

Design of sample holder for *in operando* XAS of oxidation state changes in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ electrodes

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Abstract. The design and construction of a sample holder for *in operando* X-ray absorption spectroscopy on solid oxide electrodes, like for instance the lanthanum strontium manganite electrodes, is explained. The sample holder is mounted in a test-cell, which is also described together with some preliminary test-results from temperature measurements and electrochemical characterisation performed on a “dummy” sample in the test cell. The test-cell is a modified version of a test-cell previously designed in our laboratory, and will in the future be used for X-ray absorption experiments on solid oxide electrodes.

1. Background

The perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ (LSM) has found application as electrode material in solid oxide electrochemical cells, like the solid oxide fuel cells (SOFCs), solid oxide electrolysis cells (SOECs) and cells for electrochemical gas purification. During several decades extensive research has been conducted on LSM, including work on electrical properties [1], defect chemistry [2] and the influence of electrical polarisation on segregation in LSM electrodes [3]. An overall tendency today in the research on LSM electrodes and solid oxide electrodes in general, is an increased interest in studying the electrodes at realistic operating conditions, i. e. *in operando*, or at conditions close-to realistic operating conditions, i.e. *in situ*, with optical/spectroscopic methods. For *in operando/in situ* studies the use of X-ray absorption techniques has great advantages, as they in contrast to many other analytical methods do not require vacuum conditions. The challenge in performing *in operando/in situ* studies of solid oxide electrodes is the need for operating the electrodes at elevated temperatures (300-900 °C), in controlled atmosphere and with electric contact, while still maintaining the optical access to the electrodes. To meet these requirements a careful design is necessary for any test-cell and sample holder for *in operando* studies of solid oxide electrodes. The design of a test-cell for *in operando* X-ray absorption spectroscopy of solid oxide electrodes has been described by Hagen et al. together with preliminary test-results [4]. This paper describes the design of a new sample holder for a test-cell, which is a modified version of the test-cell described by Hagen et al. [4].



2. The design of the test-cell.

The test-cell is intended for measurements in fluorescence mode, as both sample thickness and the mounting of the sample on a heat-stage make measurements in transmission mode impossible. In order to make it easy to transport the cell between different synchrotron facilities, the test-cell has a fairly compact design, with the dimensions of the main house being 8 cm x 12 cm x 12 cm. In the following the main house of the test-cell, the sample-holder and the sample, which in the future will be measured in the cell, will be described in more detail.

2.1 The main-house

The main house is made of aluminium and has a removable front plate and back plate for easy access to the sample in the inner of the house. On the two opposite sides of the test-cell are X-ray windows, and a gas inlet and a gas-outlet made with standard fittings. The front plate is dominated by a large window, 9 cm in diameter, to allow for detection of the fluorescence signal from the sample. The small X-ray windows on the sides of the house and the big X-ray window in the front is made of Kapton® foil which is clamped between the front-plate/metal rings and the main-house together with O-rings to secure the sealing. Figure 1 shows a schematic drawing of the cell design, and a front view and a side view image of the cell.

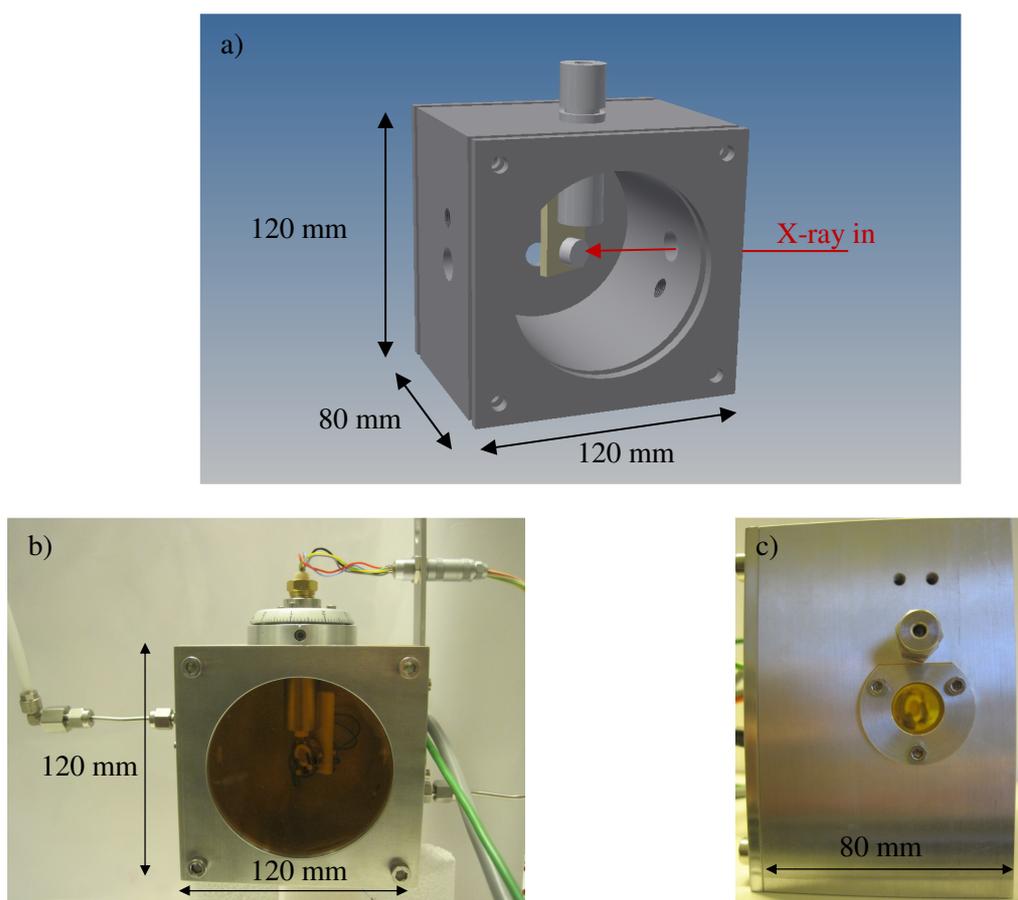


Figure 1. Illustrations of the test-cell for *in operando* X-ray absorption spectroscopy on solid oxide electrodes, a) schematic drawing, b) front view image and c) side view image.

2.2 The sample holder

The sample holder is a hollow stainless steel rod, on which a heat-stage is mounted. The stainless steel rod is mounted through “the roof” of the test-cell, where an O-ring between rod and house secure the sealing. The steel rod is turnable, meaning the angle between the incoming X-ray and the sample may be adjusted, and the actual angle may be read of on a scale ring on top of the house. In the bottom of the steel rod, inside the main house, the heat-stage is mounted. Rather than mounting the heat-stage directly on the steel rod, the heat-stage is mounted in an alumina plate mounted in the rod. This design is made to lower the heat transfer from the heat-stage to the steel rod. The heat-stage (Heatwavelabs) is made of alumina and has a diameter of 0.5”. The sample is mounted on the heat-stage with an alumina ring and to small clamps and Au mesh is used as current collector (CC) on the front side of the sample while painted Au is used for current collection on the back side.

Through the hollow middle of the steel rod is mounted a 6-hole alumina tube. This tube guides 4 leads for electrochemical characterization and 2 leads for a thermocouple to the sample on the heat-stage. The leads for electrochemical characterization are connected to a Gamry Ref600 potentiostat, thus making electrochemical characterization and electrical polarization of the sample possible. On Figure 2 is shown a close-up of the sample holder.



Figure 2. Close-up of sample mounted on sample holder. The sample is mounted below the Au mesh current collector, which is fastened to the sample by two clamps and an alumina ring.

2.3. The sample

Thin oxide films (100-1000 nm thick) are widely used as model electrodes, to study the electrochemical processes occurring in solid oxide electrodes [5]. Similarly, in the test-cell described here, thin film electrodes will be applied to monitor the effect of the electrical polarisation on the manganese oxidation state in the LSM electrodes. According to theory cathodic polarisation of LSM electrodes will cause an increase in the number of oxygen vacancies, accompanied by a decrease in average oxidation state of the manganese to retain charge neutrality [6]. Orikasa et al. [7] very briefly reported experiments, confirming this theory, but as the observed effect was close to the uncertainty of the experiments, a repetition of the experiments and confirmation of the results is desirable.

In the test-cell described here, the sample will be an electrochemical cell, (10 mm x10 mm x 0.5 mm) with 3 layers: one thin-film LSM electrode, an YSZ single crystal electrolyte, and on the opposite side of the electrolyte a porous LSM-CGO composite electrode. The porous composite electrode is used, as this electrode has a significantly lower polarisation resistance compared to the thin-film electrode. This means electrochemical impedance spectra recorded on the electrochemical cell will be entirely dominated by the thin film electrode, and thus changes in thin film electrode induced by the electrical polarisation will be detectable both on the electrochemical impedance spectra and in the X-ray absorption spectra.

3. Preliminary measurements in the test cell

So far, the described test cell has not as intended been used for X-ray absorption experiments on thin film LSM electrodes. However, preliminary tests of the cell's capability to control the sample temperature has been made, and the feasibility of performing electrochemical measurements in the cell has been investigated, in both cases using a "dummy sample" consisting of a YSZ single crystal with painted Pt electrodes on side. The results are reported in the following two sections.

3.1. Temperature control and measurement

There are three different ways to evaluate the temperature in and near the sample: a) By the thermocouple inside the heat-stage, this thermocouple is used to control the heat-stage temperature, b) By the thermocouple mounted near the sample, or c) From the ohmic resistance of the YSZ single crystal electrolyte of the sample. The latter is easily measured by electrochemical impedance spectroscopy, and from the YSZ ohmic resistance the temperature may be calculated from the correlations found by for instance Cheikh et al. [8]. It is believed using the ohmic resistance is the most accurate way to measure the sample temperature, as the method determines the temperature in the sample. In contrast, the thermocouple measurements may be inaccurate as the thermocouples either not are contacting the sample directly or by contacting the sample might affect the actual sample temperature. In Figure 3 the temperature of a dummy sample determined from the ohmic resistance is plotted as a function of the heat-stage temperature measured by a thermocouple. The difference between the heat stage temperature and the sample temperature increases from 40 °C to 125 °C in the range 400 °C to 700 °C, which is ascribed to contacting problems between sample and heat stage and heat loss from the sample to the surroundings.

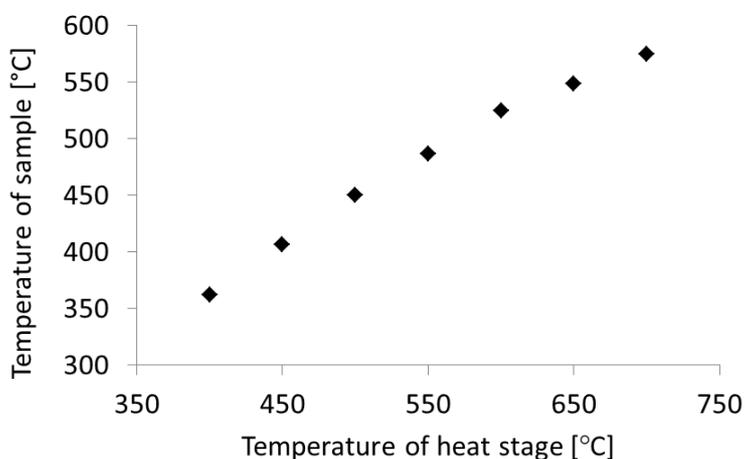


Figure 3. Temperature of a sample as function of the heat stage temperature. The sample temperature was determined from the ohmic resistance of the YSZ electrolyte, while the heat stage temperature was measured by a thermocouple mounted inside the heat stage.

3.2. Electrochemical test on dummy sample

To check the feasibility of performing electrochemical measurements in the test cell, electrochemical impedance spectroscopy was conducted on the dummy sample consisting of a YSZ single crystal with a Pt electrode on each side. As seen in Figure 4, a nice impedance spectrum was obtained, confirming the test cell can be used for electrochemical characterisation.

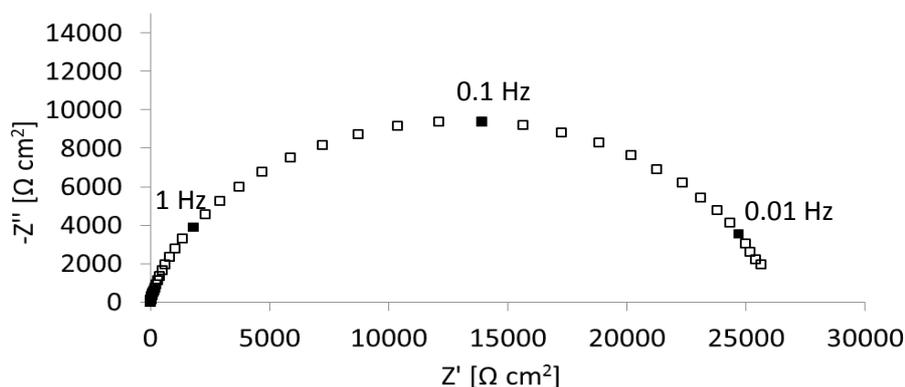


Figure 4. Electrochemical impedance spectrum recorded in the test cell on an electrochemical cell with a YSZ electrolyte and two Pt electrodes. The sample was at 525 °C in a gas flow of 50 ml/min 4% O₂ in Ar.

4. Outlook

The construction of a sample holder for *in operando* XAS on solid oxide electrodes has been described together with a description of the applied test-cell. It has been confirmed the cell is capable of controlling the sample temperature and preliminary electrochemical measurements has been made. The test-cell is a modified version of the cell previously used and described by Hagen et al. [4]. In the near future the cell will be used for *in operando* experiments on LSM thin film electrodes. The outcome of the experiments will hopefully be experimental confirmation of a decrease in the average manganese oxidation state during cathodic polarisation of LSM electrodes, as predicted by theory and indicated by the experiments by Orikasa et al. [7].

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