In situ Study of Surface Oxygen Exchange and Transport on Ceria at Different Temperatures

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Oxygen exchange and transport have important applications for renewable energy, gas sensing, chemical synthesis and many other technologies. For example, in solid oxide fuel cell (SOFC), gaseous oxygen is reduced to oxygen ion at cathode surfaces. Oxygen ion will then get incorporated into the lattice and diffuse through the solid electrolyte and oxidize fuel molecules at the anode surfaces[1]. A possible oxygen incorporation process would include O_2 molecule adsorption, molecular dissociation, electron transfer from cation, and incorporation of oxygen anion into oxygen vacancies on the surfaces. Nonstoichiometric reducible oxides, for example, ceria (CeO_2) has a fluorite structure where oxygen transport can occur via thermally activated vacancy hopping[2]. Changing the oxygen partial pressure or increasing the temperature will alter the exchange rate through surface exchange and bulk ionic conduction [3]. To improve material performance, it is desirable to develop a deeper understanding of the atomic level processes that regulate oxygen exchange and transport at different temperatures and oxygen partial pressures. Such *in situ* experiments can simulate the working condition for real applications.

Time resolved *in situ* aberration-corrected TEM was used to study the oxygen exchange/transport process at room temperature and elevated temperature on ceria surfaces. To facilitate the oxygen exchange process, oxygen vacancies were engineered by reducing the sample with a high electron beam dose rate of ~10,000 $e^{-}Å^{-2}s^{-1}$ for 20 mins. Then the sample was heated up to 200°C and then to 500°C to examine the structure changes due to increased surface oxygen exchange and bulk oxygen transport. Images were acquired using Gatan K3 direct electron detector at 7.5 frames/second with an aberration corrected Thermo Fisher Titan ETEM operated at 300 kV with a dose rate of 3750 $e^{-}Å^{-2}s^{-1}$. Time series image stacks were aligned by cross-correlation for drift correction and binned twice in time for noise reduction in digital micrograph.

Figure 1a showed an image of CeO_2 (110) surface in the [110] projection with 0.4s total exposure time at room temperature before reduction. **Figure 1b** shows the same area after reduction at 200°C. The data shows cation migration and surface reconstruction due to the high dose electron beam. Multiple (111) nanofacets have formed after reduction and heating in order to minimize the surface energy ((111) is the low energy surface). Interestingly, the cations at corner sites at room temperature appear to be more fluxional than those at similar sites at 200°C. It is possible that high oxygen exchange rate at high temperature helps cation stabilization. **Figure 2** shows a time resolved, line intensity profile recorded at room temperature from a row of sub-surface anions and cations . The oxygen peaks are the two minor peaks between major cerium peaks in the figure.

There are significant occupancy changes over time in oxygen column arising from oxygen ion hopping and migration. We are currently developing and training a segmentation convolutional neural network to detect column occupancy changes. This can be applied to the *in situ* data in Figure 2 to identify oxygen vacancy activity and cation migration. A more sophisticated machine learning algorithm is under development to map out the oxygen transport path that associated with active exchange sites.

Reference:
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[4] We gratefully acknowledge the support of the following NSF grants to ASU (OAC 1940263, 2104105 and DMR 1840841) and NYU (HDR-1940097 and OAC-2103936). The authors acknowledge HPC resources available through ASU, and NYU as well as the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

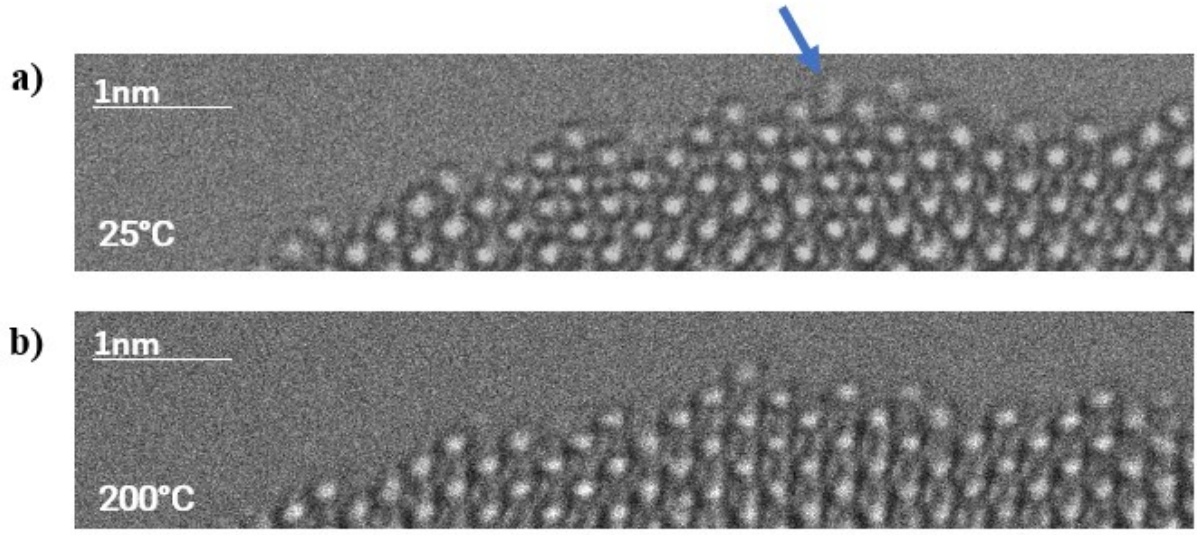

Figure 1. a) TEM image of CeO_2 (110) surface in the [110] projection with 0.4s total exposure time at room temperature. b) Same region after reduction and at a temperature of 200°C. Blue arrow indicated the highly fluxional cation corner site.

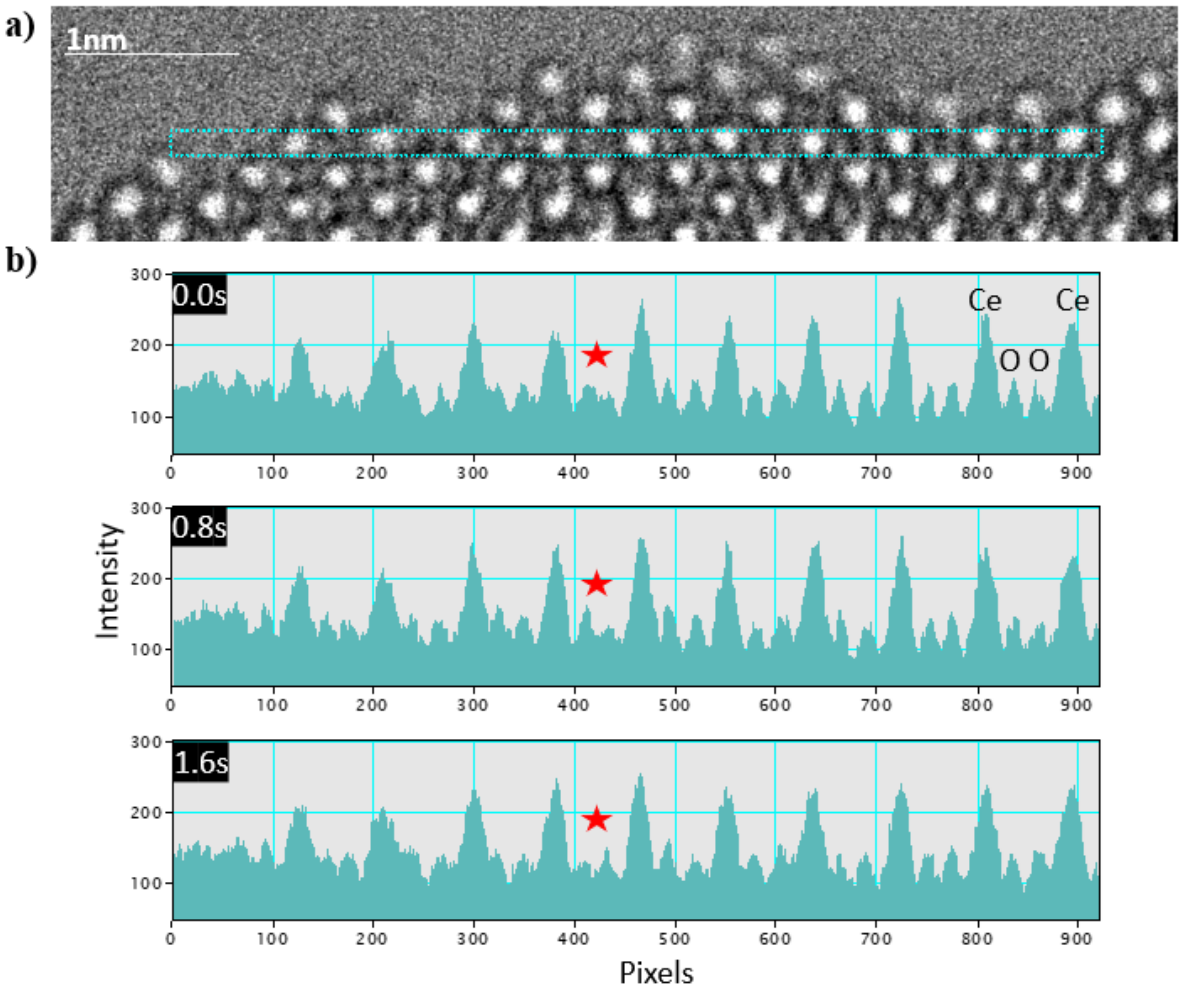

Figure 2. a) TEM image of CeO_2 (110) surface in the [110] projection with 0.4s total exposure time at room temperature before reduction (green box showed the region of interest for line profile) b) Time evolved line intensity profile of the area of interested. Oxygen column intensity changes over time.