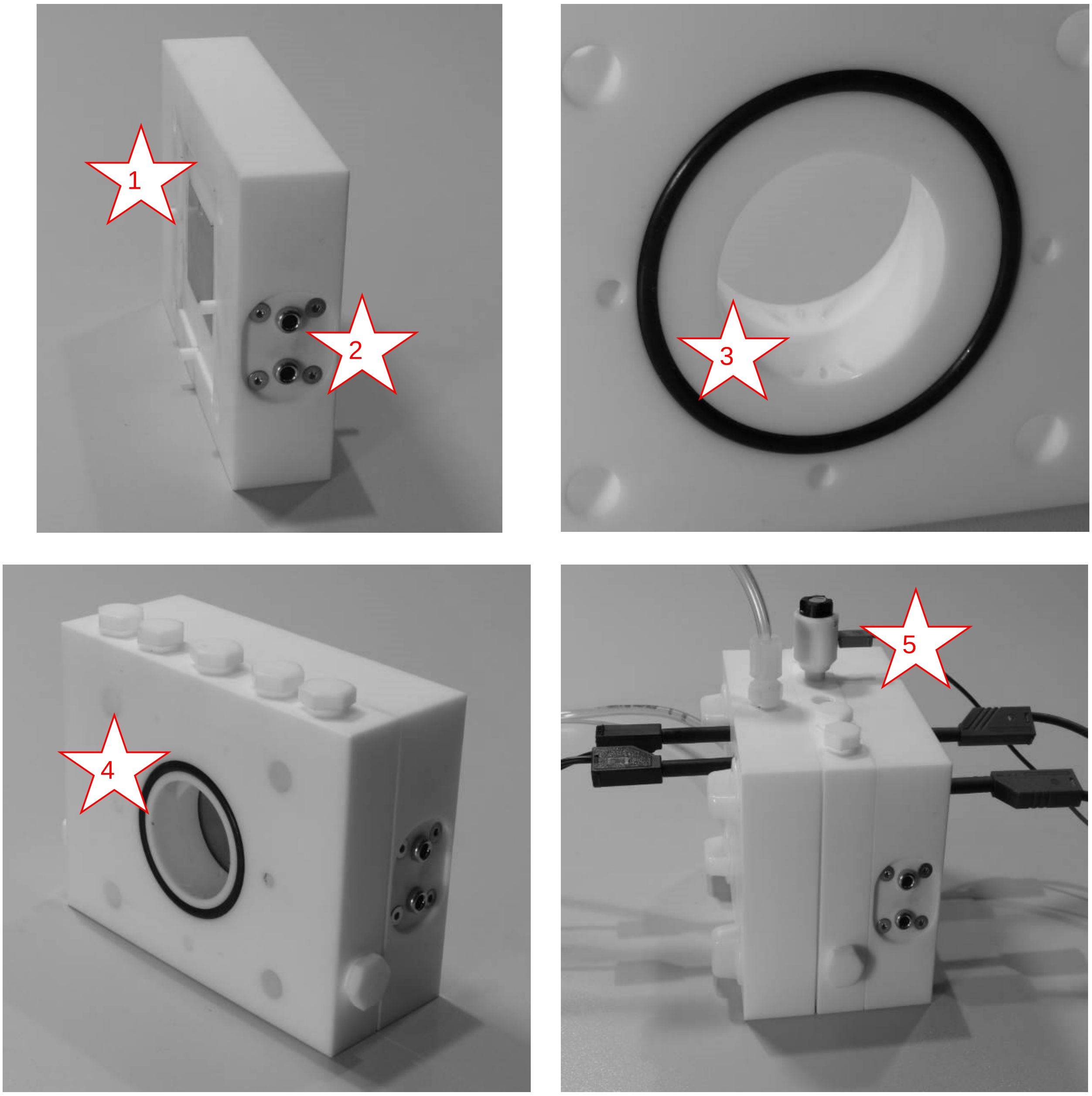

Figure 2: Top left: (1) heating element, (2) 4mm plug for heating power supply, Top right: (3) electrolyte inlet nozzles, bottom left: (4) Haber-Luggin-capillary, Bottom right: assembled cell with mounted Mini-Hydroflex reference electrode (5)

3.5 Electrolyte compartment

The following requirements belong to the electrolyte compartment:

- No disturbance of the field line distribution between working and counter electrode.
- Low water vapour loss.
- Pumping of electrolyte through the cell from the bottom to the top. Quantity <0.1 l/min preferred.

This is achieved by a tubular electrolyte compartment, covered on both sides with counter electrode and working electrode of the same size.
The electrolyte compartment has a round shaped active area of 10 cm². They are tightened towards the counter electrode with a O-ring.

The thickness of the electrolyte compartment is about 20 mm and the diameter 35,6 mm. There are integrated two Haber-Luggin capillaries half way up located very close to the working electrode.
Furthermore there is an electrolyte in- and outlet in order to allow an electrolyte flow through the cell. The electrolyte inlet is divided into 6 small nozzles facing directly towards counter and working electrode. The electrolyte outlet is at the top oft he cell provided with a cavity ensuring the removement of gas bubbles coming from the electrochemical reaction inside of the cell. This is shown in the schematic drawing of Figure 3.

1. PTFE electrolyte compartment
2. PTFE G1/8 plugs for additional devices as RHE, PT100, Pump
3. ECTFE tube connector for pumping electrolyte through the cell
4. EPDM seal on Haber-Luggin capillary side
5. EPDM seal on back side of the compartment
6. Pins for mounting the electrodes respectively membranes

In the cross section of this electrolyte compartment (Figure 4) it is shown:

- Thread G1/8 for electrolyte inlet (from above insert of PT100).
- Insert of Hydrogen Reference electrode with Haber-Luggin capillary.
- 3 nozzles for electrolyte spreading.
- Cavity a the electrolyte outlet.

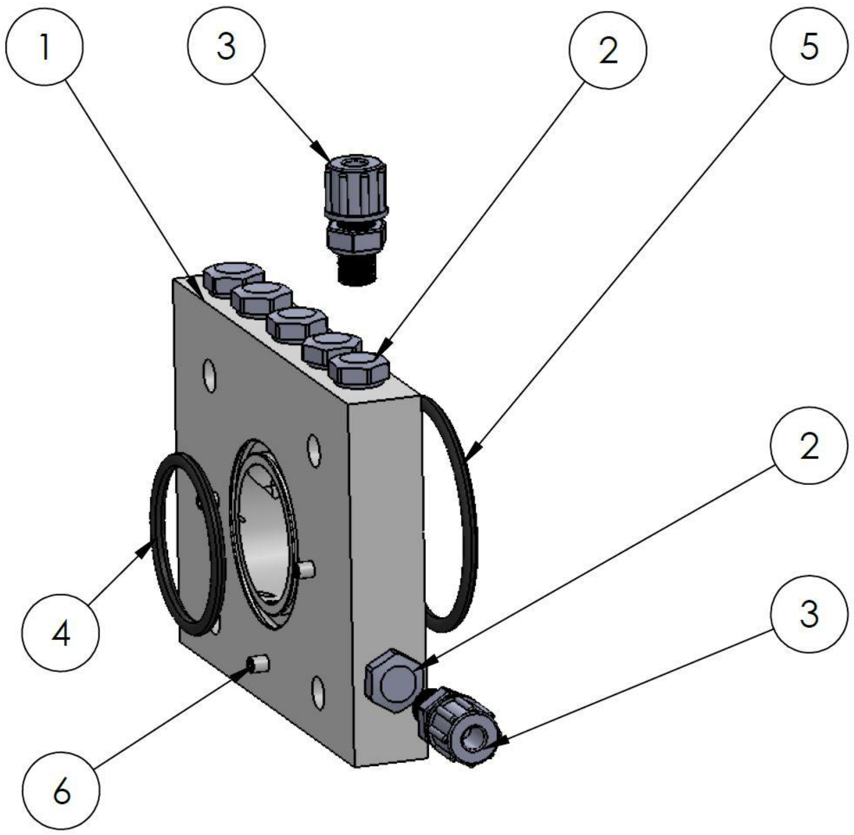

Figure 3: Schematic drawing of the analyte compartment

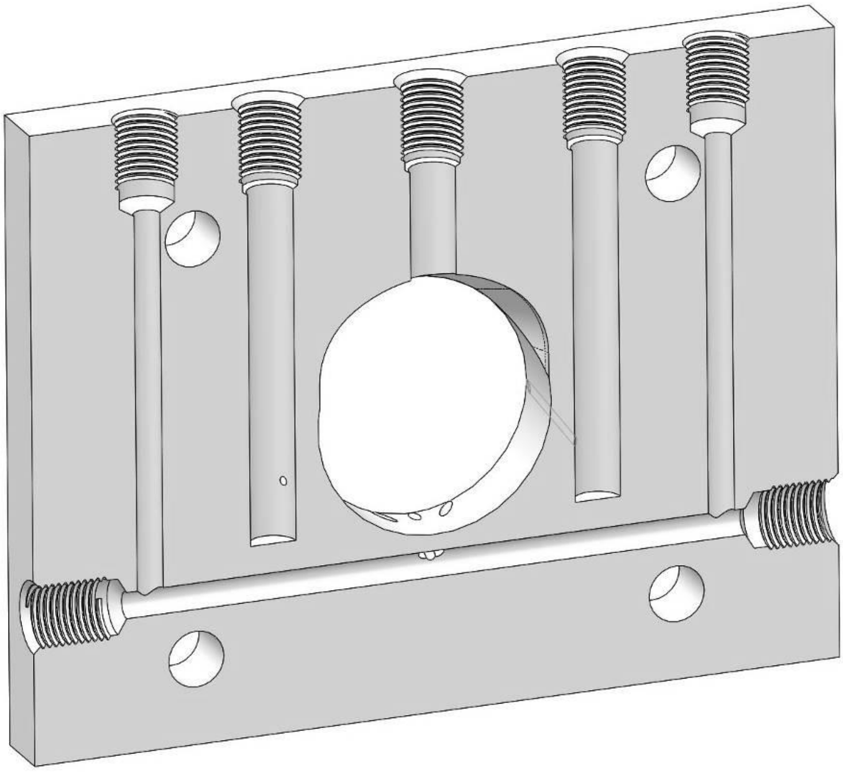

Figure 4: Cross section of the electrolyte compartment

3.5.1 Two electrolyte compartments

In the case of reactions products from the counter electrode will interfere with the working electrode, you should insert a second electrolyte compartment with a membrane separating counter electrode from working electrode.
Membranes are any kind of porous diaphragm or ion exchange membranes.
The electrolyte compartment with the Haber-Luggin capillary is still facing towards the working electrode in order to measure the potential of the working electrode with almost negligible IR drop.

3.5.2 Membrane resistance

As each electrolyte compartment has Haber-Luggin capillaries, you may use two electrolyte compartments for measuring the membrane resistance.

In order to measure the voltage drop across the membrane both electrolyte compartments have to be positioned in a way, that both Haber-Luggin capillaries will face towards the membrane.

The voltage drop across the membrane is taken as the difference of the both reference electrodes inside of the Haber-Luggin capillaries.

3.5.3 Hydrogen permeation

Hydrogen uptake and permeation is a critical effect on the mechanical stability of some metals (iron and copper based materials) during electrochemical processes.
If you like to measure the Hydrogen permeation of your conductive probe please insert this in between both electrolyte compartments.
The conductive material (working electrode) has to be cutted in a dimension of 65 x 90 mm².
You have to contact this material by alligator clamps from the top of the cell.
The AE electrode of the charging cell may be one of our below mentioned counter electrodes.
The AE electrode of the oxidation cell is a gas diffusion electrode acting as the oxygen electrode of a fuel cell. The Working electrode (your sample) acts as a hydrogen electrode. You may measure the permeating Hydrogen amperometric by discharging this oxidation cell (fuel cell)

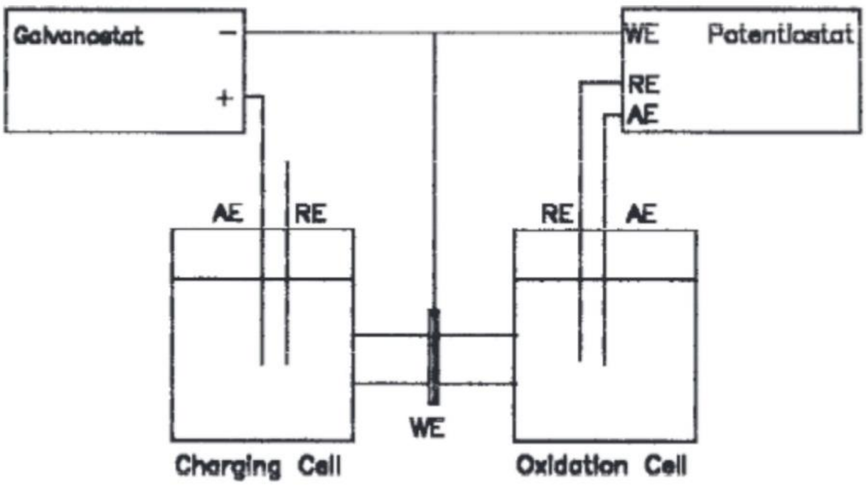

Figure 5: Figure taken from ASTM G148

3.6 Working electrode

The Working Electrode is placed in between two EPDM O-ring seals. You should cut the electrode to the dimensions.

64 x 70 mm

Then it fits perfectly in between in 3 FEP pins in the cell.

If your working electrode is a gas diffusion electrode with a non-conducting gas diffusion layer (porous PTFE) you should remove the PTFE layer at the top of the electrode, in order to ensure the contact plugs will touch the working electrode.
For the use of gas diffusion electrodes you may use your mass flow controller (if available) or you may order very precise micro valve from Gaskatel.
If you are looking for other geometries simply remove the 3 FEP pins out of the cell.
The working electrodes are connected by two gold plated 4 mm banana plugs from the back side.

3.7 Gas compartment

When characterising gas diffusion electrodes, one has to supply the GDE with gas. This is managed by the additional gas compartment with two:

- Gas inlet (top).
- Gas outlet (side).

The gas compartment is made out of PTFE.

3.8 Seals

We have implemented O-Ring seals out of EPDM in each compartment

3.9 Temperature measurement

We offer a 3-wire PT100 sensor with PTFE insulation, fitting into the electrolyte compartment.

3.10 Temperature control

You can adjust the temperature in your ElyFlow cell with our temperature control box.

3.11 Pump and reservoir (coming soon)

Pumping hot and often corrosive electrolyte in lab size is not an easy way. There are some commercial pumps available you may use: Membrane pumps, hose pumps and impeller pumps. When using hose pumps you should use EDPM or FKM tubes, In the case of membrane pumps the preferred materials are PP or PTFE for the housing and EDPM or FKM as a membrane material.
Gaskatel is offering a membrane pump out of PP housing and EPDM membrane with an internal regulated power supply.

3.12 Complete cell control / data acquisition (coming soon)

The complete cell control comes with a USB connection to your computer and a free software GCB control.The technical datas are as follows:

- Current supply 0 - 5 A.
- Volts up to 24 V.
- Two temperature control units.
- Potential measurement -1,9999 to +1,9999 volts.
- Additional sensor input for example for pressure sensors (volt or ampere signal).

4 Setting-up operation

4.1 Operating conditions

Nominal voltage

The nominal voltage applied between working and counter electrode must be below 50 V of alternating current and 75 V of direct current. The maximum power load is 5 A.

The nominal voltage applied to the PTC heating elements must not exceed 24 V of direct current.

Nominal current

The maximum approvable electrical current between working electrode and counter electrode is determined by the boiling point of the designated electrolyte and must not exceed 5 A. The brought in volume of electrolyte in relation to the yielded Joules heat determine the maximum heating up rate and end temperature, which must be below boiling temperature in any case. Please note that the Joules heat adds to a sum of environmental temperature, cell heating and the product of cell current and cell voltage.

Pressure range

At the gas inlet the maximum applicable pressure is 200mbar. Common operating pressure is well below the bubble point of the electrode.

Temperature range

The designated operation range of the half cell is respectively +160°C (PTFE)

4.2 Warnings

Hot surfaces

The cell heaters and / or the applied cell current can heat up the half cell far beyond 80° C. Do not place heat sensitive things on the half cell. Do not place inflammable things near the half cell. Pay attention to a correct lining of your measurement and heating cable. Select cable insulations with a reasonable temperature specification. Else there is a risk of an electrical shortcut and fire hazard.

Laboratory use

The half cell is defined solely for use in a laboratory environment. The laboratory environment must be conform to the safety data sheets and specifications of your electrolyte.

Protective equipment

The operator of the half cell must be dressed with adequate laboratory protective equipment according the safety data sheets and specifications of your electrolyte.
A pressure surge on the gas inlet or reach of boiling point may lead to electrolyte sputtering out of the half cell. Electrolyte vapour according vapour pressure curve is being emitted permanently by the half cell.

Prevention from leaking Electrolyte

The half cell shall be placed and operated in a catch basin, with is capable of safely carrying the complete filled in electrolyte volume in case of a leakage.

Distance to electrical / electronic equipment

Electrolyte vapour according the vapour pressure curve are constantly being emitted by the half cell. Safeguard electrical / electronic equipment by large distance, partition barriers or operating in a fume cupboard.

4.3 Assembly

Insert of the working electrode

- Cut the electrode: width. ~6,5cm, length ca. 7 cm / thickness variable.
- The active area is 10 cm².
- Unscrew the contact screws a little bit until the screws do not contact the working electrode.
- Insert the electrode or the EPDM O-Ring seals.
- Tighten the cell with a plastic wing screw equally not to leave a gap (just the thickness of the working electrode).
- Tighten the contact screws with the socket wrench until you receive a good contact.

Connecting the peripherical

In Figure 2 the electrochemical test cell with reference electrode and connecting wires is shown.

- Insert the reference electrode.
- Fill into the electrolyte compartment about 25 ml electrolyte. Use the closing plug in the cover plate. Check whether you observe also electrolyte in the reference electrode compartment. If necessary fill in also some electrolyte with a pipette into the reference electrode compartment.
- Connect the potentiostat / galvanostat.

4.4 Operation

If running the cell at higher temperatures than room temperature be aware of water vapour losses. We recommend a maximum time of 24 h. The maximum current of the cell should not exceed 3 Ampere.

Apart from that the cell may be used under conditions where the following materials:

- Main body material PTFE.
- O-Ring-seals EPDM.
- Gas compartment PTFE.

4.5 Purchased parts package

- Counter electrode compartment out of PTFE.
- DBK heating elements inside of counter Ni counter electrode 10 cm² gold plated male connector 4 mm.
- Electrolyte compartment with Haber-Luggin capillary 1 mm ± 0.12 mm.
- Solid state electrolyte inside of Haber-Luggin capillary.
- 2 EPDM O-Rings for other working electrodes.
- Gas compartment.
- Pipe fitting for tubes with 4 x 6 mm.
- Socket wrench.
- DBK PTC heating elements.
- 2 red cables for the working electrode.
- 1 black cable for the counter electrode.

5 Trouble Shooting

Error	Possible reasons	Check
Cell temperature does not exceed 100°C	Contact problems	Cable from power supply to heating elements
	PTC heating element defect	Measure the resistance of the single elements, it should be around 13 Ohm
Potentiostat indicates over voltages	Contact wires	Check the wires of the potentiostat
	Counter electrode	Disassemble and check connections
Wrong potential	Gas bubbles in front of reference electrode	Move the reference electrode in the compartment a little up and down
	Gas bubbles in Haber-Luggin capillary	Remove some electrolyte out of the reference electrode compartment with a pipette
Noisy signal	Impedance of the reference electrode or Haber-Luggin capillary too high	Current range of the Potentiostat
		Insert the intermediate plate and place the reference electrode in
Electrolyte loss	Plastic wing screws not tightened	Tighten the plastic wing screws
	O-Ring damaged	Check the position of the contact screw and the positioning pens

Table 1: Possible errors with test cells.