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Introducing and Controlling Water Vapor in Gas-Cell Microscopy Experiments

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The presence of water vapor is central to many materials applications (e.g., in steam generators, biomass-fired plants, turbine engines, fuel cells, and catalysts) [1]. The role of water vapor is of particular interest in the degradation of blades in turbines fired by coal-derived synthesis gas or hydrogen having a higher water vapor content than in conventional turbines [1]. The presence of water vapor can substantially decrease the lifetime of the thermal barrier coatings protecting turbine blades by accelerating the oxidation rates. However, there is currently a lack of basic understanding of the degradation mechanisms and a lack of reaction kinetic data at the nanoscale level, which can substantially improve computational modeling for components lifetime predictions. Thus, in situ experiments could bridge this gap. Performing in situ STEM gas reactions with water vapor in a closed-cell MEMS-based specimen holder is challenging due to condensation of vapor along the narrow (<200µm) supply and return capillaries, and inside the reactor holder, since these lines cannot be effectively heated [2,3]. We have developed methods and protocols to introduce, control, and quantify the amount of water vapor in a MEMS-based closed-cell in situ reactor system (Protochips AtmosphereTM) for studies focused on the effects of environmental exposure on high-temperature structural materials and catalysts.

The primary challenge for integrating water vapor into the reaction gas-cell is that the water vapor can only be supplied under normal room temperature conditions (e.g., ~20 °C). Saturated air (100% relative humidity) at this temperature and at atmospheric pressure (e.g., 760 Torr at sea level) holds ~2% water vapor or ~17 Torr partial pressure of water. Thus, to achieve higher water vapor contents in a reaction gas, the total gas pressure must be reduced (e.g., 10% water vapor allows a maximum gas pressure in the cell of 170 Torr). To monitor the gas composition, we adapted a residual gas analyzer (RGA) from Stanford Research Systems (SRS 100) equipped with an electron multiplier on the return side of our reactor holder. The RGA was mounted on a turbo-pumped station (Pfeiffer Hi-Cube 80 Eco) with a cold-cathode gauge attached and coupled to a computer-controlled leak valve (Pfeiffer Vacuum, D-35614 Asslar) (Figure 1a) [4]. Heating tape around the RGA chamber allows for bake-outs between experiments to remove residual water vapor and gases. An ultra-high vacuum of $< 2x10^{-8}$ Torr can ultimately be reached in the RGA chamber alone. The automatic leak valve is controlled via Atmosphere *Clarity*™ software, which is responsible for monitoring the returning gas into the RGA chamber. A return capillary to the manifold is isolated from the leak valve by a hand valve (HV). Water vapor to e.g. the experimental Tank 2 in the gas manifold is supplied by a stainless-steel supply vessel (inset, Fig. 1) initially charged with 1ml water. Figure 2 shows selected images of the gas manifold GUI in the *Clarity* software, with valves S3 and T2 being opened, permitting water vapor to flow from the supply vessel to Tank 2 reaching initially 6.47 Torr (Fig. 2a) and finally achieving 17.7 Torr (Fig. 2b). Both S3 and T2 valves were then closed and the flow of water vapor from Tank 2 through the gas holder was controlled by opening T2, H1, H2, and V1 valves (Fig. 2c) after the vacuum tank was fully evacuated. The total pressure drop from 17.7 to 16.4 Torr was due to filling all the lines of the system on the way to the holder. To support the presented schematic and actually confirm the flow of water vapor through the reactor holder, the RGA system (located by the red rectangle in Fig. 2c) was necessary. The mass spectra were recorded before, during, and after the experiments, which allows us to simultaneously perform operando experiments. The mass spectra generated with and without 100% water vapor at a total pressure of 17 Torr are shown in Fig. 3. The "fingerprint" peaks at atomic mass units (AMU) 16, 17 (OH), and 18 (H_2O) clearly show the presence of water vapor flowing through the gas-cell, which

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was not observed in the mass spectrum acquired without water vapor. Experiments are in progress to calibrate the gas compositions via RGA analysis and study oxidation reactions on structural materials in the presence of water vapor. *In situ* water vapor experiments also set the foundation for future biomass catalysts research by mixing vapors and liquids [5].

References:

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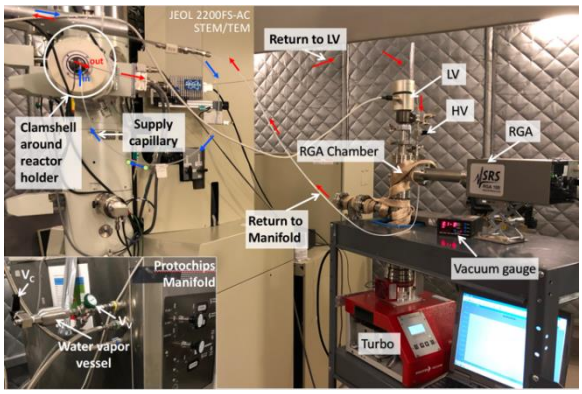

Figure 1. a) Details of RGA connection to reactor holder (inside Clamshell). Inset: Water vapor delivery fixture on adjacent Atmosphere gas manifold. b) Leak Valve (LV), Hand Valve (HV), and capillary connections.

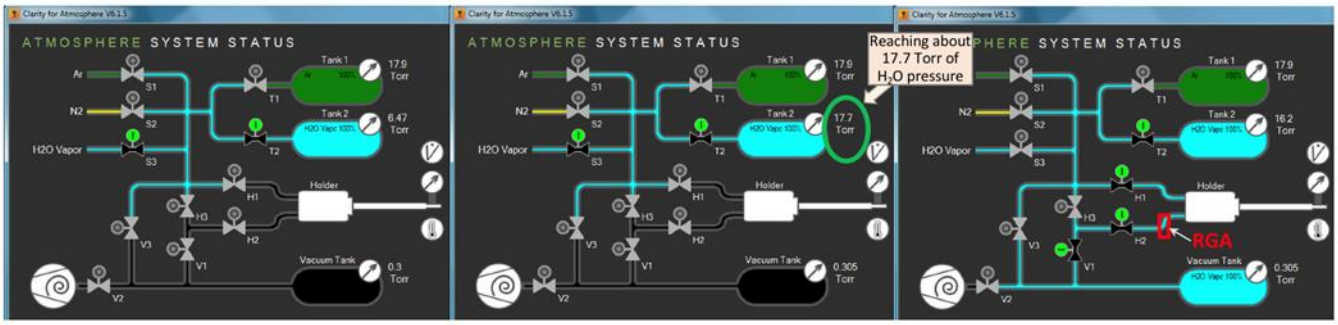

Figure 2. a) Gas manifold schematic showing selected images for introducing water vapor to gas cell via Tank 2: a) intermediate charging to 6.7 Torr, b) fully charged to 17.7 Torr, and c) with flow through the holder to the Vacuum tank via the RGA. See text for details.

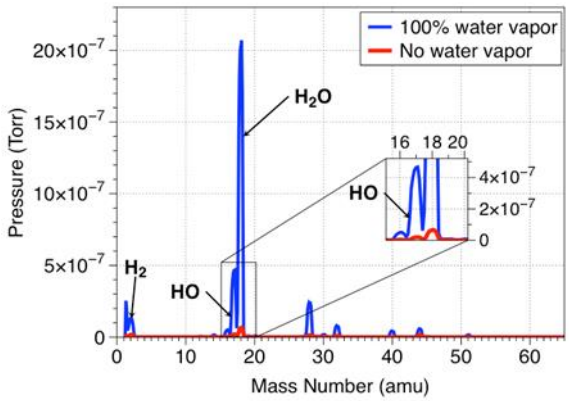

Figure 3. Detection of water vapor through gas cell is shown by RGA system before and after introduction of water vapor.

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