In situ Transmission Electron Microscopy

R E Dunin-Borkowski, M Gocyla, M Heggen, A H Tavabi, A Kovács, A Thust, J Barthel, C-L Jia, K W Urban, M Duchamp and V Migunov

Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

Ernst Ruska-Centrum für Mikroskopie und Spektroskopie mit Elektronen

ER-C

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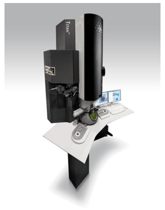
The Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), which is located in Forschungszentrum Jülich, is a national user facility open to universities and research institutions. The Institute currently operates five aberration-corrected FEI TITAN transmission electron microscopes (TEMs) and six conventional TEMs. Research topics are focused on the development of advanced high-resolution and analytical electron microscopy techniques and their application to studies of electroceramics, oxide superconductors, spintronic materials, semiconductors, nanoparticles and metallic alloys.

The FEI Titan 50-300 PICO TEM (right) is equipped with a monochromator, a Cs probe corrector, a Cs-Cc image corrector and a GIF. It has a spatial resolution of ~50 pm at 300 kV and is one of only a few chromatically-corrected high resolution electron microscopes in the world.

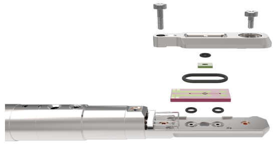
The FEI Titan G2 60-300 HOLO TEM is designed for electron holography and *in situ* TEM. It has an ultra wide pole piece gap, a C_5 image corrector, and three electron biprisms.



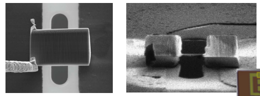
The FEI Titan 80-200 ChemiSTEM has a high brightness Schottky field emission electron gun, a Cs probe corrector, a Gatan Enfinium ER spectrometer and Super-X large solid angle EDX detector.

In situ TEM specimen holders

The ER-C has a wide variety of TEM specimen holders, including tomographic holders (Fischione Models 2020, 2040 and 2050) DENSsolutions single tilt and double tilt heating and biasing holders, a combined heating and cooling holder and a combined gas reaction and heating holder.

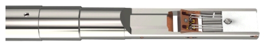


The DENSsolutions "Climate" *in situ* TEM gas and heating holder (above) provides a high pressure gas environment at temperatures of up to 1000 K inside a nano-reactor, enabling atomic resolution characterization of solid-gas reactions in real time.

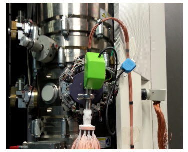


Example of an electrically contacted FIB lamella on a MEMS chip (above).

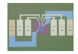
M. Duchamp, Q. Xu, R. E. Dunin-Borkowski, *Microsc. Microanal.* **20** (2014), 1638.



In situ double tilt heating holder containing MEMS heater chip (above) from DENSsolutions (Delft, NL).

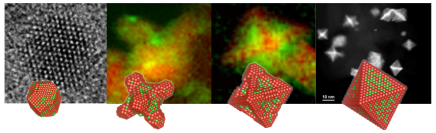


Heating and cooling holder with sub-1-Å resolution at temperatures of between 100 and 1000K with up to 6 electrical contacts to the specimen (left).



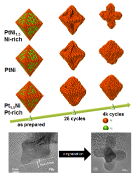
In situ single tilt heating holder containing a MEMS heater chip (above) from DENSsolutions (Delft, NL).

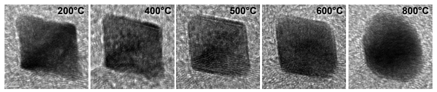
Octahedral PtNi fuel-cell catalyst nanoparticles studied by *in situ* TEM



PtNi nanoparticles after 4, 8, 16, and 42 hours of solvothermal synthesis.

Due to their highly active {111} surfaces, octahedral-shaped PtNi nanoparticles are highly promising catalysts for PEM fuel cells. A study of the growth of bimetallic PtNi alloy nanoparticles revealed a previously overlooked element-specific compositionally anisotropic growth mechanism, whereby rapid growth of Pt-rich hexapods/concave octahedra along <100> directions precedes the delayed deposition of a Ni-rich phase at the concave {111} sites (above). While the growth of Pt-rich hexapods is a ligand-controlled kinetic process, the step-induced deposition of the Ni-rich phase on the concave surfaces isa thermodynamically-controlled process that takes place over a longer time. The inferred element-specific anisotropic growth provides the underlying basis for our previously-reported compositional segregation and chemical degradation pathway for PtNi octahedra (right).

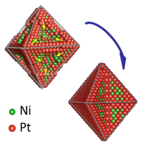




TEM image series of $Pt_{1.5}Ni$ octahedral nanoparticles during *in situ* annealing from 200 to 800 °C.

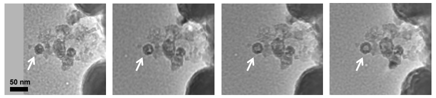
Illustration of structural changes of slightly concave $Pt_{1.5}Ni$ octahedra during annealing up to 500 °C.

Pt-rich corner atoms diffuse and subsequently fill the concave Ni-rich {111} facets, forming perfectly octahedral nanoparticles with flat Pt-rich {111} surfaces.



L. Gan, C. Cui, M. Heggen, F. Dionigi, S. Rudi, P. Strasser, *Science* **346** (2014), 1502 -1506.
C. Cui, L. Gan, H. Li, S. Yu, M. Heggen, P. Strasser, *Nano Letters* **12** (2012), 5885–5889.
C. Cui, L. Gan, M. Heggen, S. Rudi, P. Strasser*Nature Materials* **12** (2013), 765–771.
L. Gan, M. Heggen, C. Cui, P. Strasser, *ACS Catalysis* **6** (2016), 692–695.

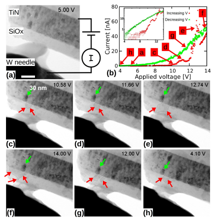
In situ oxidation of Ni nanoparticles on perovskite substrates in an oxygen atmosphere



Perovskite materials have recently emerged as promising electrocatalytic materials with a wide range of applications, including oxidation reactions, pollution abatement, hydrogenation, photocatalysis and electrocatalysis. We have studied a catalyst system of Ni nanoparticles on a $La_{0.6}Sr_{0.4}$ - FeO_3 perovskite support, focusing on the Ni-perovskite interaction and its structural consequences for methane steam reforming and methanation reactions. The image sequence above shows the oxidation of a Ni nanoparticle (arrowed) during an *in situ* heating experiment carried out at 500 °C in 1 bar of oxygen for 45 min.

R. Thalinger, M. Gocyla, M. Heggen, R. E. Dunin-Borkowski, M. Stöger-Pollach, D. Schmidmair, M. Grünbacher, B. Klötzer, S. Penner, *The Journal of Physical Chemistry C*, **119** (2015), 22050-22056.
R. Thalinger, A. Opitz, S. Kogler, M. Heggen, D. Stroppa, D. Schmidmair, R. Tappert, J. Fleig, B. Kloetzer, S. Penner, *The Journal of Physical Chemistry C*, **119** (2015), 11739–11753.
R. Thalinger, M. Gocyla, M. Heggen, B. Klötzer, S. Penner, *Journal of Catalysis* **337** (2016), 26-35.

In situ resistive switching of a SiO_x layer in the TEM using a movable probe

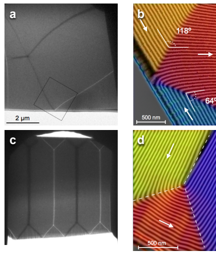


In situ observation of the formation of a conductive path in a SiO_x layer recorded while using a movable W needle in a Nanofactory specimen holder to apply a bias locally to the specimen in the TEM.

(a) Bright-field TEM image of the device recorded during the application of an initial 5 V bias, showing no visible change from the as-fabricated device. A schematic diagram of the electrical setup used during the *in situ* TEM experiment is shown on the right of the image. (b) Current-voltage (I-V) measurements recorded while performing *in situ* switching of the device using a W needle in the TEM. The red and green dots correspond to positive and negative voltage sweeps, respectively. Images (c-e) were recorded while increasing the voltage, while images (f-h) were recorded while decreasing the voltage. The red arrows in (c-h) indicate the part of the SiO_x layer that changes during the sweep. The green arrow indicates a crystal in the TiN layer that can be used as reference point during the switching process.

M. Duchamp, V. Migunov, A. H. Tavabi, A. Mehonic, M. Buckwell, M. Munde, A. J. Kenyon, R. E. Dunin-Borkowski (2016), submitted.

Soft magnetic materials for energy conversion and high frequency applications



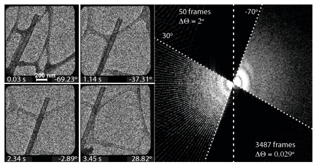
Soft magnetic materials employed in transformers, electrical machines, radio frequency and microwave applications occupy a 40% share of the global market of magnetic materials. Fe-Si alloys are used for the generation and distribution of electrical energy and in motors. Novel amorphous and nanocrystalline Fe-Si-based materials (e.g. Vitroperm and Finemet) show superior soft magnetic properties and low losses.

We have used using Lorentz TEM and off-axis electron holography to study the infulence of stress-induced anisotropy on the structural and magnetic properties of $Fe_{73.5}Si_{15.5}B_7Nb_3Cu_1$ alloys.

(a, c) Lorentz TEM images of annealed and stress-annealed samples. (b, d) Corresponding magnetic induction maps extracted from electron holograms.

A. Kovács, K.G. Pradeep, G. Herzer, D. Raabe, R.E. Dunin-Borkowski, *AIP Advances* **6** (2016), 056501.

Fast tomography for low dose characterization of nanoscale materials



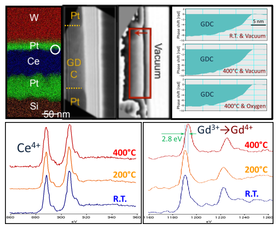
Continuous tilt series acquisition of a $(LaCeS)_{1.2}CrS_2$ nanotube on a lacey C support. The tilt series comprises 3487 images taken over a tilt range of −70° to +30° in only 3.5 s.

The filling of Fourier space with projection data according to the Fourier slice theorem, both for a subset of 50 images extracted in 2° increments and for the full tilt series of 3487 images with an increment of ~0.029°.

Continuous tilt series acquisition: By utilizing continuous tilting of a specimen and a fast and efficient detector (a direct electron detector with a frame rate above 100 fps), it is possible to decrease the electron dose required for the acquisition of a TEM tomographic tilt series by a factor of 10 compared to state-of-the-art low dose electron tomography. It is therefore possible to use this approach to perform dynamic *in situ* studies combined with 3D imaging with a temporal resolution of only a few seconds.

V. Migunov, H. Ryll, X. Zhuge, M. Simson, L. Strüder, K. J. Batenburg, L. Houben, R. E. Dunin-Borkowski, *Scientific Reports* **5** (2015), 14516.

Redox reactions and ionic conductivity in SOFCs studied by *in situ* TEM



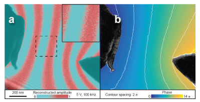
A full understanding of reaction mechanisms in solid oxide fuel cells (SOFCs) is required to optimize their performance and to overcome present limitations.

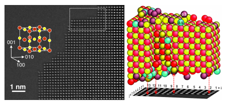
We have used *in situ* TEM to study redox reactions and ionic conductivity in SOFCs in a gas reaction environment at elevated temperature.

We studied a model Pt-GDC-Pt ultrathin cell on a Si substrate in an environmental TEM using off-axis electron holography and EELS. Changes in the activities of dopant cations in the solid electrolyte were detected during O anion conduction, demonstrating the key role of dopants in electrolyte architecture in SOFCs.

A. H. Tavabi, S. Arai, S. Muto, T. Tanji and R. E. Dunin-Borkowski, *Microsc. Microanal.* **20** (2014), 1817-1825.

Novel approaches for studies of ultrafast and dynamic processes in the TEM





The double exposure method in electron holography is presently being developed to allow differences in electrostatic potential between two states of a system that is being switched at high frequency to be recorded. (a) Double exposure electron hologram recorded during the application of a square wave with a 5 V amplitude at a frequency of 100 kHz applied between two metallic needles overlaid with its amplitude. (b) Corresponding phase image (proportional to the projected electrostatic potential) recovered from the high frequency DEEH amplitude.

V. Migunov, C. Dwyer, C. B. Boothroyd, G. Pozzi and R. E. Dunin-Borkowski (2016), submitted

Aberration-corrected TEM combined with dedicated numerical evaluation procedures allows the three-dimensional shape of a crystal to be determined from only one single high-resolution image, as shown above for an MgO crystal viewed along [001]. The sensitivity of the reconstruction procedure is not only sufficient to reveal the surface morphology of the crystal with atomic resolution, but also to detect the presence of adsorbed impurity atoms. Such a single-image approach offers possibilities to detect changes in surface morphology during *in situ* chemical reactions.

C. L. Jia, S.-B. Mi, J. Barthel, D. Wang, R. E. Dunin-Borkowski, K. W. Urban and A. Thust, *Nature Materials* **13** (2014), 1044-1049.

Conclusions

- *In situ* heating experiments in vacuum and in a gas environment in the TEM combined with analytical investigations provide crucial information about the formation and degradation of octahedral nanoparticles and nanoparticle catalysts on perovskite substrates. This information is essential for the enhancement of novel stable and efficient catalysts for future energy conversion and storage applications.
- Continuous specimen rotation allows tomographic imaging of dynamic processes such as catalytic reactions and phase transformations *in situ* in the TEM with sub-5-s temporal resolution.
- The use of MEMS-based devices is promising for future *in situ* TEM studies when both an electrical stimulus and an elevated or reduced specimen temperature stimulus are required.
- Off-axis electron holography is a powerful technique to study electromagnetic potentials in materials.
- New methodological developments promise to provide improved temporal resolution in future *in situ* studies.

Acknowledgements

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