

Concentration cell sensor using solid electrolyte support tube

The use of controlled atmospheres during measurements at high temperatures is a specialty of the ProboStat. Nevertheless, the establishment of controlled atmospheres is not entirely trivial. This is mainly done before the gas enters the ProboStat, and may require one or more of prefabricated gas mixtures, gas mixing, total pressure control, electrochemical pumping, wetting, and drying and other filtering/gettering.

We will here contribute with suggestions and advice on some of these topics.

Oxygen activity control and monitoring

In order to control p_{O_2} one usually uses mixtures of O_2 and an inert gas (e.g. Ar, N_2) for relatively oxidizing conditions, $CO+CO_2$ mixtures for more reducing conditions and H_2+H_2O mixtures for even more reducing conditions. In both the latter types of mixtures, additions of inert gas (e.g. Ar) can be done to lower the activity of carbon and hydrogen without, in principle, affecting the oxygen activity.

Monitoring of p_{O_2} can be useful to check the actual activity, to provide feedback to a mixing or pumping system, or to provide information of instantaneous p_{O_2} in transient experiments. However, one should be aware that monitoring methods may have flaws just like control (mixing and pumping) methods.

Systems may be built with different levels of sophistication. For instance a gas containing water vapour or CO_2 may be led through three cells: The first has an oxygen sensor and an oxygen pump by which an appropriate amount of oxygen is pumped in or out to reach the desired p_{O_2} . The second cell has the actual sample and is where the measurement is done. The third has a sensor where the p_{O_2} of the gas leaving the measurement cell is monitored, as a check. One or more of the sensors may be integrated with the measurement cell if possible.

However, most users will settle with a simpler system, using a mixing or pumping stage and one sensor.

Integration of sensors in a ProboStat

Integration of sensors that are to be placed in the high temperature zone, close to the sample, is not part of the standard furnishment for ProboStats. However, the versatility of the ProboStat offers several ways of including sensors:

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The most obvious type of sensor is a tube of yttria stabilized zirconia (YSZ) or other solid electrolyte. Two of the ProboStat electrode connections are used to measure the voltage over the sensor tube, while 2, 3, or 4 electrode connections are used to measure the sample in 2-, 3-, or 4-electrode geometry. The inner gas supply is used for a reference gas for the sensor (e.g. air) while the outer gas is used for the sample compartment that is monitored by the electromotoric force of the sensor.

The solid electrolyte tube functions as a support tube for the sample in this setup, and one may for instance use a small alumina cylinder and plate to form a platform for a disk sample on top of the usually rounded electrolyte tube end.

The spring load of the ProboStat holds the sample and its electrode contacts in place and also the top electrode of the solid electrolyte tube.

The inner electrode of the solid electrolyte tube is contacted using the hose compression force via the inner gas supply tube, as in normal ProboStat operation.

The solid electrolyte tube must be equipped with electrodes; this is typically done by painting with Pt paste. On the inside this can be tricky. Be aware that solid electrolyte tubes such as YSZ are very expensive and very vulnerable to mechanical and thermal shocks and thermal gradients compared to e.g. alumina tubes.

One may use two thermocouples to ensure that the temperature inside the sensor tube is close to that outside. If using only one thermocouple, care should be taken to ensure thermal homogeneity throughout the sample and sensor area.

The setup of such a cell requires adjustment of wire lengths and some special use of electrical feedthroughs, but is otherwise straightforward. The sensor signal may for instance be taken out on feedthrough 10 (TCT-) vs feedthrough 2 (TCB-). One must be aware of the limitations in the accuracy of YSZ as sensor electrolyte, and of the cost of the YSZ tubes.

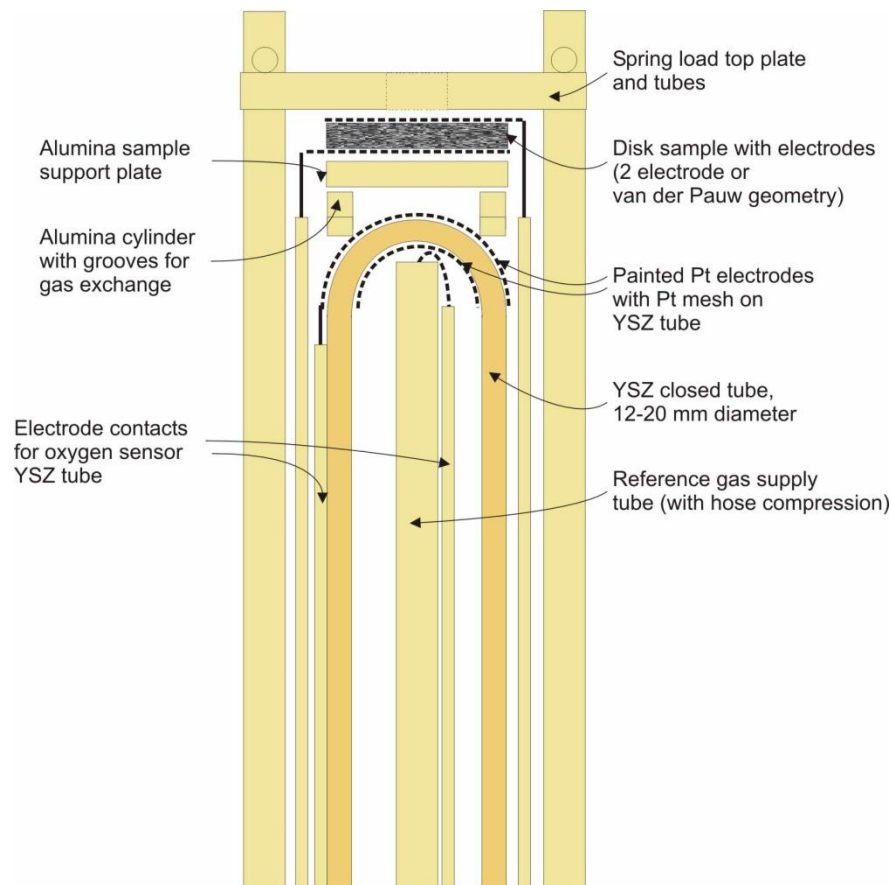


Figure 1. Suggested schematical setup of ProboStat with YSZ sensor tube as support tube. Measurements on disk sample can comprise up to 4 wires (e.g. 2-electrode or van der Pauw measurements) provided sensor connections are taken out through used TCT thermocouple feedthrough. Outer enclosing tube, outer gas supply tube, thermocouple, and base unit are not shown for clarity.



1. Insert the inner electrode contact into the inner gas tube. Estimate the length so that the electrode contact touches the inner wall of the YSZ tube when mounted.



2. Mount the YSZ sensor tube. Be careful in order to prevent scratching of the inner electrode by the inner electrode contact.



3. For connecting to the outer electrode, use a GP1 1.5cm longer than standard. Bend the Pt wire all the way over the top of the sensor tube.



4. Place the alumina cylinder with grooves on top of the tube. Make sure that the Pt wire is firmly pressed down by the cylinder.



5. Place the sample support plate well aligned on top of the alumina cylinder.



6. Bend one 2-wire hand electrode contact with Pt net (H2N20) carefully on top of the support plate. It will now serve as the lower electrode contact for the sample.



7. Place the sample on top of the hand electrode contact.



8. Bend the upper hand electrode contact (H2N20) carefully on top of the sample. Then connect the thermocouple (TCC/D).



9. Mount the spring load assembly. Use preferably soft springs. Check that the setup is well aligned. Cover optionally the thermocouple tip by the thermocouple cap.



10. The outer gas tube can now be mounted (here, the bent quartz model).



11. Finally close the outer gas compartment by mounting the outer tube.

Figure 2. Step by step example setup of ProboStat with YSZ sensor tube as support tube.

Other types of sensors

Resistance-type sensors

By using two or four of the otherwise unused electrode or thermocouple connections one may include a 2- or 4-electrode resistance-type sensor. These are not commercial, but NorECs and others are working on the development of these.

Sensor/pump inserted through a top-flange in an open-end outer tube

One may use an open-end enclosing tube and use a flange (e.g. a separate ProboStat unit) to insert a sensor or pump this way, approaching the sample from the top.

Sensor/pump attached to the gas stubs (from version A6).

From the ProboStat version A6 the center gas stub is detachable (threaded) and similarly one or two detachable stubs (by sliding O-ring seals) can also be attached to the outer chamber. Onto these can be glued YSZ tubes of inner diameter 4 mm and outer 6 mm. If equipped with Pt electrodes, an electrode connect on the outside, contact to the inner electrode via a noble metal wire fed through the gas connect, and a reference gas, sensors and pumps can be envisaged.

Separate ProboStat units used for sensor/pump applications

One may of course use a separate ProboStat unit in its own furnace for sensor or pump applications, using closed YSZ tubes and/or resistance-type sensors.