1131
doi:10.1017/S1431927615006443 Paper No. 0565 Microsc. Microanal. 21 (Suppl 3), 2015

Materials Science Applications of Aberration Corrected TEM and/or STEM.

Gustaaf Van Tendeloo[1], Artem Abakumov[1], Sara Bals[1], Sandra Van Aert[1], Jo Verbeeck[1]

[1.] EMAT Research Group, Department of Physics, University of Antwerp, B-2020, Belgium

The introduction of aberration corrected (AC) lenses has evidently introduced large changes in the electron microscopy world. Even more important though are the changes in the world of materials science, solid state physics and solid state chemistry. The new possibilities of AC-EM have boosted the development of new materials and new products or provided extra information about the functioning of these products. Major improvements originate from the combination of an increased signal to noise ratio, the possibility to work at variable voltages, the development of better detectors, the improvement of algoritms for 3D electron tomography, the incorporation of monochromators for EELS analysis and the improved recording of EDX spectra.

A recent example is the search for the origin of voltage decay in high capacity layered oxide electrodes in Li-based batteries. Lithium rich layered oxides ($Li_{1+x}Ni_yCo_zMn_{1-x-y}O_2$) are attractive electrode materials with very high energy densities (16% over todays commercial cells). However they are known to suffer from voltage decay upon cycling. Using a double corrected TEM-STEM instrument we could study the migration of cations between the metal layers and the Li-layers and prove unambiguously that the trapping of the metal ions in the interstitial tetrahedral sites is at the origin of the voltage decay (see figure 1). Expanding the study to $Li_2Ru_{1-y}Sn_yO_3$ and Li_2RuO_3 we could figure out that the slowest decay occurs for cations with the largest ionic radius [1].

Also more fundamental aspects in nanoscience can now be tackled. The combination of electron tomography and EELS has allowed us to map the valency of the Ce ions in CeO_{2-x} nanocrystals in three dimensions. There is a clear facet-dependent reduction shell at the surface of the ceria nanoparticles; {111} surface facets show a low surface reduction, whereas at {001} surface facets, the cerium ions are more likely to be reduced over a larger surface shell (see figure 2). Our generic tomographic technique allows a full 3D data cube to be reconstructed, containing an EELS spectrum in each voxel. This possibility enables a three-dimensional investigation of a plethora of structural and chemical parameters such as valency, chemical composition, oxygen coordination, or bond lengths, triggering the synthesis of nanomaterials with improved properties [2].

Even in identifying or restoring famous paintings advanced EM can now play a crucial role. We investigated the deterioration of historical chrome yellow paint in the paintings of Van Gogh, in order to allow an optimal reconstruction of his works. This is particularly done by a quantitative analysis and mapping of the EELS data of chromium. The original pigments in late 19th Century consisted of $PbCrO_4$, $PbCr_{1-x}S_xO_4$, and $PbSO_4$ particles. During aging, the particles have gradually evolved to core–shell $PbCrO_4$–Cr_2O_3, or core–shell $PbCrO_4$–$PbSO_4$ particles together with some remaining PbSO4. An artificial aging process speeds up the evolution and shows that they will evolve towards Cr_2O_3, $PbCrO_4$–$PbSO_4$– Cr_2O_3, or $PbSO_4$– Cr_2O_3 core–shell structures. Greenish Cr_2O_3 deteriorates the originally clean yellow colour. All those intermediate or final states have been observed and analysed by AC STEM [3].

The authors acknowledge financial support from the European Research Grants (ERC Grants) for GVT, SB and JV.

[1] M. Sathiya et al. Nature Materials (2014) DOI: 10.1038/NMAT4137
[2] B. Goris et al. ACS Nano **8** (2014) p. 10878
[3] H. Tan et al. Angew. Chem. Int. Ed. **52** (2013) p. 11360

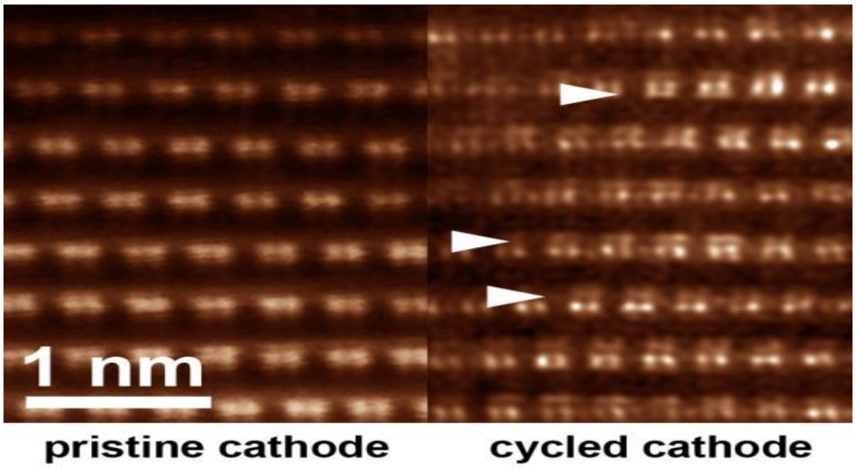

Figure 1. [1$\bar{1}$0] HAADF-STEM image of pristine $Li_2Ru_{0.75}Ti_{0.25}O_3$ (left) and after 50 charge-discharge cycles. Extra cations at the tetrahedral interstices locally appear after cycling (marked with arrowheads).

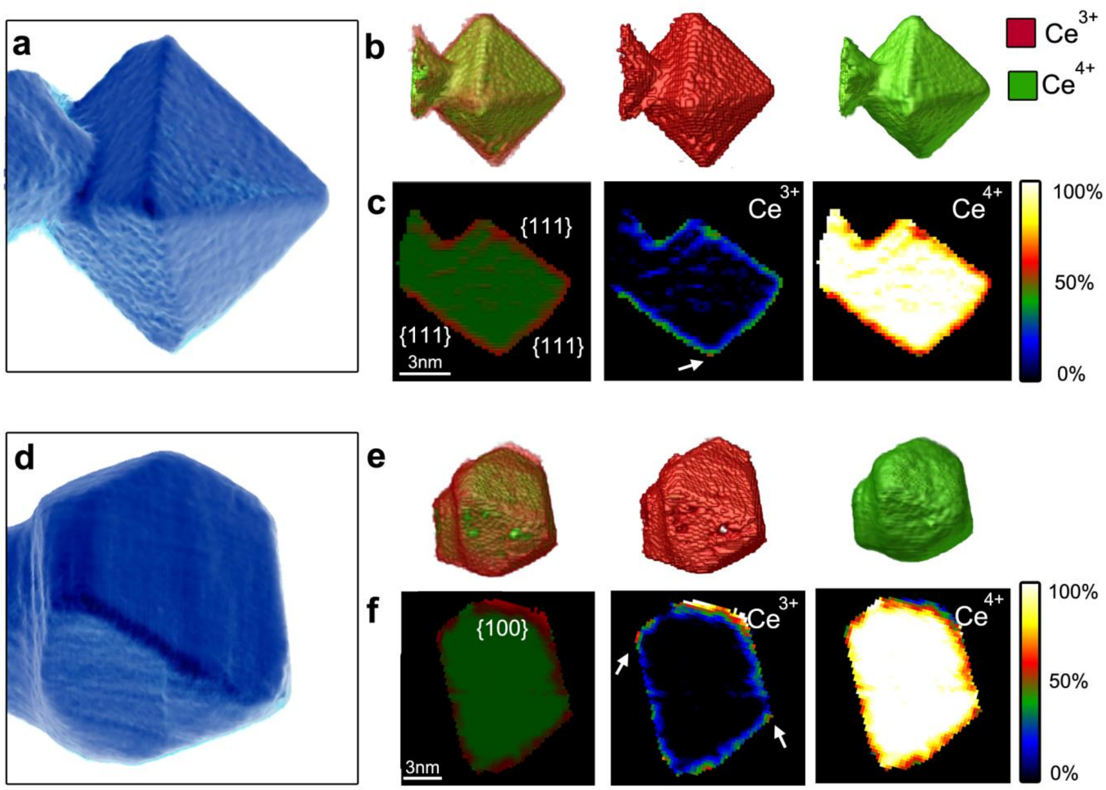

Figure 2. (a and d) HAADF-STEM reconstructions of near-perfect and truncated octahedral ceria nanoparticle. (b and e) The corresponding 3D visualizations and slices through the 3D reconstructions showing the valency results for Ce^{3+} and Ce^{4+}, indicating a thicker Ce^{3+} layer with more oxygen vacancies at the {001} truncation. (c and f) Slices through the Ce^{3+} and Ce^{4+} volumes.