In Situ X-ray-based Imaging of Nano Materials

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Abstract

Functional nanomaterials are heterogeneous and understanding their behavior during synthesis and operation requires high resolution diagnostic imaging tools that can be used *in situ*. Over the past decade, huge progress has been made in the development of X-ray based imaging, including full field and scanning microscopy and their analogs in coherent diffractive imaging. Currently, spatial resolution of about 10 nm and time resolution of sub-seconds are achievable. For catalysis, X-ray imaging allows tracking of particle chemistry under reaction conditions. In energy storage, *in situ* X-ray imaging of electrode particles is providing important insight into degradation processes. Recently, both spatial and temporal resolutions are improving to a few nm and milliseconds and these developments will open up unprecedented opportunities.

Introduction

Within the past few decades, nanomaterials have been increasingly used in products ranging from sunscreen to antimicrobial treatments to catalysts to rechargeable batteries, and as new nanomaterials continue to be developed, they will find increasing use especially for sustainable energy conversion and storage, such as quantum dots (QDs), batteries and new catalysts. In order to develop better functional nanomaterials, it is essential to understand how they are formed during synthesis and how they operate in realistic environments. To this end, many *in situ* diagnostic approaches are being used, but since nanomaterials are often heterogeneous (energy storage, fuel cells, catalysts on supports) imaging these processes is required – “seeing is believing” to quote the old adage.

Over the past few years, X-ray based imaging or microscopies (XMs) have been developing rapidly and have been increasingly applied to *in situ* imaging of functional nanomaterials. The current spatial and time resolutions are approximately 10 nm and sub-seconds and are steadily improving. Due to the penetration power of X-rays and excellent spatial and temporal resolutions, XMs can visualize materials in realistic synthesis environments and operating conditions for real time investigations far from equilibrium. While *in situ* transmission electron microscopy (TEM) has far better spatial resolution, TEM requires the use of less realistic environments because of strong interaction between electrons and the material. For example, TEM observations of lithiation of silicon nanowires (a promising anode for Li-ion batteries) required the use of a solid state Li_2O electrolyte rather than the organic liquid electrolyte used in Li-ion batteries. [1] Thus, TEM and XM are complementary [2].

This review covers a brief overview of XM based *in situ* imaging of nanomaterials with a focus on catalysis and energy storage and how nanomaterials evolve during operation. There are

two major modalities of XM, scanning and full field, which are conceptually illustrated in Fig. 1. In scanning mode, images are acquired pixel-by-pixel using a finely focused (10-100 nm) X-ray beam; fluorescent (providing elemental sensitivity) or transmitted (morphology) X-rays are collected, frequently simultaneously, to form an image. Auger electrons can also be collected for mapping surface-sensitive elemental distributions. If a 2D segmented detector is used, dark field images or differential phase contrast images can be measured. In full field, a large, typically incoherent, X-ray beam is focused onto the sample, defining the field of view, and the scattered and transmitted X-rays are collected by the objective lens that forms a real-space, absorption contrast image on an area detector in a single shot. A phase ring can be used to measure Zernike phase contrast. The full field mode allows rapid image acquisition which is ideal for tomography. In both modalities, chemical mapping is obtained using X-ray absorption spectroscopy (XAS), where the incident X-ray energy is scanned across an absorption edge to measure chemical signatures. Both modes have advantages and disadvantages as discussed in Refs. [2] and [3]. Additionally, the two modes have coherent diffractive imaging (CDI) analogs (Fig. 1 yellow), where the use of coherent illumination and oversampling of the data allow the use of iterative algorithms to reconstruct the complex-valued image at a resolution finer than limited by the imaging optics. [4] The remainder of this perspective discusses XMs as applied to catalyst nanomaterials, energy storage electrodes, porous fuel cell electrodes, and nanomaterials synthesis electrodeposition. We finish with some thoughts on future directions.

Catalyst

In order to characterize nanoparticle catalysts *in situ*, they should be observed within their porous support and under reactive conditions. Standard imaging techniques, such as visible light

and electron microscopies, struggle to resolve nanometer structures on support particles which are tens to hundreds of microns in diameter, especially at high temperature and pressure. However, with its relatively large penetration depth and high resolution, *in situ* X-ray microscopy is uniquely poised to tackle this challenging problem.

With soft X-rays (defined here as X-rays having energies below ~ 2 keV), the chemical and morphological changes in individual supported catalytic nanoparticles should be able to be tracked, although current microscope resolutions are limiting. Due to their relatively large scattering cross-section, soft X-rays are ideal for mapping chemistries of thin samples such as nanoparticle catalysts. On the other hand, the limited working distance between the optics and the sample (hundreds of microns to a few millimeters), makes *in situ* sample environments more difficult to design. A proof of technique demonstration of *in situ* scanning transmission X-ray microscopy (STXM) (Fig. 1a), allowing temperatures up to 350°C and various gas environments at 1 bar, mapped the Fe L-edge chemistries of supported iron oxide particles during reduction and the Fisher-Tropsch synthesis. [5] The resolution of the chemical maps was limited to ~ 40 nm. The oxygen and carbon chemistries were also measured in specific locations, but not spatially mapped.

Hard X-rays (above ~ 2 keV) can penetrate thicker samples making them ideal for studying catalysts in their intact support. Working distances are also longer (tens of millimeters or longer) allowing more complex sample environments, such as high pressure. *In situ* hard X-ray transmission X-ray microscopy (TXM) (Fig. 1b) was used to track the Fe K-edge chemistry of a Ruhrchemie catalysts under reaction conditions (350°C , 10 bar, and various gas environments) (Figure 2) [6]. The ~ 30 nm resolution limit of the microscope again prevented resolving individual nanoparticles.

The most promising emerging microscopy to push the resolution down to a few nanometers is ptychography. [4] A proof of principle demonstration of *in situ* ptychography at high temperature (620°C) and in a CO₂ environment imaged aggregates of Li₂ZrO₃ particles for CO₂ capture and storage with a resolution of only ~200 nm. [7] With a carefully designed sample environment and a stable sample positioning system, the resolution using ptychography could be below 10 nm under reaction conditions. Thus, in the near future, *in situ* ptychography will enable nanoparticle catalysts to be tracked on supports and under operating conditions.

Energy storage

Energy storage devices such as Li-ion batteries are complex, hierarchical systems that have heterogeneities that span length scales from Ångströms to millimeters. Studying the dynamics of nanoscale heterogeneities under active biasing illuminates how specific heterogeneities lead to particular failure pathways. For example, local defects at the primary particle level can lead to dramatic differences in the local charge density at the nanometer scale.

Two modes of *in situ* X-ray imaging, tomography and chemical mapping, have proven to be especially valuable to energy storage research in recent years. Tomographic imaging allows the 3D structure to be visualized and can give quantitative measurements on density and volume changes. Measuring these changes is particularly important for studying the failure mechanisms in alloying anode materials such as Si, Ge, and Sn (recent examples include Li-Ge [8], Li-Sn [9], and Na-Sn [10]).

In addition to standard absorption contrast tomography, where the image contrast is given by the differences in how different materials absorb the X-rays, phase contrast imaging has been successfully utilized to image low-Z materials (such as Li or C) in 3D. Work by Eastwood *et al.*

demonstrates the value of phase contrast tomography in mapping lithium metal dendrite growth. [11] This work is limited to ~1 micron resolution, however, we expect to see *in situ* higher resolution phase contrast tomography on energy storage systems in the near future, especially considering its unique capability of low dose, high contrast imaging of materials which are effectively transparent to most X-rays.

Recently *in situ* Bragg coherent diffractive imaging (CDI) was utilized to map the 3D strain in a single metal oxide particle within an operating battery. [12] Mapping 3D strain can be an indirect measure of ion diffusion into the particle and can be extremely valuable in visualizing the strain propagated by local defects. However, this technique is limited by sample constraints such as only one particle is imaged and this particle must remain crystalline and fixed in position. Nevertheless, a related, but non-imaging, Bragg coherent diffraction technique for measuring the phase transition of an assembly of particles has shown promise in unambiguously distinguishing between solid solution and two phase transitions. [13]

The second valuable *in situ* imaging mode, 2D **chemical** mapping, gives an indirect measure of ion diffusion and current density by mapping the chemical changes in active material during biasing. These chemical changes can be measured by tuning the energy across an absorption edge and measuring the changing intensity in transmission in both full field (see for example [14-16]) and scanning modes or with fluorescence [17] in scanning mode.

The current limitation to *in situ*, high resolution (tens of nanometers) tomographic and chemical imaging of batteries is predominately radiation dose. Presently, high resolution tomography is done in a quasi *in situ* manner where tomography data sets (requiring a few to tens of minutes) are recorded at limited voltages during electrochemical cycling. In the future, limited angle, dynamic tomography [18] or very low dose projection (dose fractionation)

tomography [19] could substantially reduce the dose per data set and increase the speed of data collection. Similar dose limiting efforts are already underway for chemical imaging by reducing the number of energy points needed in an XAS scan to identify the chemical state of each pixel [20]. Typically for XAS microscopy, images are collected at a number of different energies across a particular absorption edge and linear combination fitting using known chemical standards is performed on each pixel to determine the pixel's chemical makeup. Already, L-edge chemical maps, where the spectral signatures of specific transition metal chemistries tend to be dramatically different compared to their K-edge counterparts, have been successfully performed with only two energy points. For example, Yu *et al.* [21] (Figure 3) accurately distinguished between LiFePO_4 (Figure 3B, red) and FePO_4 (blue) by taking the difference between images recorded at 708 and 710 eV X-ray energy.

Additionally, *in situ* ptychography would allow high resolution imaging using a lower resolution scanning probe [22]. Current examples of *ex situ* ptychographic chemical mapping utilize soft X-rays [21, 23]. This severely limits the maximum thickness of the imaged material to avoid multiple X-ray scattering within the material, which would violate the assumptions of the Born Approximation utilized in the iterative image reconstruction algorithms. Depending on the degree to which the approximation is violated, image resolution can suffer or image reconstructions are not reproducible. Additional complications arising from samples which are too thick manifests as a dampening of the peaks in the X-ray absorption spectrum (Figure 3C). Nevertheless, we expect the emergence of *in situ* ptychography on more complex systems such as those for energy storage in the immediate future.

Fuel cells

Tracking the changes in the nano- and microstructure as well as chemistry at the nanoscale in fuel cells under operating conditions such as high temperature or an O₂ environment gives a more complete understanding of how these changes contribute to the efficiency of operation and failure pathways. Some *ex situ* high resolution X-ray tomography results have given insight into the pore network in solid oxide fuel cells (SOFC) (see for example [24-26]). However, few examples of *in situ* X-ray microscopy or tomography of fuel cells are published at present. Shearing *et al.* measured the microstructural changes of a SOFC near room temperature (14 °C) and operating temperature (695 °C) [27]. More recently, Bozzini *et al.* imaged model (half-cell) nano proton exchange membrane fuel cells (PEMFC) with applied cathodic or anodic polarization and 2.5x10⁻⁵ mbar O₂ [28]. Local Fe L₃ absorption spectra show a spatial variation in the relative ratio between different Fe oxidation states in the cell containing NaBH₄ in the electrolyte. On the other hand, cells containing no NaBH₄ in the Nafion-ionic liquid electrolyte had Fe only in the high oxidation state (Fe^{3+,4+}) under anodic polarization of the working electrode at +2V.

In situ imaging of fuel cells would also benefit from the significant spatial resolution improvement with coherent imaging techniques. 3D near-field ptychography (a CDI technique that measures the near-field, rather than far-field, diffraction) has been demonstrated on an *ex situ* SOFC anode with ~120 nm resolution. [29] The reconstructed microstructure (pore, metal, and ceramic phases) agrees with standard inline holography tomography (holotomography) on the same sample. In the future, near-field ptychography will allow tomography on samples at a much lower X-ray energy and without the *a priori* knowledge required for in-line holography.

Nanostructure synthesis

X-ray microscopy is a promising *in situ* characterization technique for visualizing the nucleation and growth/dissolution of nanostructures because X-rays penetrate sample environments such as liquid electrolytes [30]. Electrochemical syntheses are especially of interest because of the variety of nanostructures that can be deposited, such as nanorod, plates, or films. Bozzini *et al.* have designed a microcell with varying current density for *in situ* electrodeposition imaging studies combining fluorescence mapping and μ XAS (see for example [31]).

X-ray microscopy has also been utilized to watch the morphological and chemical transformation of previously synthesized nanostructures over time following the introduction of a solution. The galvanic replacement of Ag wires, with diameters mostly in the 70 to 90 nm range, into hollow Au was tracked in a flow cell after the injection of aqueous solution of HAuCl_4 . [30] The nanowires undergo multiple steps during the process including local pitting, etching of Ag and deposition of Au on the outside of the wires, and finally the reconstruction of nanotube walls via Ostwald ripening. In a similar study, the hollowing of Cu_2O nanocubes to form Cu_2S nanocages with 10-20 nm wall thicknesses by sulfidation was tracked also as a function of time. [32] Immediately before X-ray imaging, Na_2S solution was added to Cu_2O nanocrystals and within 360 s most or all of the Cu_2O cores were removed, leaving the Cu_2S nanocages. Currently the number of *in situ* microscopy studies of nanostructure synthesis is small; however, we anticipate a growing interest as these X-ray imaging techniques become more broadly known and spatial resolutions continue to improve.

Conclusion and Future Perspective

In the next few years, we anticipate that both full field and scanning X-ray microscopies will be increasingly important for *in situ* studies of a diverse range of nanomaterials as more researchers become aware of the capabilities of (S)TXM and as additional instruments become accessible. We also anticipate that spatial and temporal resolution will improve. Figure 4 shows a simplified illustration of space and time scales important in nanomaterials function and their accessibility with X-ray imaging. The right side shows microstructure that is accessible with current capabilities; these typically span times of seconds to hours and >10 nm length scales. Examples of these are given in the text above. In the near future, the spatial resolution will improve to <5 nm (about 2 nm in heroic efforts) and the time scales may approach milliseconds. More importantly, we anticipate that improvements in data collection will enable more 3D and chemically specific imaging. These developments will allow, for example, probing of surface layers on nanoparticles, nanoparticle aggregation, and triple phase boundaries. One limitation may be X-ray induced beam damage to the small particles, especially in reactive environments as found in batteries or catalysis or in typical synthesis conditions. It is important to find ways to mitigate this, perhaps by approaches like fly-scan ptychography as already demonstrated with visible light and X-rays [33-35]. It will also be important to adopt approaches to address a range of complementary diagnostic modes, including coupling techniques such as Raman and IR [36], as these can add chemical sensitivity not obtainable with X-rays. One method to address the relevant range of length scales from atoms to particles is correlative microscopy where TXM and STXM are used at a >10 nm scale to identify interesting regions in a nanomaterial and then the same location analyzed with TEM. Achieving this goal *in situ* will present challenges.

Further into the future, new fourth generation X-ray sources will become operational with significantly enhanced brightness as compared to the present sources. These include NSLS II

(USA, presently operating), Max IV (Sweden, 2016), SIRIUS (Brazil, 2019), and the upgraded Advanced Photon Source (USA, 2020s). These new sources and the X-ray imaging instruments that they enable should facilitate an improvement in resolution, potentially to Ångströms, for CDI approaches. This will now begin to address near atomic scale issues (e.g., reaction sites), illustrated on the left side of Figure 4, and may enable Holy Grail experiments of atomic scale observations of individual nanoparticles, such as catalysts, during operation. The advent of free electron lasers, such as the Linac Coherent Light Source (USA) and XFEL (Germany), enables shorter time scales to be probed, possibly approaching atomic motions (nucleation, reactions). However, with these high intensity, small spot probes it will be essential to develop effective ways to address and limit X-ray beam damage. Nevertheless, *in situ* X-ray microscopy will continue to play an increasingly vital role in understanding the synthesis of functional nanomaterials and their the behavior during operation.

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- [1] Liu XH, Huang JY. **In situ TEM electrochemistry of anode materials in lithium ion batteries.** *Energy Environ. Sci.* 2011, **4**:3844-60.
- [2] Nelson Weker J, Toney MF. **Emerging In Situ and Operando Nanoscale X-Ray Imaging Techniques for Energy Storage Materials.** *Adv. Funct. Mater.* 2015, **25**:1622-37.
- [3] Falcone R, Jacobsen C, Kirz J, Marchesini S, Shapiro D, Spence J. **New directions in X-ray microscopy.** *Contemp. Phys.* 2011, **52**:293-318.
- [4] Chapman HN, Nugent KA. **Coherent lensless X-ray imaging.** *Nat. Photonics* 2010, **4**:833-9.
- [5] de Smit E, Swart I, Creemer JF, Hoveling GH, Gilles MK, Tyliczszak T, et al. **Nanoscale chemical imaging of a working catalyst by scanning transmission X-ray microscopy.** *Nat.* 2008, **456**:222-5.
- [6] Gonzalez-Jimenez ID, Cats K, Davidian T, Ruitenbeek M, Meirer F, Liu Y, et al. **Hard X-ray Nanotomography of Catalytic Solids at Work.** *Angew. Chem., Int. Ed.* 2012, **51**:11986-90.
- [7] Høydalsvik K, Bø Fløystad J, Zhao T, Esmaili M, Diaz A, Andreassen JW, et al. **In situ X-ray ptychography imaging of high-temperature CO₂ acceptor particle agglomerates.** *Appl. Phys. Lett.* 2014, **104**:241909.

Using *in situ* ptychography, the authors image agglomerates of catalytic nanoparticles, demonstrating for the first time the potential benefit of the coherent imaging technique in tracking nanoparticle catalysts under operating conditions.

- [8] Weker JN, Liu N, Misra S, Andrews JC, Cui Y, Toney MF. **In situ nanotomography and operando transmission X-ray microscopy of micron-sized Ge particles.** *Energy Environ. Sci.* 2014, **7**:2771-7.

Using *operando* 2D TXM, the authors observed a significant size dependence on the cycling characteristics of micron-sized Ge particles. With *in situ* tomography, the complete fracturing of alloying anode materials into separate pieces was unambiguously demonstrated for the first time.

[9] Wang J, Chen-Wiegart Y-cK, Wang J. **In Situ Three-Dimensional Synchrotron X-Ray Nanotomography of the (De)lithiation Processes in Tin Anodes.** *Angew. Chem., Int. Ed.* 2014, **53**:4460-4.

••[10] Wang J, Eng C, Chen-Wiegart Y-cK, Wang J. **Probing three-dimensional sodiation-desodiation equilibrium in sodium-ion batteries by in situ hard X-ray nanotomography.** *Nat. Commun.* 2015, **6**:7496.

The authors track the microstructure of tin anode particles in sodium-ion batteries throughout ten electrochemical cycles. They find that particles with diameters below 0.5 μm do not show signs of fracturing while particles above 1.6 μm show significant fractures.

••[11] Eastwood DS, Bayley PM, Chang HJ, Taiwo OO, Vila-Comamala J, Brett DJL, et al. **Three-dimensional characterization of electrodeposited lithium microstructures using synchrotron X-ray phase contrast imaging.** *Chem. Commun.* 2015, **51**:266-8.

The microstructure of electrodeposited lithium metal “dendrites” has been imaged for the first time using *in situ* phase contrast tomography. This work lays the foundation for higher resolution *in situ* phase contrast imaging in energy storage.

•[12] Ulvestad A, Singer A, Clark JN, Cho HM, Kim JW, Harder R, et al. **Topological defect dynamics in operando battery nanoparticles.** *Sci.* 2015, **348**:1344-7.

The authors utilized Bragg coherent diffraction to track the 3D strain of individual crystalline particles under operating conditions. They mapped the edge dislocations within the particles as a function of charging and discharging.

•[13] Singer A, Ulvestad A, Cho H-M, Kim JW, Maser J, Harder R, et al. **Nonequilibrium Structural Dynamics of Nanoparticles in LiNi_{1/2}Mn_{3/2}O₄ Cathode under Operando Conditions.** *Nano Lett.* 2014, **14**:5295-300.

The competing transformation mechanisms: solid solution and two-phase reactions were directly observed using coherent X-ray diffraction under fast (dis)charging conditions. The occurrence of the different transformation mechanisms depended on the lithium concentration and the direction of the biasing.

[14] Li L, Chen-Wiegart Y-cK, Wang J, Gao P, Ding Q, Yu Y-S, et al. **Visualization of electrochemically driven solid-state phase transformations using operando hard X-ray spectro-imaging.** *Nat. Commun.* 2015, **6**:6883.

[15] Nelson Weker J, Li Y, Shanmugam R, Lai W, Chueh WC. **Tracking Non-Uniform Mesoscale Transport in LiFePO₄ Agglomerates During Electrochemical Cycling.** *ChemElectroChem* 2015, **2**:1576-1581.

[16] Yu Y-S, Kim C, Liu Y, van der Ven A, Meng YS, Kostecki R, et al. **Nonequilibrium Pathways during Electrochemical Phase Transformations in Single Crystals Revealed by Dynamic Chemical Imaging at Nanoscale Resolution.** *Adv. Energy Mater.* 2015, **5**:1402040.

••[17] Li Y, Weker JN, Gent WE, Mueller DN, Lim J, Cogswell DA, et al. **Dichotomy in the Lithiation Pathway of Ellipsoidal and Platelet LiFePO₄ Particles Revealed through Nanoscale Operando State-of-Charge Imaging.** *Adv. Funct. Mater.* 2015, **25**:3677-87.

In situ soft X-ray fluorescence STXM was demonstrated for the first time to track the differences in the lithiation pathways in ellipsoidal and platelet LiFePO₄ particles. Ellipsoidal particles intercalate sequentially, while platelets particles intercalated simultaneously.

[18] Myers GR, Kingston AM, Varslot TK, Turner ML, Sheppard AP. **Dynamic tomography with a priori information.** *Appl. Opt.* 2011, **50**:3685-90.

[19] Hong YP, Gleber SC, O'Halloran TV, Que EL, Bleher R, Vogt S, et al. **Alignment of low-dose X-ray fluorescence tomography images using differential phase contrast.** *J. Synchrotron Radiat.* 2014, **21**:229-34.

[20] Nelson Weker J, Li Y, Chueh WC. **Low dose, limited energy spectroscopic x-ray microscopy.** In *X-ray Nanoimaging: Instruments and Methods II*. Edited by Lai B. SPIE; 2015:95920N-N-8.

••[21] Yu Y-S, Kim C, Shapiro DA, Farmand M, Qian D, Tyliczszak T, et al. **Dependence on Crystal Size of the Nanoscale Chemical Phase Distribution and Fracture in Li_xFePO_4 .** *Nano Lett.* 2015, **15**:4282-8.

Soft X-ray ptychography was used to image the chemical and morphological changes in different sized LiFePO_4 plates after partial chemical or electrochemical delithiation.

[22] Shapiro DA, Yu Y-S, Tyliczszak T, Cabana J, Celestre R, Chao W, et al. **Chemical composition mapping with nanometer resolution by soft X-ray microscopy.** *Nat. Photonics* 2014, **8**:765-9.

•[23] Li Y, Meyer S, Lim J, Lee SC, Gent WE, Marchesini S, et al. **Effects of Particle Size, Electronic Connectivity, and Incoherent Nanoscale Domains on the Sequence of Lithiation in LiFePO_4 Porous Electrodes.** *Adv. Mater.* 2015, **27**:6591-7.

The authors employed soft X-ray ptychography, STXM, and TEM to determine how the carbon black loading affects the sequence of lithiation in partially discharged LiFePO_4 .

••[24] Harris WM, Lombardo JJ, Nelson GJ, Lai B, Wang S, Vila-Comamala J, et al. **Three-Dimensional Microstructural Imaging of Sulfur Poisoning-Induced Degradation in a Ni-YSZ Anode of Solid Oxide Fuel Cells.** *Sci. Rep.* 2014, **4**:5246.

Tomography was used to map the spatial distribution of Ni, Ni-S, and YSZ phases in a SOFC anode after exposure to hydrogen sulfide at elevated temperatures. The authors found that the nickel-sulfur layer covered most of the exposed nickel surface, thereby blocking the reaction sites.

[25] Julie V, Jérôme L, Peter C, Pierre B, Gérard D, Heikki S, et al. **3D phase mapping of solid oxide fuel cell YSZ/Ni cermet at the nanoscale by holographic X-ray nanotomography.** *J. Power Sources* 2013, **243**:841-9.

[26] Kennouche D, Chen-Wiegart Y-cK, Cronin JS, Wang J, Barnett SA. **Three-Dimensional Microstructural Evolution of Ni- Yttria-Stabilized Zirconia Solid Oxide Fuel Cell Anodes At Elevated Temperatures.** *J. Electrochem. Soc.* 2013, **160**:F1293-F304.

[27] Shearing PR, Bradley RS, Gelb J, Lee SN, Atkinson A, Withers PJ, et al. **Using Synchrotron X-Ray Nano-CT to Characterize SOFC Electrode Microstructures in Three-Dimensions at Operating Temperature.** *Electrochem. Solid-State Lett.* 2011, **14**:B117-B20.

[28] Bozzini B, Gianoncelli A, Kaulich B, Mele C, Prasciolu M, Kiskinova M. **In Situ Soft X-ray Microscopy Study of Fe Interconnect Corrosion in Ionic Liquid-Based Nano-PEMFC Half-Cells.** *Fuel Cells* 2013, **13**:196-202.

•[29] Stockmar M, Hubert M, Dierolf M, Enders B, Clare R, Allner S, et al. **X-ray nanotomography using near-field ptychography.** *Opt. Express* 2015, **23**:12720-31.

Near-field ptychography was used to image the 3D microstructure of a SOFC. The quality of the results was compared to conventional holography tomography. This work demonstrates a method for high resolution tomography imaging on strongly absorbing and refracting samples.

[30] Sun Y, Wang Y. **Monitoring of Galvanic Replacement Reaction between Silver Nanowires and H₂AuCl₄ by In Situ Transmission X-ray Microscopy.** *Nano Lett.* 2011, **11**:4386-92.

[31] Bozzini B, Gianoncelli A, Mele C, Kiskinova M. **Electrochemical fabrication of nanoporous gold decorated with manganese oxide nanowires from eutectic urea/choline chloride ionic liquid. Part II – Electrodeposition of Au–Mn: A study based on soft X-ray microspectroscopy.** *Electrochim. Acta* 2013, **114**:889-96.

[32] Kuo C-H, Chu Y-T, Song Y-F, Huang MH. **Cu₂O Nanocrystal-Templated Growth of Cu₂S Nanocages with Encapsulated Au Nanoparticles and In-Situ Transmission X-ray Microscopy Study.** *Adv. Funct. Mater.* 2011, **21**:792-7.

[33] Pelz PM, Guizar-Sicairos M, Thibault P, Johnson I, Holler M, Menzel A. **On-the-fly scans for X-ray ptychography.** *Appl. Phys. Lett.* 2014, **105**:251101.

[34] Deng J, Nashed YSG, Chen S, Phillips NW, Peterka T, Ross R, et al. **Continuous motion scan ptychography: characterization for increased speed in coherent x-ray imaging.** *Opt. Express* 2015, **23**:5438-51.

[35] Huang X, Lauer K, Clark JN, Xu W, Nazaretski E, Harder R, et al. **Fly-scan ptychography.** *Sci. Rep.* 2015, **5**:9074.

[36] Gibson EK, Beale AM, Catlow CRA, Chutia A, Gianolio D, Gould A, et al. **Restructuring of AuPd Nanoparticles Studied by a Combined XAFS/DRIFTS Approach.** *Chem. Mater.* 2015, **27**:3714-20.

Figure 1: Schematics of different X-ray microscopy geometries. In a scanning technique (a), the beam is focused to a very small spot size and the sample is scanned through the X-ray beam. Transmitted X-rays, fluorescence X-rays, or Auger electrons (or several of these) are collected to form an image and allow for elemental or chemical mapping. If a coherent beam is used, then scattered intensity patterns can be collected either in transmission or near a Bragg diffraction peak and reconstructed into an image with a resolution below the beam size. In the full field technique (b), a beam is focused onto the sample and the scattered and transmitted X-rays are collected with an objective lens onto an area detector forming the image. If a coherent beam (yellow) is used without any focusing optics, the scattered intensity pattern can be collected either in transmission or near a Bragg peak for higher resolution imaging.

Figure 2. Imaging catalysis in real time. *In situ* chemical mapping of Fischer–Tropsch-to-Olefins catalyst particle (fresh) and during the reaction (10 bar, $H_2/CO = 1$ and 350 C) as a function of reaction time. Color denotes the different Fe chemistries as follows: Fe_2TiO_5 is green, Fe_2O_3 is red, and Fe_3O_4 is blue. For the maps after 6 h and 7 h under reaction conditions: Fe_2TiO_5 is green, FeC_x is red, and Fe_3O_4 is blue. a) Bulk Fe XANES spectra of the fresh particle, b–d) single pixel at the three different denoted regions. Fits are solid lines. Reproduced with permission. [6] Copyright 2012, Wiley.

Figure 3. Chemical mapping of LiFePO_4 . A) Optical density (OD) map at 709.2 eV and B) difference map between OD maps at 708 and 710 eV of Li_xFePO_4 crystal obtained by ptychography. Blue indicates FePO_4 and red is LiFePO_4 . C) Single pixel X-ray absorption spectra (solid lines) showing intensity saturation from the expected spectra (dashed lines) due to the large optical thickness of the particle. Reproduced with permission. [21] Copyright 2015, American Chemical Society.

Figure 4. Current and future imaging capabilities. Schematic of the current and future capabilities of imaging different length scales relevant to nanomaterials ranging from reaction sites, such as adsorption, intercalation, and nucleation, to interfaces, such as segregation, formation of solid electrolyte interface, and triple point boundary, to particles microstructure, such as porosity/tortuosity and grain orientation. The relevant time scales are indicated at the bottom.

Figure 1

Figure 2

Figure 3

Figure 4