

Development and Initial Applications of Double Aberration Corrected (AC) ETEM and (AC) ESTEM at York

Edward D Boyes^{1,3,4}, Michael J Walsh^{1,4}, Michael R Ward^{1,4}, and Pratibha L Gai^{1,2,4}

Departments of Physics¹, Chemistry² and Electronics³, York JEOL Nanocentre⁴, University of York, York, YO10 5DD, UK

The design of the modern ETEM^{1,2} has proved to be very successful in fulfilling the ambitions of the initial agenda for dynamic in-situ atomic resolution HRTEM imaging studies of reactions under controlled conditions of specimen temperature and gas atmosphere. The operational functionality is now combined with aberration correction for both ETEM and ESTEM with a full range of imaging and analytical capabilities.

As well as continuous dynamic reaction sequences, the controlled conditions support access to intermediate states or phases which may be metastable with respect to reaction conditions of gas atmosphere and/or temperature, and they are therefore not reliably accessible through ex-situ or discontinuous experiments.

The original high resolution ETEM HRTEM has been widely replicated commercially around the world to support studies of a range of heterogeneous solid state catalysts under gas reaction conditions. In the process the advanced instrumentation has led to a revolution in the science²; contributing to a much fuller and more accurate account of key processes in industry. These often use complex combinations of materials and the in-situ studies make clear they are in detail subject to multiple competing processes. With new developments we are beginning to have the tools to engage directly and constructively with the atomic scale complexity of the real world of solid state heterogeneous catalysis of gas reactions; better informed by careful complementary designs of model system experiments.

In particular, we are beginning to address one of the central dilemmas of supported metal particle solid state heterogeneous catalysis. This is that particles with the most active sites may well also be those which are at the same time inherently the most unstable in configuration; leading to drastic deleterious changes in both site type selectivity and site number activity. Such behaviour is clearly undesirable and must be characterised using minimally invasive methods before it can be managed on a rational basis.

The original ETEM was designed principally, and in practice almost exclusively, for HRTEM. The design is compatible with EELS but has serious limitations for several other analytical techniques. It has been used very successfully for AC ETEM but it is compromised for (AC) ESTEM in regard of (a) HAADF Z-contrast STEM imaging, (b) wide angle electron diffraction including CDBP HOLZ rings and (c) EDX; to the extent no previous AC ESTEM is known to be operational at this time.

A revised design at York enables AC ESTEM with a full range of analytical tools operational in dynamic in-situ experiments, currently at more modest gas pressures up to ~0.1mbar which are still sufficient to flood the sample surface with upwards of 100,000 monolayers of gas per second.

The operating pressure is expected to be increased into the mbar range with further revisions to the design, including especially the planned investment in an extra stage of differential pumping, but more gas may restrict performance at the highest resolutions of <0.1nm; especially in HAADF STEM. We need enough gas to dominate the surface chemistry, but no more, in order to avoid as far as is possible the introduction of artefact gas ionisation by the beam and its general scattering or absorption by the gas.

In terms of the 'pressure gap' between catalyst analysis³ and operations, the situation with EM is a good deal more favourable than, for example, with many surface science methods; allowing higher but still modest gas pressures and continuous exposure and analysis rather than the discontinuous or pulsed methods typically used in surface science analyses. We are in the process of evaluating the gas pressure compatibility of the various operational modes; recognising that for HAADF STEM crystal orientations with respect to the electron beam direction may be more critical than for phase contrast applications.

The elimination of restrictions on performance and capability in the AC ESTEM provide the full range of STEM imaging and analytical facilities for experiments with gas and allow uncompromised dual function use of the core instrument, to demonstrated resolutions to below 0.08nm without changing the microscope gas compatible configuration for operations in high vacuum. The latter currently reach down to $<5 \times 10^{-8}$ mbar high vacuum pressure in the column; somewhat paradoxically due in large part to the improved pumping installed for gas operations.

The powerful new tool is being used to innovate and develop key aspects of catalysis science, and the practical applications of it in industry and in the laboratory; in pursuit of more effective, lower cost (broadly defined) and generally more sustainable processes⁴⁻⁷ with reduced resource and environmental impacts. We are currently working with the initial proof-of-principle rig which we aim to develop further in the future.

References

1. E D Boyes and P L Gai, *Ultramicroscopy*, 67 (1997) 219
2. P L Gai, E D Boyes, S Helveg, P L Hansen, S Giorgio and C R Henry, *MRS Bulletin*, 32 (2007) 1045
3. G A Somorjai, et al, *Phys Chem Chem Phys*, 9 (2007) 3500
4. P L Gai et al, *Catal. Lett.* 132 (2009) 182
5. P L Gai and E D Boyes, *Microscopy Res and Tech*, 72 (2009) 153
6. P L Gai and E D Boyes, *J Physics, Conf Ser*, 241 (2010) 012055
7. M J Walsh et al, *Nanoletters*, (2012), <http://dx.doi.org/10.1021/nl300067q>