Controlled Atmosphere High Temperature SPM for electrochemical measurements

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Abstract. A new controlled atmosphere high temperature SPM has been designed and build for the purpose of performing electrochemical measurements on solid oxide fuel cell materials. The first tests show that images can be obtained at a surface temperature of 465°C in air with a standard AFM AC probe. The aim is to produce images at a surface temperature of 800°C with electrically conducting ceramic probes as working electrodes that can be positioned at desired locations at the surface for electrochemical measurements.

1. Introduction

Solid oxide fuel cells (SOFC) and electrolyzer cells (SOEC) are all solid devices under development for electrochemical power conversion of gaseous fuel to electricity and vice versa. Both may be based on the very same cell operating at temperatures between 500 and 1000°C. The performance of the cells is mainly limited by the electrodes.

The structure of the composite electrodes consists of a three dimensional structurally stabilizing network of an oxide ion conducting phase and a second network of an electron conducting electrode phase. The electrochemical reactions take place at the three phase boundary between the electrolyte, the electrode and the supplied gas. The grain sizes are in the range of 1 μm and there is thus a multitude of contact points between the two phases.

Electrochemical tests of cells and model electrodes average over these points or alternatively over areas of a few hundreds of microns in diameter. Microstructures can only be studied after the electrochemical tests have been performed and proper samples have been prepared. This does not allow any detailed study of the dynamic interaction, which takes place at elevated operation and fabrication temperature.

The exact mechanisms for the electrode processes have not yet been fully established. We believe that the study of interfaces between the electrode particles is the key to understanding the composite electrodes. Monitoring the development of surfaces exposed to high temperatures and in-situ selecting points for electrochemical characterization are important aspects necessary for the detailed investigation of electrode processes. Other properties such as sintering, cohesive forces and contact area size are also of interest and should be studied as a function of time, temperature, contact pressure and atmosphere.
The aim with the CAHT-SPM is to be able to study surfaces at 800°C which is around the operation temperature for solid oxide fuel and electrolyzer cells. We report on the initial tests and experiments with the CAHT-SPM where we successfully have obtained AFM images at a surface temperature of 465°C in air.

A study of the literature reveals that high temperature atomic force microscopy studies are commonly performed on polymer materials at temperatures typically up to 130°C or in a special case up to 233°C [1-6]. One example was found where 400°C was reached but this was with samples much less than half a millimeter laterally [7]. No references to higher temperatures could be retrieved.

The CAHT-SPM will, by being able to perform atomic force microscopy at higher temperatures, make it possible to study surface properties of a much larger group of materials than polymers.

2. Description of the CAHT-SPM

The CAHT-SPM consists of a detector part and a scanner part (Figure 1). The laser-probe-detector is a fixed system. The CAHT-SPM is designed to high temperature measurements, up to 800°C, and only materials stable at high temperatures are used.

![Figure 1](image.png)

Figure 1. An image and a sketch of the CAHT-SPM showing the basic elements.

The shield between the scanner part and the detector part can be water cooled and the quartz window can easily be replaced. The sample is placed on a steel cylinder, which again is placed in a small furnace that is located at the largest possible distance from the piezo translator. The sample is kept in place by three springs. Five thermocouples can be placed at desired locations e.g. the piezo translator, the sample surface and the probe.

The samples may be up to 2 mm in thickness and 1.5 cm in diameter. The maximum scan area is 100 µm by 100 µm and the Z-range is 30 µm. The sample and the probe can be viewed by two cameras during operation; one is a top view CCD camera, which is also used when adjusting the laser light on the probe. The second CCD camera shows a side view image of the sample and the probe and is especially useful when manually adjusting the sample height.

It is possible to use both standard AFM probes and custom designed probes. The aim for the desired high temperature electrochemical measurements is electrically conducting ceramic probes. The probe holder is designed to accommodate probes which are up to 1 mm in width and up to 9 mm in length. Custom designed probes made of an electrically conducting ceramic material that can withstand the high temperature will be fabricated and used.

Electrical and electrochemical measurements can be performed with the probe as the working electrode, and with the possibility to apply large forces to the probe in order to make good contact with the substrate.
For mounting samples, probes and placing thermocouples, the detector part can be lifted off and placed bottom up next to the scanner part. This allows for easy access and working space for all procedures.

The CAHT-SPM is equipped with an inlet and outlet for gasses such that any controlled atmosphere can be used.

3. Results

The sample was in all cases a 2 mm thick, disk shaped (Ø=1.5 cm) ceramic sample made of Sc-Y-stabilised zirconia (Sc-YSZ). The sample was heat treated for 10 hours at 1700°C, which produced grain sizes around 10-30 microns and ensured structural stability of the surface at all experimental temperatures.

3.1. Probe instability due to heat

The thermal expansion of the probe material is an important factor that can influence image quality at high temperatures. The stability of the probe was studied by monitoring the movement of the reflected laser beam on the detector. The probe was left away from the sample surface and the furnace was heated to a temperature of 300°C. This resulted in a temperature of the probe of 61°C and a sample surface temperature of 232°C. The sample underside is then 263°C. These temperatures are stable with time within 1-2°C. Figure 2 shows a graph of the temperature and the X and Y movements (as voltages) of the laser spot with time. It was found that under the above mentioned conditions it takes approximately 5 hours before the voltages are stable. It is possible to acquire images during the stabilization period but they may show effects of the movements.

3.2. Temperature gradients

The temperatures of the piezo translator, the probe and both sides of the sample have been measured as a function of the temperature set point of the furnace (Figure 3). The bottom of the sample is situated on the steel cylinder in the furnace. Heat loss from the sample to the surrounding atmosphere can take place from the sides and surface of the sample. At a furnace temperature of 600°C the difference between the furnace and the sample surface is about 170°C. For a 2 mm thick ceramic Sc-YSZ sample, there is a gradient across the sample of 80°C. The temperature of the piezo translator is 66°C for a furnace temperature of 600°C and is thus about to become critical.

3.3. First high temperature images

Figure 4 shows a reference image obtained at room temperature. A weak pattern of the interference between two frequencies caused by vibrations is present in the image but it does not influence the basic results of the experiment. All temperatures referred to are sample surface temperatures.
Two high temperature experiments have been performed. The first ran to a sample surface temperature of 360°C. Severe disturbances were found in the scanned images at temperatures above 290°C. They were found to be related to thermal vibrations of the standard AFM DC probe. Below 290°C the acquired images were similar to Figure 4. Between 233°C and 290°C the grain boundaries were still visible but the images were becoming more and more blurred. The scan area was, however, stable with time once temperature was reached. The setup was left at high temperature overnight, and the images obtained after a quick probe change were better than the day before (Figure 5).

![Figure 4. The Sc-YSZ surface at 26°C.](image)

![Figure 5. The Sc-YSZ surface at 290°C. Notice the different scan area.](image)

The second experiment could be taken to a much higher temperature due to the use of a standard AFM AC probe. The AC probe is shorter and thicker than the DC probe. Unfortunately the probe was slightly damaged early in the experiment. Thermal expansion between room temperature and 276°C caused the sample to touch the probe. Images could, however, be obtained even though the quality was less than desired. Figure 6-Figure 9 show the images from the second experiment. Figure 4 is still the reference room temperature image.

Grains, grain boundaries and grooves with the same degree of details are found in all images. At temperatures above 400°C the silicon probe started to deposit material. The time for stabilization at the different temperatures has not been long enough to reach thermal stability. At 465°C the piezo translator reached a temperature around 80°C and very little time was spent at this temperature before cooling was initiated.

4. Discussion
The very first images made at high temperature with the CAHT-SPM show the recognizable pattern of grains and grain boundaries with grooves even though the probe was damaged. The degree of details is satisfying for the initial testing but the surface structures are very coarse. More testing on the resolution at high temperatures will be performed to explore the limits of the SPM.

The CAHT-SPM in the present state can be operated at temperatures up to 400°C in air. Higher temperatures will require a probe of a different material and some cooling or insulation to keep the temperature of the piezo translator down.

Thermal stability takes several hours to establish. Drift of the sample during heating of the surface prevents making images until the furnace temperature and sample surface temperature are stable. It is highly likely that drift compensation must be implemented even though similar images can be acquired a short time after the furnace has reached its set point.
Conclusion

It is possible to obtain high quality images with the CAHT-SPM at high temperatures. The resolution is less than for conventional SPM but sufficient for the tasks, which the CAHT-SPM was designed for. There are still some problems to overcome such as stable probes and reducing the piezo translator temperature, and there is a large number of testing experiments to be performed with respect to the possibilities of the CAHT-SPM. The first results are, however, very encouraging for the further use.

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