Spectroscopic Imaging Using Transmission X-ray Microscopy

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&
TXM Team

- Instrumentation & Background
- 2D and Tomographic Imaging
- XANES Imaging
  - Experimental Procedure
  - Data Analysis
- In-situ studies with Xanes
**Imaging: X-ray Microscopy**

Imaging systems: Need various length scales for functional materials

- **g** - Scanning μ-XRF microprobe (hard X-ray, focused with K-B mirrors to ~ 1 micron spot)

- **d, f** - Zone-plate-based STXM
  - Zone-plate focused to very fine spot (tens of nm)
  - Soft X-rays: transmission at C, O K-edges and metal L-edges
  - Hard X-rays: K edge fluorescence
  - Scanning methods can be slow to cover a large area, tomography is difficult

- **e** - Full-field TXM
  - Hard and soft X-ray
  - Resolution: micro-CT ~1 micron, nano-CT tens of nm
  - Hard x-rays give good depth of focus and sample penetration

Full-Field Microscopy

Fuel cell micro-CT Data
F DeCarlo, UNICAT report, Argonne Lab 2004

Fuel cell nano-CT Data

Porosity Segmentation & quantification

Resolution: 140 nm

Mokso, Stampanoni et al. (2012) J Struc Biol 177:233
The zone plate:

\[ r_n = \sqrt{n \lambda f + \frac{n^2 \lambda^2}{4}} \]

\[ f = \frac{2 r_N \Delta r_N}{\lambda} \]

It is a lens that works at X-ray regime.
Because it is a lens, it follows the thin lens equation
\[ \frac{1}{s} + \frac{1}{s'} = \frac{1}{f} \]

Where \( f \) is the focal length; \( S \) is the distance from the sample to the zone plate; and \( S' \) is the distance from the zone plate to the detector.

The magnification achieved by this zone plate can be written as:
\[ M = \frac{S'}{S} \]

If you measure the distances in our system, you will see that the magnification achieved by the zone plate is around 50.
Functional Schematic of Transmission X-ray Microscope

- Data storage & reconstruction
- Fast camera
- Motion control & data acquisition
- Computer cluster (if available)
- Rotation stage
- Zone plate
- Scintillator
- Objective lens
- Mirror
- Our camera box

X-rays
Visible photons
Camera: commercially available, with pixel size approximately 7 microns.

Scintillator: converts X-rays into visible light for detection

Mirror: 45 degree mirror

Objective lens: additional magnification of 10x or 20x
Pixel size, magnification, and resolution

\[
\text{Pixel}_{\text{effective}} = \frac{\text{Pixel}_{\text{real}}}{M_X \times M_V}
\]

Where \(\text{pixel}_{\text{real}} = 7\) microns
- \(M_X = 50\); is the magnification achieved in the X-ray regime
- \(M_V = 10\) or 20; is the magnification achieved in the visible light regime

As a result, the effective pixel size is around 7 nm (with 20X) or 14 nm (with 10X).

However, the real imaging resolution is not as small as the pixel size because the limitation in the quality of the zone plate adds a point spread function to your image.

The quality of the zone plate limits the resolution to be around 30 nm. In other words, we are oversampling at the detector plane, which gives us flexibility to upgrade when better X-ray optics are available.
Transmission X-ray Microscope – Full-Field Imaging

Full Image (2Kx2K pixels) in single shot

Spatial resolution $\sim 30$ nm  
Energy $\sim 5$ keV – 14 keV  
FOV 30µm

2D imaging and Tomography in absorption and Zernike phase contrast
SSRL BL6-2C: Full Field Hard X-ray

Spatial resolution: 30 nm
FOV 30+ um
Energy: \(~4.5\) keV – 14 keV
2D imaging and Tomography
Energy scanning for XANES imaging
Fluorescence microprobe (micron-scale)
Typical exposure: ½ second
CCD array: 2048 x 2048
TXM image of Siemens star test pattern at 9 keV

30 nm Siemens star
9 keV absorption contrast
Stacked 30-200 zone plate
Unique Imaging Capabilities

3D – mosaic tomography
  • pore structures, surface/core

Elemental sensitive TXM imaging
  • Nanoscale heterogeneity, promoters/active sites

Chemical sensitive TXM imaging
  • Chemistry vs. morphology/heterogeneity

In-situ, in operando

J Gonzalez-Jimenez et al. (2012) Angew Chem Int Ed 51: 11986-11990


Imaging of Mineralized Tissue

Imaging nanoscale bone damage

Scientific Achievement

Nanoscale evidence of bone damage due to stress loading was viewed with X-ray microscopy, not previously seen with microCT.

Significance and Impact

Diseases such as osteoporosis alter bone remodeling and may weaken tissue. Ability to image details in bone structure in response to stress provides new insights into skeletal damage mechanisms and future avenues for research.

Research Details

- Pillars from bone were subjected to stress loading, and stained with uranyl acetate to indicate damage.
- Damaged areas had altered morphology including staining of existing bone features and cross-hatching.

Work performed at SSRL and Cornell University

Representative TXM absorption contrast image (acquired at 7.1 keV) of rat cortical bone illustrating details in bone structure at 30 nm resolution. Features include lacunae and canaliculi present with grey areas indicating bone, and black areas indicating background, lacunae and canaliculi. Left: 6x9 mosaic of low resolution images. Right: single high resolution image of region. No staining is present in this image; grey-scale variation represents attenuation differences in the tissue.

Effects of Tooth Strain on Surrounding Bone

• Nanoscale structural properties of bone-ligament-jawbone show relationships between strain and bone disease.
• Jaw strain (e.g. grinding or clenching of teeth or orthodontic treatment) exerts stresses on teeth & surrounding bone. These strains can alter bone structure and cause problems with bone health.
• Nanoscale imaging of mineralized tissue in bone-ligament-jaw with X-ray microscopy and other techniques showed changes in structure due to strain.
• Sites of tension lead to changes in physiology of ligament space, which can stress health of the bone-ligament-jaw system.

Figure. Images of adapted jaw bone using transmission x-ray microscopy at SSRL Beam Line 6-2 (30 nm resolution) Highly attenuating bands within bone matrix (block black arrows), are formed due to strain. Darker regions (less than 30 mm in size) are lacunae, which house bone cells.


Work performed at SSRL, LBNL, and UCSF School of Dentistry
μ-XRF – Complementary Elemental Mapping

Elemental distributions correlated with disease

SP Ho et al. (2013) *Bone* 57, 455-467
Data from Geological sequestration of carbon dioxide is an important component of global greenhouse gas emission reduction strategy.

Considerable amount of CO₂ generated by large stationary sources, making it feasible to capture and treat.

It is critical to understand and ultimately identify suitable reservoir zones for CO₂ injection and storage.

Need for CO₂ Sequestration

Geological sequestration of carbon dioxide is an important component of global greenhouse gas emission reduction strategy.
The density measured using medical CT indicates different CO$_2$ concentration throughout the core.

Why do samples 1 and 2 show difference in CO$_2$ saturation?
Multiple Length scale study – breaking into representative smaller samples

Physically broken down into smaller pieces for μ-CT experiment (limited field of view)

Numerically broken down into smaller pieces for analysis (we have limited computational power)

• Several positions on the sample were scanned.
• Each scanned area results in a 3D volume, which is still too big for the computer to handle.

S1 and S2 (cm size) taken from the core cylinder.

~1 cm

However, we need to be careful when doing this. The boxes must be large enough to be meaningful.
Segmentation beyond histogram-based thresholding

Separation and labeling

give each individual grain an ID, enabling a lot of sophisticated statistical analysis.

Histogram helps for identifying different minerals.
Single grain mounted on a needle for nano-CT investigation

Morphology at sub-grain scale

30 µm

10 Micron
Conclusions: Shale CO₂ Sequestration

• More and Smaller skeleton grains
• Harder for small grains to penetrate
• Less small grains
• Larger porosity
• Smaller complexity in the connected pore structure
• Less pore throats
• Wider secondary throats

High concentration of CO₂ in CO₂ saturation experiment

Low concentration of CO₂ in CO₂ saturation experiment

• Less and larger skeleton grains
• Easier for small grains to penetrate
• More small grains
• Smaller porosity
• Larger complexity in the connected pore structure
• More pore throats
• Tighter secondary throats
Related Study: how do fluids flow through rocks?

Tomography determines porosity and connectivity to allow for modelling of fluid flow through the connected channels—this has relevance to oil exploration and extraction.
X-ray Absorption Spectroscopy (XANES, EXAFS)

Tunable source enables:

- Element specific ID
- Chemical speciation
- Structural determination

Excites core electrons (mainly s, p)
Using X-ray Absorption to Characterize Materials

Tunable source enables:

• Elemental identification
• Chemical speciation
• Structural determination

Can couple to X-ray imaging for 2D, 3D, in situ and time resolved imaging
Adding Chemistry: XANES imaging

2D and 3D XANES Microscopy

1) Collect one high resolution absorption image at each energy
2) Trace the absorption value for each pixel to get single pixel XANES
3) ~1 million XANES per energy stack!
XANES: Linear Combination Fitting

Li-ion NiO battery electrode at the Ni K-edge (J Cabana LBNL)

F Meirer, J Cabana, Y Liu, A Mehta, P Pianetta (2011)
J Synchrotron Rad 18: 773-781

Spectra of pure compounds
excellent agreement with Lytle database
How do we analyze ~ million XANES?

Processing pre- and post-edge data:

Average Region value
Pixel with maximum absorption in area
Pixel with maximum absorption in image

Edge jump
FF TXM XANES: 2D & 3D chemical info

Linear combination fit using principal components to determine ratio of chemical phases for each pixel:

one XANES spectrum for each pixel

Normalized $\mu(E)$

$E_1, E_2, E_n$

$x,y,E$ (θ)

3D distribution of NiO (red) and Ni metal (green)

$\theta_1, \theta_2, \theta_n$

$0, \mu_{max}$

$E_{max}$

$x,y (E)$

$15 \mu m$

Pixelsize ~15 nm

$15 \mu m$

$x,y,E$

$3D$ reconstruction of phase maps

Probable Processing Steps for production of *Attic ceramic (Greek)*

**Levigation →** Fractionates the Clay into three component
1. Finest + K-rich for **Black Gloss**
2. Middle Fractionate for **Red Gloss**
3. Coarsest aggregates for the **Body**

**Firing in the Reducing environment at >850°C**
Vessel reduces to all black
Black Gloss densifies/vitrifies

**Oxidative pre-firing at 800°C**

**Plug**

**CO/CO₂**

**Slow Cooling in oxidizing environment from ~800°C**
Denser/impermeable black remains black

**Porous red reoxidizes**
Nanostructure & phase imaging of Sigilatta

Campanian (Roman)
Brown/red body, Black high-gloss coating

Phase map deduced from $\mu$-XRF measurements at ID21 (ESRF) with huge FOV including Raman spectra recorded at various points

Nanostructure (TXM) & phase imaging of Sigillatta

Different types of pottery show different chemistry

Campanian (Roman)
Brown/red body,
Black high-gloss coating

Pre-sigillata (Roman)
Brown/red body,
Black high-gloss coating

Sigillata (Roman, Italian workshop)
Brown/red body,
Red high-gloss coating

Hematite

Maghemite

Hercynite

Slip

Body

5 μm
LiFePO$_4$ batteries

- Specific capacity 170 mAh/g
- Energy density 220 Wh/L
  - But long cycle life
  - Safe – low fire hazard

- Operation depends on efficient insertion/removal of Li
- Ability to accomplish phase changes determines
  - electrode utilization
  - cycle life

- Improved with smaller particles – but why?
  - Surface effects/ contact?
  - Crystal morphology?

Roehr Motorcycles 2011 eSuperSport Electric Sportbike –
- AC Induction Motor, 50Kw (67Hp) power, 80 lb/ft torque.
- 100+ MPH, strong acceleration.
- Roehr battery: high discharge LiFePO$_4$ battery chemistry
- Safe & reliable, industry leading cycle life, high energy density
- 7.7Kwh capacity - 75 mile range. Recharged in <7 hours.

http://www.roadracingworld.com
Delithiation/ lithiation of LiFePO₄ (ex situ)

- Phase transformations
determined by crystal and electronic structure
- Channels (1D) allow Li transport for charge/discharge
- Particle size and morphology can lead to kinetic barriers
  - modify reaction mechanism and rate

LiFePO$_4$ – phase transformation

- LiFePO$_4$/FePO$_4$ 1$^{st}$ order phase transition ~3.4 V vs Li$^+/\text{Li}^0$
- On Li extraction: **anisotropic** changes in lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
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<tbody>
<tr>
<td>LiFePO$_4$</td>
<td>10.334</td>
<td>6.002</td>
<td>4.695</td>
</tr>
<tr>
<td>FePO$_4$</td>
<td>9.826 (-4.9%)</td>
<td>5.794 (-3.5%)</td>
<td>4.784 (+1.9%)</td>
</tr>
</tbody>
</table>

G Chen, X Song, TJ Richardson 2006, Electrochem Solid-State Lett 9, A295
Electron Microscopy – defects are interior

STEM HAADF:
Intensity exponentially proportional to mass thickness

Dark features: cracks or voids

SEM: Shows surface
Less defects seen – they are in the interior

Q: What is the chemistry?

Crystals: $2 \times 0.2 \times 4 \ \mu m \ (a,b,c)$
TXM: Spatially resolved chemistry

Left: XANES of LiFePO$_4$ & FePO$_4$ (averaged over full FOV containing multiple single-phase particles)

Right: single pixel XANES

Verifying principle components: LiFePO₄ & FePO₄

Q: Is there a transition chemistry or just a 2-component system?

- **Left:** principle components analysis: First 2 account for 99.2%
- **Right:** Overclustered k>N, k-means clustering
  - a) score plot
  - b) Cluster index image displaying the distribution of pixels assigned to each of 5 clusters.
  - c) Average XANES of all pixels in each cluster.
- Clusters of 2 most distinct XANES fit to LiFePO₄ and FePO₄. The rest fit to these 2 compounds.

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Heterogeneity in structure affects delithiation

a) FF TXM @7080eV; nominal composition Li$_{0.74}$FePO$_4$
Defects: dark areas

b) Chemical phase map - LC fitting of single pixel XANES
Delithiation seen on defect-free denser edges

Nearly fully delithiated crystal shows progression

- FF TXM image of a selected crystal in a sample with nominal composition Li$_{0.5}$FePO$_4$ collected @ 7080eV.
- Chemical phase map obtained by LC fitting of XANES data at each pixel.
  - The white arrows – FePO$_4$ elongated domains in c direction correlate with distribution of cracks (seen also in TEM, right)
- Fits to Li$_{0.06}$FePO$_4$, thus kinetic factors control ultimate phase ratio
LiFePO$_4$ - summary

- STEM revealed macroscopic defects
  - dominates kinetics of phase transition
- Stresses of delithiation lead to mechanical failure along c-axis particularly in defective center
  - dense edges remain more intact
- Microstructure important role as kinetic factor during phase transformation
- Larger particles fail due to effects within the interior, thus smaller particles are needed
- Operando studies now in progress (W Chueh, Stanford)
In Situ / Operando Imaging

Condenser Lens

Pinhole

Zone Plate Objective Lens

Battery Cell
High Pressure work

(a) Condenser Sample Zone Plate
    Pinhole

(b) Scintillator CCD

(c) Capillary Condenser Chamber Cross DAC
    Mounted on sample stage
    X-rays Fresnel Zone Plate
Understanding formation of the earth’s core

Model for iron and silicate in the earth’s core.
Magma ocean and percolation might be dominant mechanisms over different pressure–temperature ranges during Earth’s core formation.

Fe in silicate at different pressures

- As pressure increases, Fe begins to form a network, suitable to allow for percolation.

TXM tomography above and below Fe K-edge, to distinguish Fe from silicate matrix.

Characterizing channels in the iron network

3D renderings of the interconnected network iron alloy melt prepared at high pressure (64 GPa) and temperature (3300 K). a,b, The channel in a has been confirmed to be iron-rich material by element-sensitive nanoscale tomographic imaging; the channels labeled in blue in b are contiguous, as determined by using a 3D flood-fill algorithm. c, The channel line set extracted from the reconstructed 3D volume; the color map represents the relative thickness of the channel, with warmer colors indicating thicker channels.

Visualization of pressure induced phase transition in BiNiO$_3$

Observing 3D Chemical phase changes at high pressure

Visualization of chemical phases at nanometer resolution

5D visualization of pressure induced phase transition in BiNiO$_3$

The 5D (x, y, z, Energy, Pressure) visualization of chemical phase transition upon compression.

The phase transition pathway within the material visualized over virtual slices from tomography

In-situ battery cells

In-situ battery Cell – follow structural & morphological changes:

- In-situ, in real time (slow – hours)
- X-ray “transparent” cell
Ge particle battery anodes

Ge anodes:
- Ge -> Li\(_{≈4}\)Ge
- Large theoretical capacity (1600MAh g\(^{-1}\)); > 4x vs graphite
- Ge: Li diffusivity ~ 400X Si
- ~300% volume changes induce cracks and pulverization
- Leads to low cycle life

Goals – studying Ge micron particles:
- Understand Li\(^+\) insertion mechanism into Ge
- Quantify volume changes
- Visualize crack formation
- Quantify porosity changes
- Understanding can yield insight into Si and Sn also

Morphology changes during (de)lithiation of micron Ge

1. Cracks form in larger particles
2. Cracks fill as lithiation continues
3. Cracks reappear during delithiation
4. After delithiation larger particles are porous

In situ nanotomography of Ge batteries

- Fresh
- Lithiated (320% expansion)
- Delithiated

 Particle fractures into completely isolated pieces

Summary: Ge particle anodes

- Structure (XRD) & local chemistry (XAS) [*not shown*]
  - phase sequence to GeLi alloys – sharp and gradual
- Morphology (TXM):
  - End 1st lithiation: Smaller particles begin expansion earlier
  - 2nd (de)lithiation: Only large particles remain electronically connected

After expansion during lithiation, during contraction some particles lose contact with conductive polymer. Flexible polymer binders are being developed to counteract this.

a. Before cycling  b. Lithiated state  c. Delithiated state
Operando Chemistry: Tracking Li-ions during cycling

Deep discharge of LiCoO₂ battery – see Co reduction with delithiation
Operando Catalysis: Fischer-Tropsch at full T & P

Fischer-Tropsch catalysis

- Biomass, Natural gas, Coal
  → S-free, aromatic-free fuel

- Hydrocarbon distribution: methane to heavy waxes. Depends on catalyst and promoters.

- Typically Fe or Co catalyst
  - Addition of promoters can improve catalytic activity, selectivity

- Deactivation mechanisms:
  - Metal chemical changes?
  - Sintering/ morphology changes?

- Which initial chemical forms are most active?

US Dept of Transportation

Activity of 10 wt% and 15 wt% Co/TiO₂ catalysts vs. time on stream.
BL6-2 SSRL: Operating conditions 10-20 Bar/ to 500 °C

- Elliptical capillary condenser
- Water-cooled heater
- Zone plate (behind heater)
- To CCD camera (2Kx2K, ~15-21 nm pixel size)
- Fluorescence detector
- Gas inlet from mass flow control
- Sample high-pressure capillary
3D Fe catalyst – promoters, support, pore structure
Ruhrchemie Catalyst (70Fe₂O₃/20TiO₂/6ZnO/4K₂O)

3D elemental distribution (Fe in Red, Zn in Green, Ti in Yellow). Particle~20 um
Selected volume 3.8×6.7×6.5 µ³: solid phase = 143.5 µ³ (86.7% of volume)

Testing: activity, selectivity

- **Catalytic activity data**: (bench data)
  - FTO material at 10 bar, 350°C, H₂/CO = 1
  - a) Carbon conversion with time on stream
  - b) Normalized product yield
    - Selectivity towards methane, butane, propene, ethylene, CO₂
    - Maximum olefin production matches time for max CO conversion
    - From growing amount of Fe₃O₄ ? Carbides?

[Graphs and data plots depicting carbon conversion and normalized product yield for different compounds like CH₄, C₂H₆, C₃H₆, C₄H₁₀, CO, H₂, H₂O, CO₂, and He under conditions of 10 bar, 350°C, H₂/CO = 1.]
Initial Chemical Imaging of Fe Catalyst

High resolution single pixel Fe K-edge XANES

- Red: \( \text{Fe}^{3+} \)
- Green: \( \text{Fe}^{2+} \)
- Blue: \( \text{Fe}^{2,3+} \)

a: Averaged XANES
b-d: Single pixel XANES (21x21nm)

% Phase composition:
- \( \text{Fe}_3\text{O}_4 \): 100%
- \( \text{Fe}_2\text{TiO}_5 \): 54%
- \( \text{Fe}_2\text{O}_3 \): 42%

Operando Fischer-Tropsch Catalysis

Reaction over 5 h @10 bar and 450 °C

Initially Fe$_3$O$_4$ is formed, and lastly Fe carbide (purple, at 7h).

- Active Fe carbide and Fe$_3$O$_4$ control conversion rates.

Comparing timing with bench catalysis chemistry and mass spec data (maximum activity & selectivity at ~2h):

- Fe$_3$O$_4$ quite active, even before much Fe carbide formed.

Active forms of Fe appear on Fe$_2$O$_3$ (red), not Fe$_2$TiO$_5$ (green).

- Formation of Fe$_2$TiO$_5$ during calcining should be avoided.
Conclusions from Fe FT study

• **Activity Identified:**
  - Of main starting materials in fresh catalyst, Fe$_2$O$_3$ best reduced to Fe$_3$O$_4$
    - Formation of Fe$_3$O$_4$ in 1-2 hours: is active, selective catalyst
    - Small amounts of active Fe carbides formed on surface of Fe$_3$O$_4$

• **Failure pinpointed:**
  - No sintering seen – not a cause for failure
  - Fe$_2$TiO$_5$, formed during calcining with TiO$_2$, was not as chemically active.

• This type of spatially resolved chemical information, revealing **nanoscale heterogeneity in full industrial conditions** can inform synthesis protocols for FTO and other catalysts, for optimized activity.
Imaging Strengths of TXM

- Wide range of applications and multimodal imaging
- 50 micron depth of focus: whole samples or slices 50 microns thick
- Best on fixed, dried tissue; with support for heat sink
- Use of synchrotron tunable energy
- Software for automated collection, sophisticated data analysis and quantification
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