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2016

Ng, C. S., Baek, J. D., Zade, V., Villegas, A., Lee, T.-H., Su, P.-C., . . . Lee, M. H. (2016). Scanning probe-based in situ high temperature electrical and electrochemical measurements in atmospheric pressure. *ECS Transactions*, 72(28), 11-20. doi:10.1149/07228.0011ecst

<https://hdl.handle.net/10356/85348>

<https://doi.org/10.1149/07228.0011ecst>

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Scanning Probe-based *in-situ* High Temperature Electrical and Electrochemical Measurements at Atmospheric Pressure

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Atomic force microscopy (AFM)-based study of electrical and electrochemical properties of a material/system at an elevated temperature in atmospheric pressure has been limited to ~250°C in conventional AFM setups. In this report, we have demonstrated the viability of a new approach for high temperature electrical and electrochemical studies (up to 700°C) in a conventional AFM setup by employing a combination of a micro-heating stage (MHS) and custom-made all-metal tips. We present the design, fabrication process and characterization of the MHS and the all-metal tip. A temperature dependent impedance measurement on an MHS-integrated half-cell was then successfully demonstrated with a custom-made Pt-Ir tip. Issues and possible room to improve regarding the new approach are also discussed.

Introduction

The bulk property of a material is a combination of its local properties. In a microscopic view, local properties of a sample can be distinctly different from one region to another. To further understand the electrical and electrochemical properties of a system affecting the macroscopic properties, it is often important to directly characterize the properties of interest in a highly localized manner. One of the examples is ionic transport property of solid oxide electrolytes, in which grain region is known to have substantially higher ionic conductivity than their interfaces or grain boundary regions¹. Another example can be found in the oxygen reduction reaction (ORR) on oxide-based electrolytes. Despite earnest efforts to elucidate the ORR process on solid electrolytes in the last century, there are still many uncertainties remaining even for the Pt/yttria-stabilized zirconia (YSZ) system, one of the most well-studied system². Although an electrochemical reaction is intrinsically a nanoscale process, most studies have relied on bulk-type (i.e., area-averaged) measurements²⁻⁵. Direct nanoscale observations will be highly valuable in clarifying the remaining uncertainties such as the effective width of triple phase boundary⁶⁻⁸ and impact of defects on reaction kinetics. True nanoscale *in-situ* observations of oxygen transport and reaction may promote clearer understanding of these phenomena and potentially lead a breakthrough.

In order to understand highly localized transport and electrochemical properties of these materials, AFM can be used to characterize the local electrical signals on the

material using a conductive probe. To achieve proper measurements of oxygen transport and ORR kinetics on an oxide electrolyte, a very high temperature $> 500^{\circ}\text{C}$ is needed. Assuming a Pt tip is in contact with a YSZ (the most widely used oxygen-conducting solid electrolyte) with an estimated contact radius of 10 nm, in excess of 10 G Ω of resistance is expected at such a low temperature. However, a resistance of $\sim 1\text{ M}\Omega$ is expected at 500°C , well within the measurable bandwidth considering the usual stray capacitance of AFM systems (10 - 100 pF)⁹. Despite the need for an operational temperature of $> 500^{\circ}\text{C}$ for these studies, this is intrinsically very challenging in a conventional AFM setup because considerable heat convection occurs from the hot chuck to the AFM cantilever and scanner due to the large size (cm-scale) of heating chuck. The cantilever is subject to thermally-induced vibration/deflection at this high temperature, which results in an unstable tip-sample contact. Heated scanner may cause unexpected non-linear positioning and malfunctions. These limit the maximum allowable temperature only up to $\sim 250^{\circ}\text{C}$ in a non-vacuum environment. The high temperature operation is also expected to cause significant tip degradations. It is known that the melting temperature of a metal decreases sharply as the size reaches critical dimension (usually $< 50\text{ nm}$).¹⁰⁻¹² Given that commercially available conductive tips are usually coated with $\sim 10\text{ nm}$ thick metals on Si-based probes, it is not surprising to see a partial evaporation and/or peel-off of the metal at high temperatures.

In order to overcome these issues, in this report, we prepared a micro-heating stage (MHS)¹³⁻¹⁵ with an area roughly a million times smaller than that of a conventional AFM heating stage to minimize this thermal convection issue. A variety of thin film heating devices has been realized on a Si platform for different applications such as sensors¹⁶⁻¹⁸, micro-fluidity device¹⁹ and phase change memory device²⁰. Electrical current is flown through a patterned resistive element made of noble metals, oxides or doped Si to incur Joule heating. Lee *et al.* reported a micron-scale Pt heater patterned on top of a phase-change memory element demonstrating a rapid heating up to 700°C in 50 ns¹⁵. In another study, Broekmaat *et al.* used a Pt heating filament embedded in a $2 \times 2\text{ mm}^2$ of ceramic plate to reduce the total heating power by locally heating up the sample²¹. We leveraged these studies to design and implement a MHS-integrated solid oxide half-cell. We also fabricated AFM probes made of all-metal to avoid the peel-off issue during high temperature operation. A temperature dependent impedance measurement on an MHS-integrated half-cell was then successfully demonstrated with a custom-made all-metal (Pt-Ir) tip. Issues and possible room to improve regarding the new approach are also discussed.

Design and Fabrication

Figure 1 shows a conceptual drawing of an MHS-integrated AFM measurement on solid oxides. The narrow metal pattern (the shaded area in the figure) acts as a micro-heater. A bilayer of oxide/metal deposited on top of this heater serves a solid oxide-based half-cell, and a conductive AFM probe can be used a mobile/nanoscale electrode. In this experimental section, we present the fabrication of micro-heater integrated half-cell chips and all-metal AFM probes, and share a preliminary high-temperature EIS measurement using this setup in AFM.

Figure 1. A conceptual drawing of the intended high temperature AFM setup. A nanoscale metal/oxide/metal cell (implemented by the conductive AFM tip/oxide/back electrode) sits on a micro-heating stage passivated by a Si_3N_4 layer.

Figure 2. (a) The schematic drawing of the chip design. A YSZ/Pt BE bilayer sits on a micro-heater. Between the Pt BE and Pt-based micro-heater, a Si_3N_4 layer is added to prevent electrical cross-talk. (b) An optical image of a fabricated chip. (c) A photograph of the chip mounted on the AFM sample holder.

Design and Fabrication of Micro-Heating Stage

A schematic drawing of the samples with an MHS is shown in Figure 2(a). On top of a SiO_2 (400 nm)/Si wafer, a patterned Pt thin film (200 nm thick) was deposited as the heating element. The temperature of the heating element is measured *in-situ* from its

electrical resistance value by utilizing the fact that the electrical resistivity of a metal increases with temperature²². After characterizing the relationship between the electrical Pt resistance and temperature in a fabricated MHS, we could obtain the temperature of Pt heater element by measuring its electrical resistance. For an accurate measurement of electrical resistance through the heating element, electrical leads for 4-probe measurement were incorporated in the chip design. P3 and P4 shown in Figure 2(a) are the two electrical leads for flowing currents to incur Joule heating while P1 and P2 are for measuring the voltage drop (and thus the temperature) across the heating element. On top of this micro-heater, a half-cell (i.e., a 200 nm thick YSZ layer on a Pt-based back electrode) was deposited. P5 in the figure is the electrical pad leading to the Pt back electrode (BE). It is noted that an AFM tip will act as the working electrode. To prevent electrical crosstalk between the half-cell and its underlying heating element, a layer of silicon nitride was deposited between them. Figure 2(b) shows a photograph of an actual chip fabricated based upon the aforementioned design.

The fabricated MHS was placed onto an AFM sample plate (Keysight Technologies 5500 AFM), with additional modification for spring-aided electrical connections to the micro-heater and the BE as shown in Figure 2(c). The micro-heater was heated in an open-loop condition where a fixed voltage is applied and the resulting resistance (and temperature) is measured, or in a closed-loop condition where the applied voltage was continuously tuned to match the heater temperature to a set value. This circuitry was implemented by a combination of passive electrical elements, microchips and LabView (National Instruments) modules.

Figure 3. The sequence of fabricating an all-metal AFM tip using a Pt-Ir wire.

Fabrication of Pt-Ir AFM Tip

All-metal AFM probe was fabricated using a commercial Pt-Ir scanning tunneling microscopy (STM) tip wire. The fabrication of Pt-Ir AFM tip can be divided into two different processes: an electrochemical etching process of the Pt-Ir tip and a transformation of the metal wire into a structure compatible with an AFM setup. The

fabrication of Pt-Ir tip starts with short segment of Pt-Ir wire. Roughly half of the cut wire was pressed between two flat steel surfaces to create the cantilever part of an AFM tip. The flat cantilever was further polished for an ideal reflection of laser beam in the AFM scanner. The polished tip was then attached to the bulky chip of a standard AFM probe using an epoxy adhesive. The probe was then checked for laser reflection in the AFM equipment before making the other side of the tip electrochemically etched. The reflective part was covered and painted with a sealant to prevent contamination from the etching solution, and removed after the etching process was completed. The overall process is depicted in Figure 3.

Figure 4. Electrochemical tip etching process. (a) Crude etching with a high ac voltage (28 – 35 V_{ac}). Note the lower tip is a mirror image reflected on the aqueous solution. (b) Fine etching with a low ac voltage (10 V_{ac}). For the fine etching, a wire with a diameter of ~1 mm was used to hold the electrolyte in a small volume.

For etching Pt-Ir tips, two-step electrochemical etching process is adopted²³. During the initial rough etching, the wire was dipped into calcium chloride (CaCl₂) solution and a high voltage (28 V – 35 V) was applied until a thin neck is formed on the Pt-Ir tip as indicated by red arrows in Figure 4(a). The Pt-tip was then moved to the following fine-etching step. The Pt-Ir tip was inserted into a spherical CaCl₂ solution suspended by a round tungsten loop (Figure 4(b)), which also acts as the counter electrode for a fine etching. Much lower ac voltages ranging from 5 V to 8 V were applied to selectively etch the neck region. When the neck is broken into two pieces during the fine etching step, the applied power was immediately discontinued to prevent over-etching.

MHS and Tip Characterization

Micro-Heater Characterization

The temperature dependency of heater element resistivity was used for the measurement and control of temperature. In order to characterize the dependency, a fabricated MHS was placed into a temperature-controlled chamber and its electrical resistance was measured at different temperatures. The resistance of the Pt heater was measured using 4-probe measurement technique, with a constant current (1 mA) applied

to the heater while measuring the voltage drop across the heating element. Figure 5 shows the resulting resistances measured at various temperatures up to 700 °C. The data points were fitted to a second-order polynomial in the following form where R_0 is the resistance at 0 °C, and α and β are fitted coefficients.

Figure 5. The resistance of the MHS heating element at different temperature in controlled temperature environment. The data point is fitted with 2nd order polynomial equation curve, where the coefficient will be used to obtain temperature from resistance value during heating.

Figure 6. The temperature of the heating element as a function of output power supplied from variable DC power source.

$$R(T) = R_0 (1 + \alpha T + \beta T^2) \quad [1]$$

The equation is then used to quantify the heater temperature based upon any given measured resistances. For Figure 6, various powers were applied to the heater, and the resulting heater temperature was obtained by measuring the resistance in the 4-probe setup. From the figure, ~7 W of power was sufficient to bring the heating element to

700 °C. The required heating power to reach a set temperature decreases with time due to continuous heating of the underlying substrate. It was roughly calculated that ~50% of power output is used to heat the heating element while the other 50% is dissipated due to the contact resistances and connectors attached to the heater.

Pt-Ir Tip Characterization

The etched Pt-Ir tips were characterized using scanning electron microscopy (SEM) imaging to observe the tip shape and apex radii, and employed to scan a substrate in contact mode to test the functionality as an AFM probe. Figure 7 shows SEM images of two tips prepared by the electrochemical etching described above. Successfully etched Pt-Ir tips have apex radii of ~100 nm. Figure 8(a) shows a typical topography image obtained in the contact mode using an etched Pt-Ir tip. From these, custom-made Pt-Ir tips were found to function properly as an AFM probe and have decent apex radii to be used as a nanoscale electrode.

Figure 7. SEM images of Pt-Ir tips fabricated through the electrochemical etching.

High-Temperature Impedance Measurement in AFM

The MHS and Pt-Ir tip were integrated together in AFM equipment, with impedance measurement instrument (Biologic, SP-200) connected between the Pt-tip and the Pt BE. The temperature of the sample is raised by applying different voltages through the heater and the resistance values of the heater were measured in an open-circuit manner. The Pt-Ir tip was placed on the YSZ electrolyte, which is sitting right on top of the heating element. Figure 8(b) shows a series of preliminary impedance spectra acquired at elevated temperatures in this setup. While the measured impedance showed decreasing trend with temperature as expected, the positive phases obtained in the scanned frequency range (200 kHz – 0.1 Hz) indicates that this may not be originated from the cell of interest (Pt-Ir/YSZ/Pt BE) where resistive and capacitive behaviors are expected to

dominate. In-depth electrical and electrochemical characterization is reserved for subsequent reports.

Figure 8. (a) An AFM image obtained using a custom-made Pt-Ir tip. (b) Nyquist plot of impedance measurements on a MHS-integrated chip with 200 nm thick YSZ/Pt from 490 °C to 520 °C.

Figure 9. (a) An optical image of a micro-heating stage damaged during AFM contact mode scanning at high temperature using custom-made Pt-tip due to high stiffness of the cantilever. (b) A heating element burned on its right side due to a high current applied to the heater. Damaged area marked with dashed rectangles.

Discussion and Conclusion

While the stiffness of commercially available AFM probes ranges from ~ 0.05 N/m to 50 N/m, the stiffness of our custom-made Pt-Ir tip is estimated to be a few thousands of N/m based upon the cantilever geometry and the Young's modulus of the material. Due to the limited sensitivity of laser-based deflection sensing module in AFM, it is hard to maintain a small pressing force with these stiff probes. This comes as a problem because a high pressing force would readily result in a significant degradation in the tip apex geometry and damage the substrate surface where the tip scans/probes on. Further, at elevated temperatures, the nanoscale materials of both the tip and substrate will be more susceptible to deformation. Figure 9(a) shows examples of sample damage done by a

contact mode AFM scanning at elevated temperatures using the custom-made tip. This caused shorting of the counter electrode with the Pt-Ir tip inhibiting further electrical measurement on the chip. There is also possibility of shorting the Pt BE with its underlying heating element. These issues can be resolved by reducing the cantilever stiffness with different cantilever dimensions. A thinner, narrower and/or longer cantilever will make the stiffness smaller. For easier fabrication, a modification in these dimensions for a small fraction of the cantilever, as opposed to the whole cantilever length, can be considered as well. The heater element can also be damaged by an excessive current flow or heating. Figure 9(b) shows an optical image of a burnt heating element due to a high current flown to the heating element. Unexpected local irregularities or non-uniformity in the heating element layer may also cause a higher current density and thus a higher temperature locally and degrade the heater readily. This would limit the maximum temperature of the MHS that could provide to heat the sample. Therefore, each MHS should be tested for its maximum allowable output power before using it to prevent permanent damage to the heating element.

In conclusion, we presented a viable solution for high temperature conductive AFM measurements by the use of a micro-patterned heater and custom-fabricated Pt-Ir tips. The MHS minimizes the amount of heat convection to the thermally sensitive AFM scanner and AFM probes, and Pt-Ir tips are free of thermal peel-off problem, the main issue of commercially available Pt-coated tips for high temperature measurements. We demonstrated that a micro-patterned heater can be heated up to 700°C and its temperature can be sensed real-time by reading the resistance of Pt heating element. A Pt-Ir tip was successfully custom-fabricated by electrochemical etching to render the apex radius of ~100 nm and demonstrated to function as an AFM probe in a commercial AFM setup. We also performed an impedance measurement using the custom-made all-metal probe on a thin film oxide electrolyte (YSZ) deposited on a micro-heater at elevated temperatures ranging from 490 – 520 °C in atmospheric temperature.

Acknowledgments

This work was supported by the US AFOSR (Grant # FA9550-15-1-0256) and AcRF Tier 2 Project by Singapore Ministry of Education (Grant No. ARC20/14 M4020202).

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