

## ***In Situ* Environmental STEM for Dynamic Nanochemical Analysis**

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Many nanostructures strongly interact with ambient gas environments and undergo significant structural and chemical modification. This is particularly true for materials related to catalysis, sensors, aerosols, liquids and life sciences. Moreover, nanoscale phase transformations that take place during materials synthesis and processing may involve gas-solid reactions (e.g. CVD). The scanning transmission electron microscope (STEM) is a powerful technique for elucidating the structure and chemistry of nanostructures at atomic resolution. However, conventional STEMs operate under high vacuum conditions that may cause significant modification to the structure and chemistry of a material and will preclude observation of gas-solid reaction processes. To address this problem it is necessary to modify either the microscope or the sample holder to create an environmental cell permitting reasonably high gas pressures to be maintained around the sample while observations are performed.

We have modified a Tecnai F20 to permit gas pressures of up to 8 Torr to be maintained around the sample during observation [1]. This environmental scanning transmission electron microscope (ESTEM) operates at 200 KV and has a field emission gun (FEG) permitting probes as small as 0.2 nm. It is equipped with standard STEM detectors and a Gatan Imaging Filter for electron energy-loss analysis permitting us to explore the nanostructure and chemistry of materials under reactive gas conditions. The environmental cell does introduce a number of compromises in the STEM performance. To maintain high pressures in the cell while maintaining high vacuums in the electron gun we have installed differential pumping apertures in the upper and lower pole pieces of the objective lens. These apertures restrict the convergence and detector collection semi-angles to about 50 mrad. This does not impact the probe formation optics or the EELS performance but it does negatively impacting the performance of Z-contrast imaging. However, despite this limitation, the instrument is a powerful tool for *in situ* high spatial resolution chemical analysis at high temperatures and pressures.

We are using ESTEM to study the factors that control the redox activity of ceria zirconia based catalysts [2]. The activity of this catalyst is directly related to the ability of cerium to reversible change its oxidation state with changes in the oxygen chemical potential. We can vary the oxygen chemical potential by changing the hydrogen pressure in the cell and control the temperature by using a hot stage. The high surface area oxides are prepared at relatively low temperatures and may be chemically heterogeneous on the nanometer level. The impact of the heterogeneity on the redox behaviour is unknown and is a topic of considerable interest. Figure 1 is an example of ESTEM imaging and *in situ* EELS analysis of ceria zirconia recorded at 740°C in 1 Torr of H<sub>2</sub>. The energy-loss spectra were quantified in the standard way to determine the compositional variation within and between nanoparticles. The Ce M<sub>45</sub> white lines were used to determine variations in the local oxidation state of the Ce. The ESTEM analysis suggests that particles showing composition uniformity are more easily reduced than those with a high degree of compositional heterogeneity.

The combination of a focused electron beam and an environmental cell provides an opportunity to explore gas-induced materials synthesis and modification at the nanometer level with ESTEM. The focused electron beam can be used to deposit material directly onto the substrate surface (electron beam induced deposition (EBID)) or it can be used to locally transform the

substrate. We have been able to conduct ultrahigh spatial resolution EBID using the very small focused probes present in the STEM [3,4]. The ESTEM allows the evolution in local chemistry to be followed while a gas induced phase transformation takes place. Figure 2 shows the changes that takes place at the nanometer level when a nanometer size probe is held stationary on a  $\text{Si}_3\text{N}_4$  membrane in an  $\text{H}_2\text{O}$  environment. This time-resolved EELS clearly shows the evolution of a nanoscale domain of  $\text{SiO}_x$  embedded in the  $\text{Si}_3\text{N}_4$  matrix.

## References

[1] Sharma, R. et al, *Microscopy and Microanalysis*, **9** Sup.02, (2003) 912.

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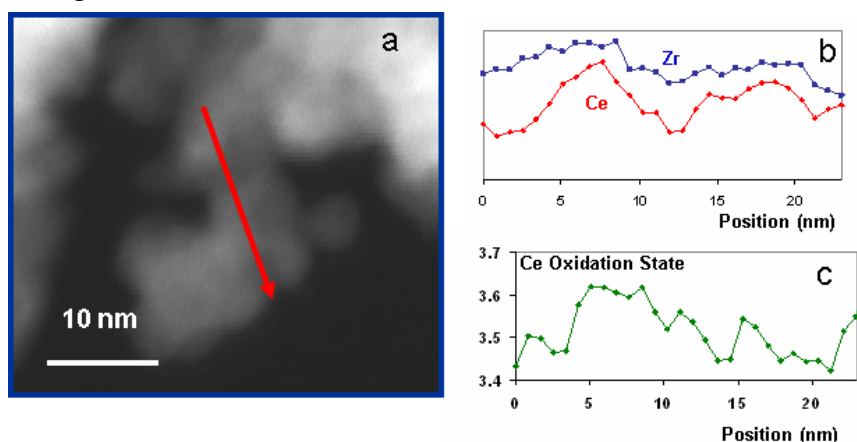


Figure 1: a) *In situ* annular dark-field STEM image recorded at  $740^\circ\text{C}$  in a hydrogen atmosphere. Arrow show path traversed by the beam to during EELS line scan. b) Ce and Zr signals from EELS data and c) derived Ce oxidation state recorded *in situ* at  $740^\circ\text{C}$  in a hydrogen atmosphere.

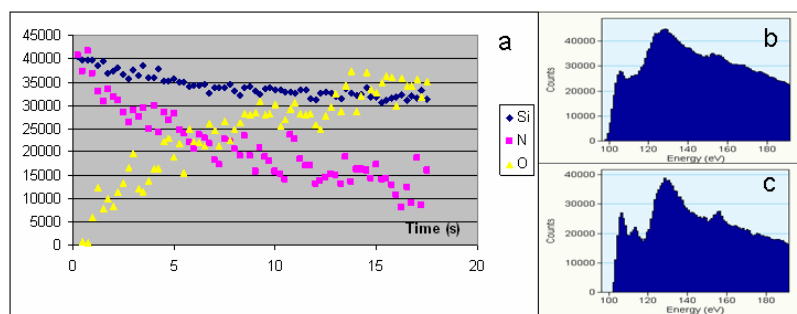


Figure 2: a) Change in relative composition of nanodomain as a function of time during localized electron irradiation of 30 nm thick  $\text{Si}_3\text{N}_4$  film in 0.4 Torr of  $\text{H}_2\text{O}$  at  $150^\circ\text{C}$ . EELS near-edge structure of Si  $L_{23}$  edge at b) beginning and c) near end of phase transformation showing formation of  $\text{SiO}_x$ .