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Scanning Probe Microscopy at 650°C in Air

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High temperature surface imaging with atomic force microscopy (AFM) is usually performed at temperatures up to 130°C on polymer materials. Only a few references are found on AFM at higher temperatures, e.g., Ref. 5, where 400°C was reached, and the very first results are reported here. Recent advancements have made it possible to study surfaces at temperatures at least up to 650°C in air at a resolution below 500 nm for contact mode measurements.

High temperature surface imaging with atomic force microscopy (AFM) is usually performed at temperatures up to 130°C on polymer materials. Only a few references are found on AFM at higher temperatures, e.g., Ref. 5, where 400°C was reached, and the very first results are reported on AFM at 500°C in air, where atomic force resolution was reported by Broekmaat et al. Several techniques for the characterization of the electrical properties of surfaces in combination with a scanning probe microscope (SPM) exist. The method used for the generation of electrical property images in the present article corresponds to the nanoimpedance microscopy technique described in Ref. 7.

The results reported here are the imaging capability at 650°C and the simultaneous acquisition of topographical and electrical data from the surface area.

Experimental

The controlled atmosphere high temperature scanning probe microscope (CAHT-SPM) was designed for in situ study of electrical/electrochemical properties of surfaces at elevated temperatures in a controlled atmosphere especially with regard to solid oxide fuel cell (SOFC) electrodes. The main purpose of this instrument is to enable a study of chemical and physical properties of surfaces down to a scale corresponding to single particles of the porous composite electrodes. These are usually of submicrometer size. It is intended to perform a variety of electrical/electrochemical experiments, and the very first results are here reported. Recent advancements have made it possible to study surfaces at temperatures at least up to 650°C in air at a resolution below 500 nm for contact mode measurements.

Conductivity imaging was performed with a setup similar to that used in Ref. 8. The conductivity was determined by an ac signal in the range of 1–10 kHz with a suitable amplitude. The ac signal was passed from the generator output of the lock-in amplifier (Stanford Research Systems, SR 830) through the probe and the spring-loaded platinum counter electrode into the current input of the lock-in amplifier. With a scan rate of 256 pixels/s, the time per pixel was 4–40 full periods, and a sufficient signal to noise ratio could be achieved with a filter time constant of a few milliseconds without reduction in the image quality.

The voltage read from the color scale in the images was proportional to the current through the probe. Thus, the color scale could read as a conductivity scale. Due to differences in tip dimensions, conductivity values could only be compared qualitatively from image to image.

Results

Figure 1 shows conductivity images of the sample with the gold pattern. At 225°C, the conductivity image shows straight edges (Fig. 1a). The first sample in the present work was a polished and sintered stabilized zirconia (SZ) disk with a 250 μm thick NiO/SZ support on both sides. The dimensions of the cell were 5.0 × 5.0 × 0.5 mm. The symmetrical cell was mounted in a special stainless steel sample holder where the cell was positioned in a slit. The cell was polished on end such that a cross section of the cell could be analyzed in the microscope. The sample holder was then mounted in the furnace.

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The current amplifier analog output giving the real part of the probe current was fed into an auxiliary input of the CAHT controller, and a conductivity image supplementing the topography image was obtained.

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Figure 1. Conductivity images (a) at 225°C, (b) 650°C first scan, and (c) 650°C second scan 30 min later. Image parameters: Scan speed of 25 μm/s, resolution of 256 × 256, and frequency of 10 kHz.
A polished cross section of a symmetrical cell are shown in Fig. 3. As time and temperature increase, the edges become wavy. Figure 1b shows the first scan at 650°C, and Fig. 1c shows the second scan 30 min later. Shortly after this, the gold pattern breaks up into irregular areas.

Figure 2 shows images of the thermally etched SZ sample acquired at 650°C. Comparing the topographic and conductivity images, the grain boundary pattern is reproduced precisely. The grain boundary consists of two shoulders and a groove in which the gold is high compared to that of the SZ. Furthermore, in situ measurements of a very mobile surface can be depicted with nanoimpedance microscopy at 650°C.

The conductivity images of the thermally etched SZ presented show that grain interiors have a higher conductivity than grain boundary regions. During heat-treatment of SZ impurities accumulate at surfaces and in grain boundaries.9,11 and grain boundary conductivity depends on the amount of impurities.9 The surface distribution of impurities on SZ heat-treated at high temperatures has been imaged with time-of-flight secondary-ion mass spectrometry12 and depth profiling shows that the grain boundaries are rich in impurities. This distribution of impurities may be a determining factor for electrical properties found with the CAHT-SPM.

Symmetrical cells are used in the SOFC research for electrochemical and microstructural studies on porous electrodes as they resemble, in composition and structure, the electrodes on full cells. The conductivity image of the symmetrical cell shows that the CAHT-SPM can visualize electrical features that cannot be distinguished in the topographical image. The complex microstructure of the electrodes and support layer is reproduced, and features below 500 nm can be distinguished.

**Conclusion**

The results presented above demonstrate the capability of the CAHT-SPM to image surface topography at 650°C. The results also show that the CAHT-SPM can be used for electrical measurements with the probe and can scan the surface simultaneously for topographical and electrical data. The resolution is currently below 500 nm.

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