Nanometer to Micrometer Void Microstructure Characterization of SOFC Layers and Interfaces by Small Angle Scattering (SAXS) and Computed X-ray Microtomography (XMT)

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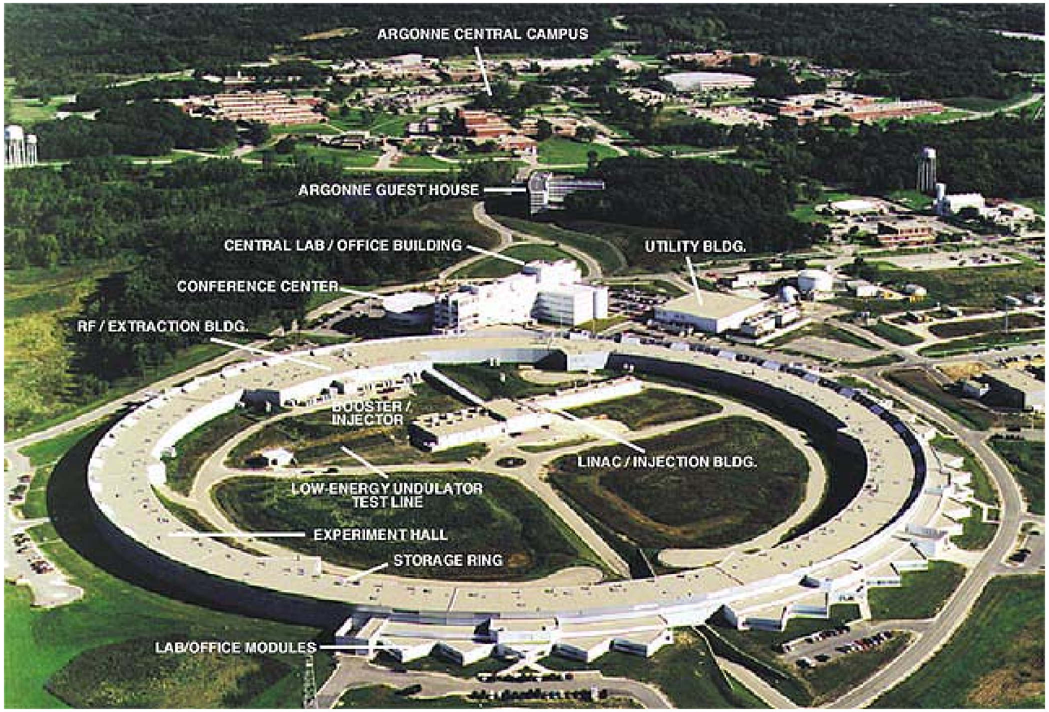
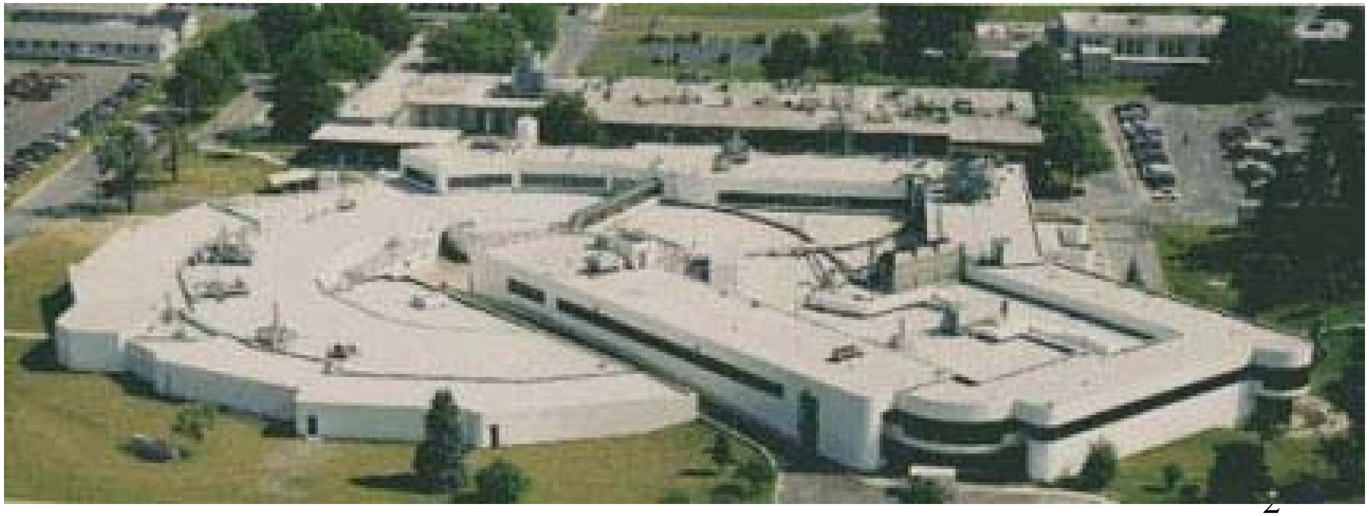
{quantitative void microstructure characterization using unique national facilities to provide links between processing and properties}

- Experiments performed at the UNICAT and SRI-CAT sectors of the Advanced Photon Source, Argonne National Laboratory, in collaboration with F. DeCarlo, and J. Almer.
- SOFC section: $La_{(1-x)}Sr_xMnO_3$ (LSM) cathode; YSZ electrolyte; and Ni(YSZ) Cermet anode supplied through Advanced Technology Program.

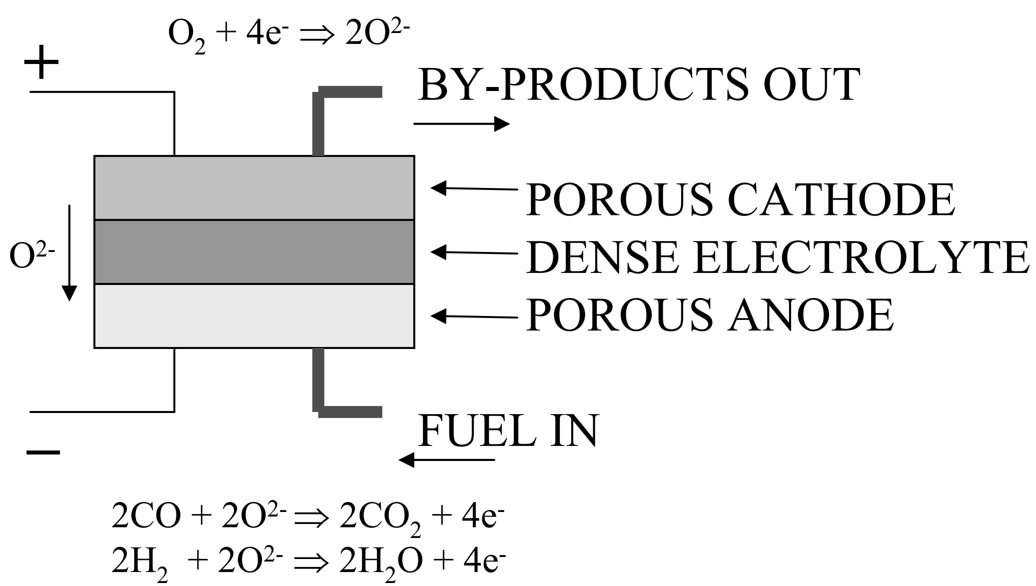


Advanced Photon Source
Argonne Nat'l. Lab., Illinois

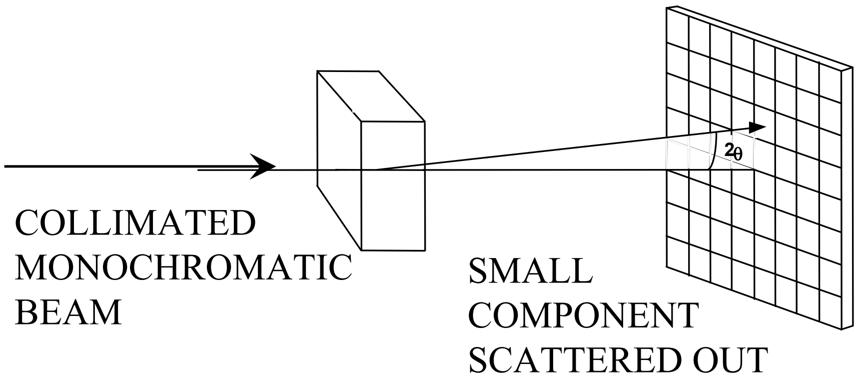
National Synchrotron Light Source
Brookhaven Nat'l. Lab., New York

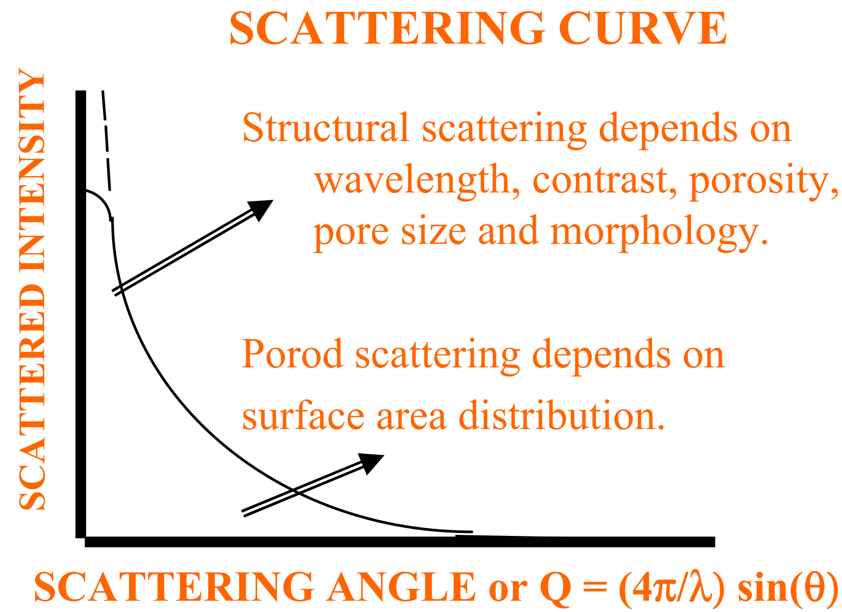


- surface x-ray scattering – catalysis/reactivity:
  – SOFC performance
- TEM/x-ray/neutron diffraction – interface phase equilibrium:
  – SOFC stability
- **XMT / SAXS – void microstructure characterization:**
  – SOFC transport properties, performance



SMALL-ANGLE SCATTERING



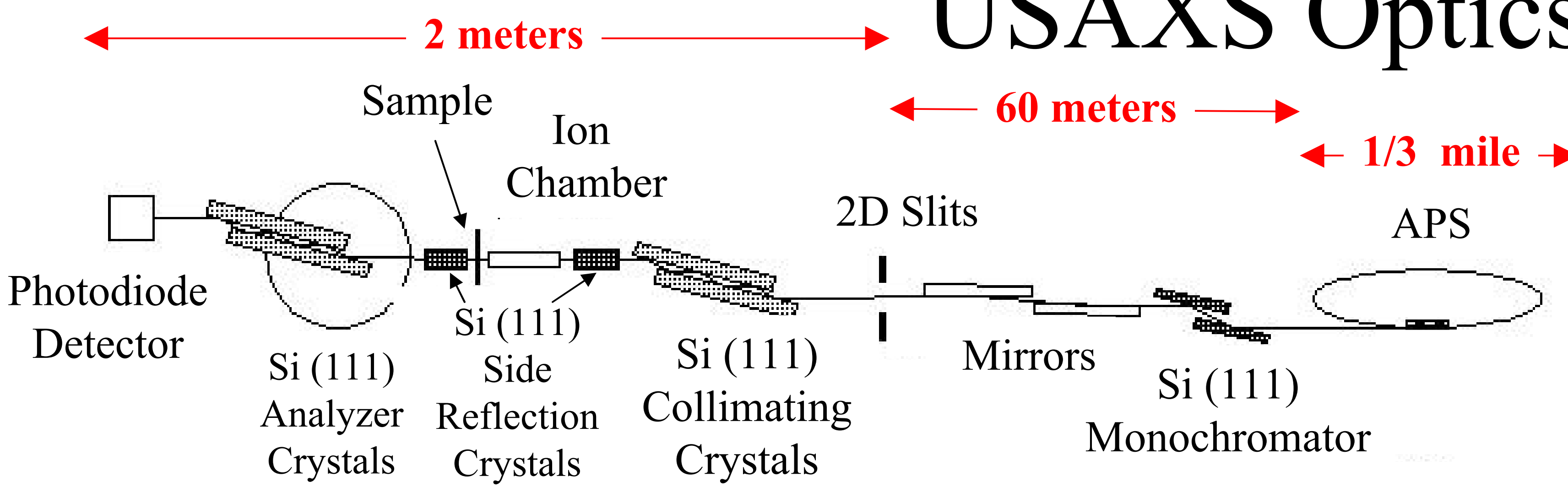


Scattered intensities for voids proportional to scattering contrasts.
Calculated Scattering Contrasts for x-rays ($|\Delta\rho|^2$) :

$|(\rho_{\text{La0.8Sr0.2MnO3}} - \rho_{\text{AIR}})|^2$	1624×10^{28} m^{-4}
$|(\rho_{\text{YSZ (3 mol \% Y2O3}} - \rho_{\text{AIR}})|^2$	2110×10^{28} m^{-4}
$|(\rho_{\text{0.3Ni+0.7YSZ}} - \rho_{\text{AIR}})|^2$	2800×10^{28} m^{-4}

- Modified ultrasmall-angle x-ray scattering (USAXS) with pin-hole collimation
- X-ray energy = 16.9 keV (wavelength = 0.0735 nm)
- Slit height (spatial resolution perpendicular to the interfaces): 41.3 μm
- Sample thickness: 248 μm

USAXS Optics



<u>Bonse-Hart USAXS Optics at 33ID</u>

•Si (111) Monochromator – X-ray Beam Energy Selection

• Mirrors – Harmonic rejection

• 2D Slits – Beam Size Definition

• Collimating Crystals – Vertical Beam Collimation

• Ion Chamber – Intensity Monitor

• Side Reflection Crystals – Horizontal Beam Collimation

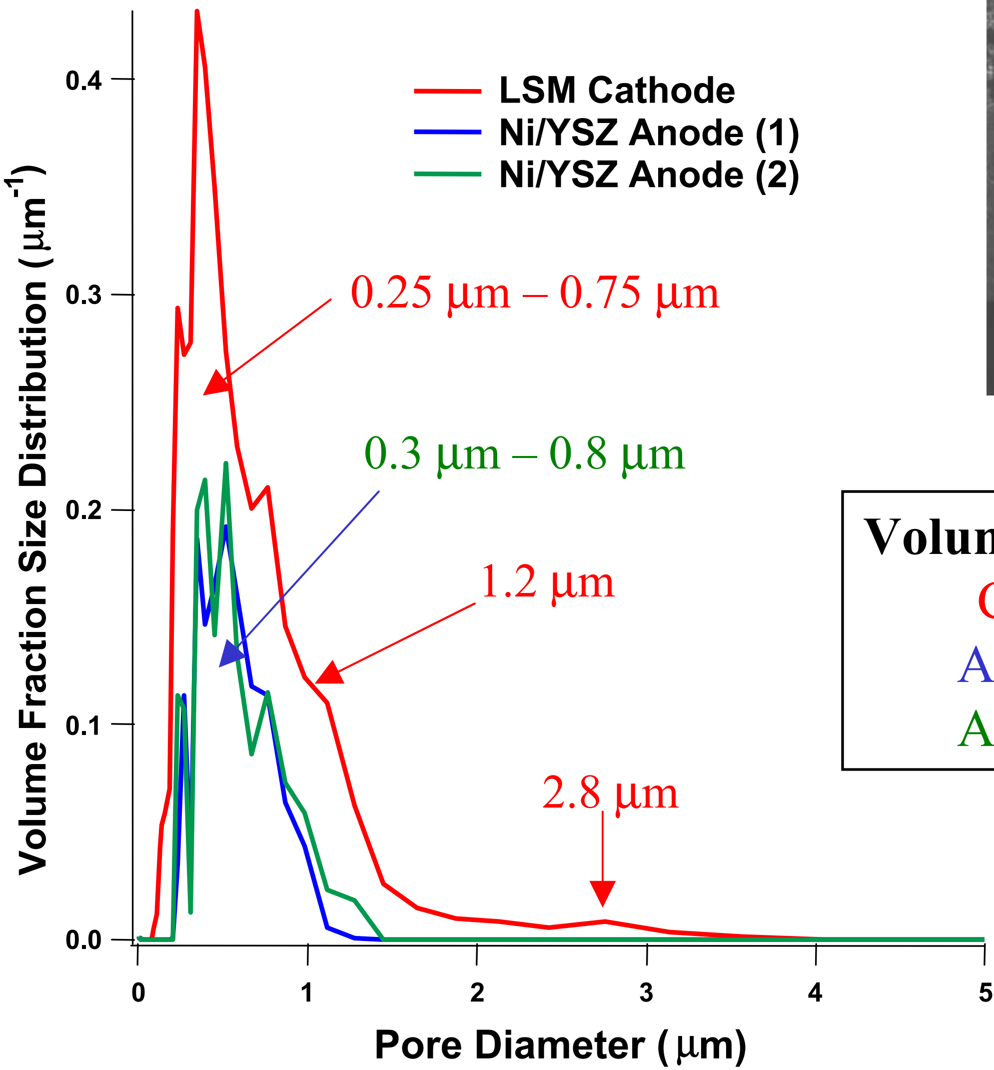
• Analyzer Crystals – Rotate to scan scattered x-rays

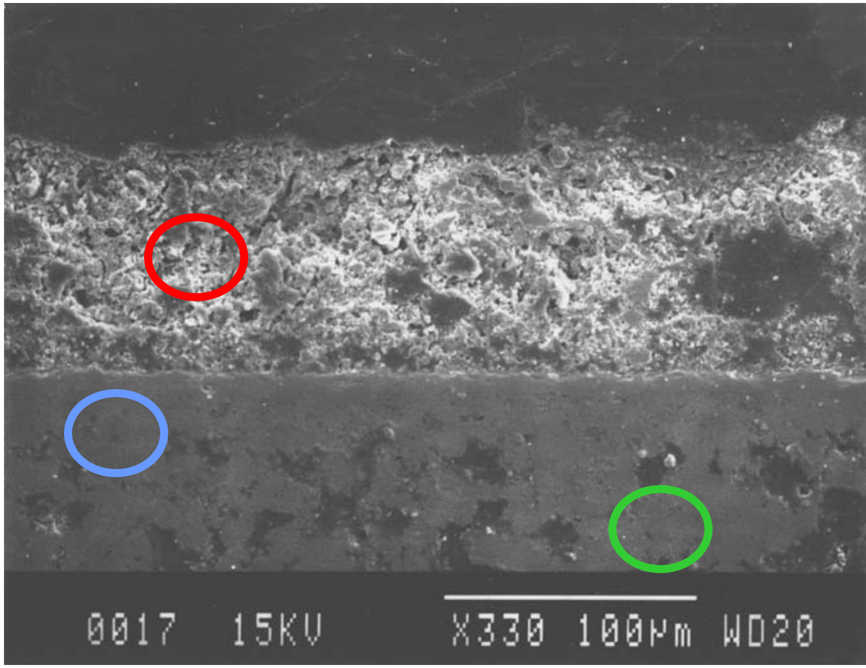
• Photodiode Detector – Linear Dynamic Range of 10 Decades

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

J. Ilavsky, A.J. Allen, G.G. Long, P.R. Jemian, "Effective Pin-hole collimated ultra-small angle x-ray scattering instrument for measuring anisotropic microstructures", *Review of Scientific Instruments* **73**[3] 1660 (2002).

Preliminary Void Size Distributions obtained from Maximum Entropy Analysis of SAXS Data:





SEM micrograph near interfaces.

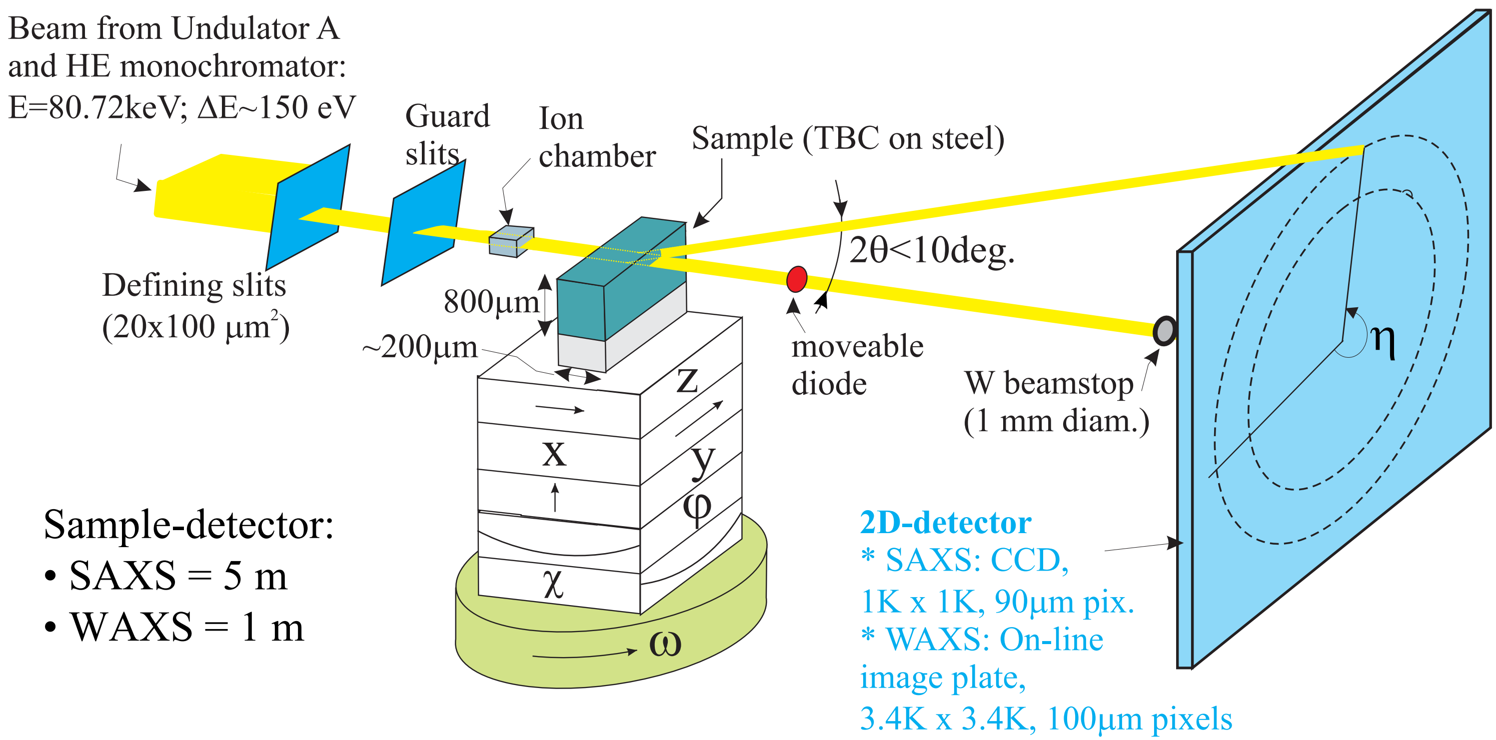
Volume Fractions (%):
Cathode: 24.6
Anode (1): 10.0
Anode (2): 10.5

Surface Areas ($m^2\ cm^{-3}$):
Cathode: 3.39 ± 0.01
Anode (1): 1.06 ± 0.01
Anode (2): 1.20 ± 0.01

High Energy SAXS (HESAXS)

{can be combined with wide-angle x-ray scattering (WAXS)}

- with J. Almer and D. Heffner *(Argonne National Laboratory)*
at SRI-CAT, sector 1-ID.

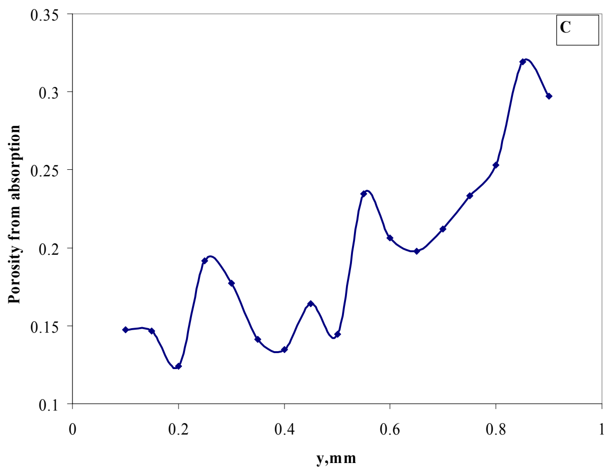


Features

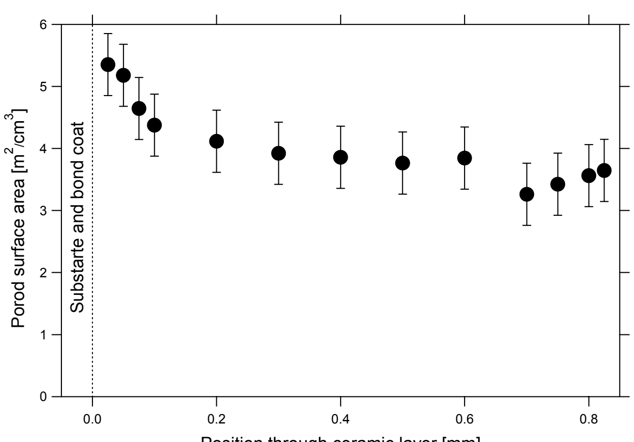
- *Direct* depth resolution to ~10µm possible (without focussing)
- Perform WAXS,SAXS (and imaging) with little change in setup
- $t_{exposure}$~ 5 sec (both WAXS and SAXS)

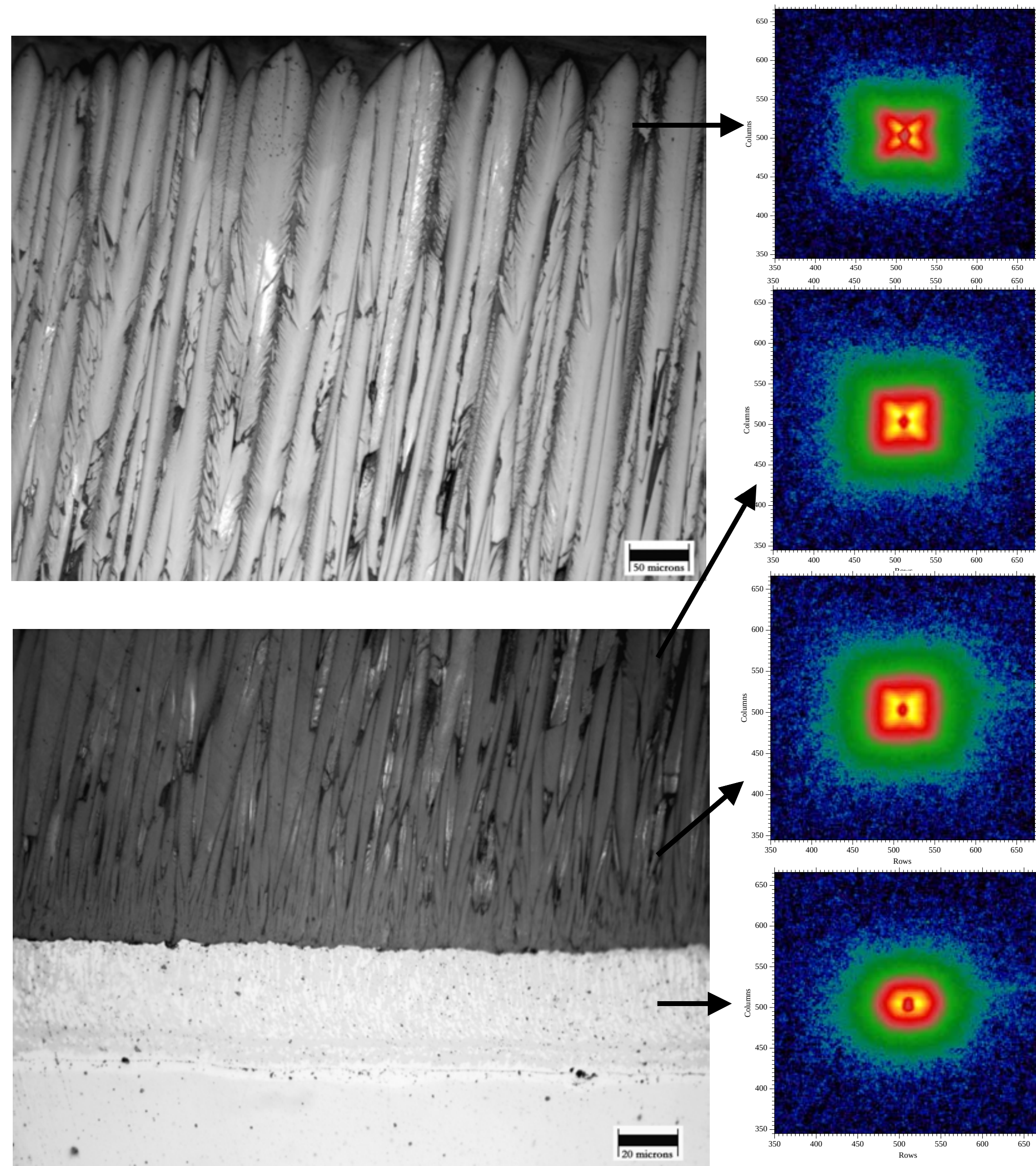
HESAXS

- Use of 50-80 keV X-rays
- Small beam size
- High penetration (up to 1 mm)



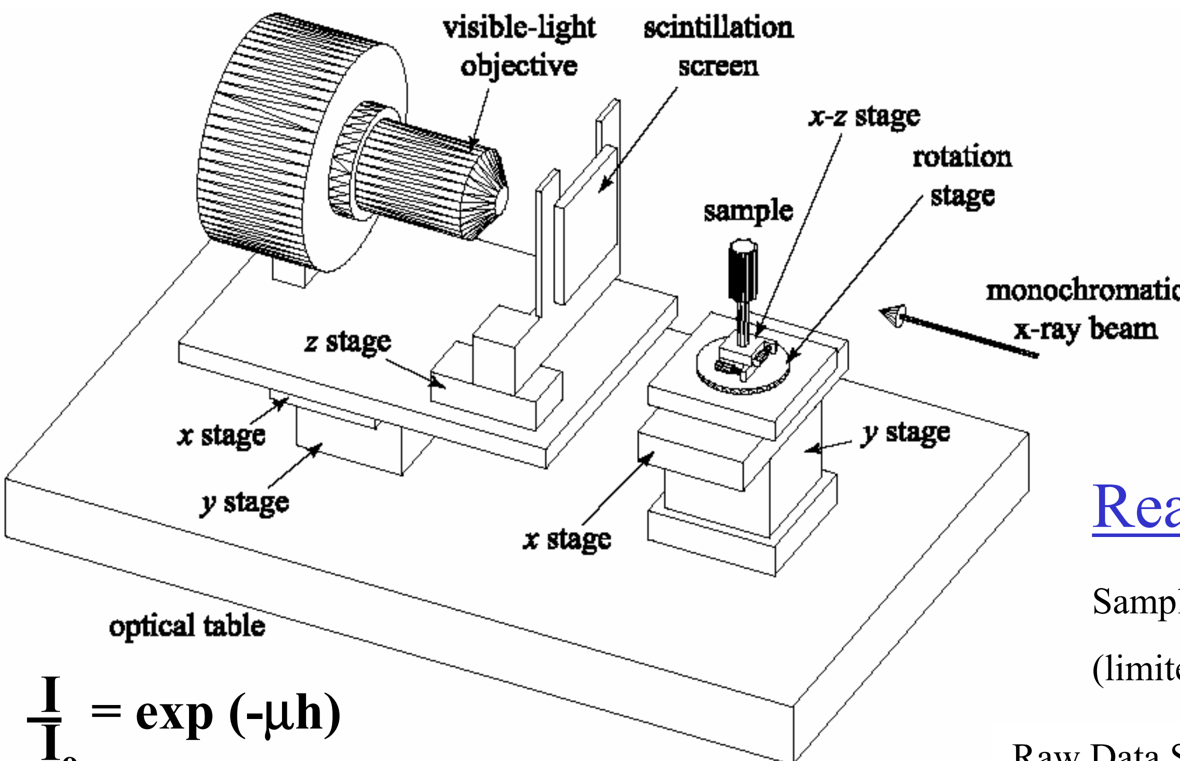
Through thickness porosity variation
Through thickness porosity surface area variation





X-ray Microtomography (XMT)

Instrument Setup



$$\frac{I}{I_o} = \exp(-\mu h)$$

where I_o is the incident x-ray intensity
I is the intensity remaining after the x-ray passes through a specimen of thickness h, and
μ is mass absorption coefficient.

In next few years, XMT resolution will greatly improve due to addition of x-ray optics between sample and scintillation screen. This will result in much larger dataset requirements than present ones are given below:

Real-Time Reconstruction:

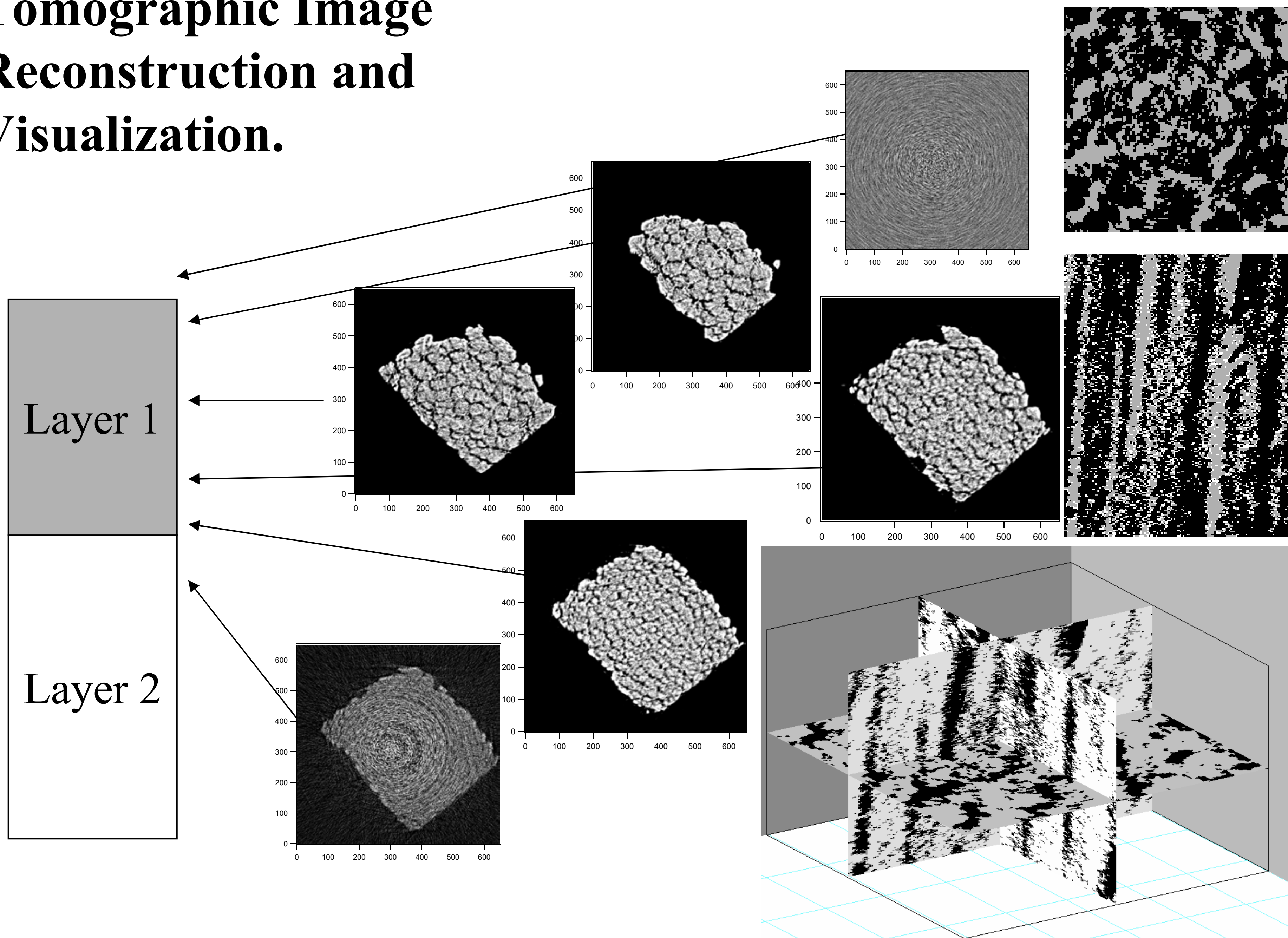
Sample measurement time 10 ~ 120 min

(limited by flux and CCD readout)

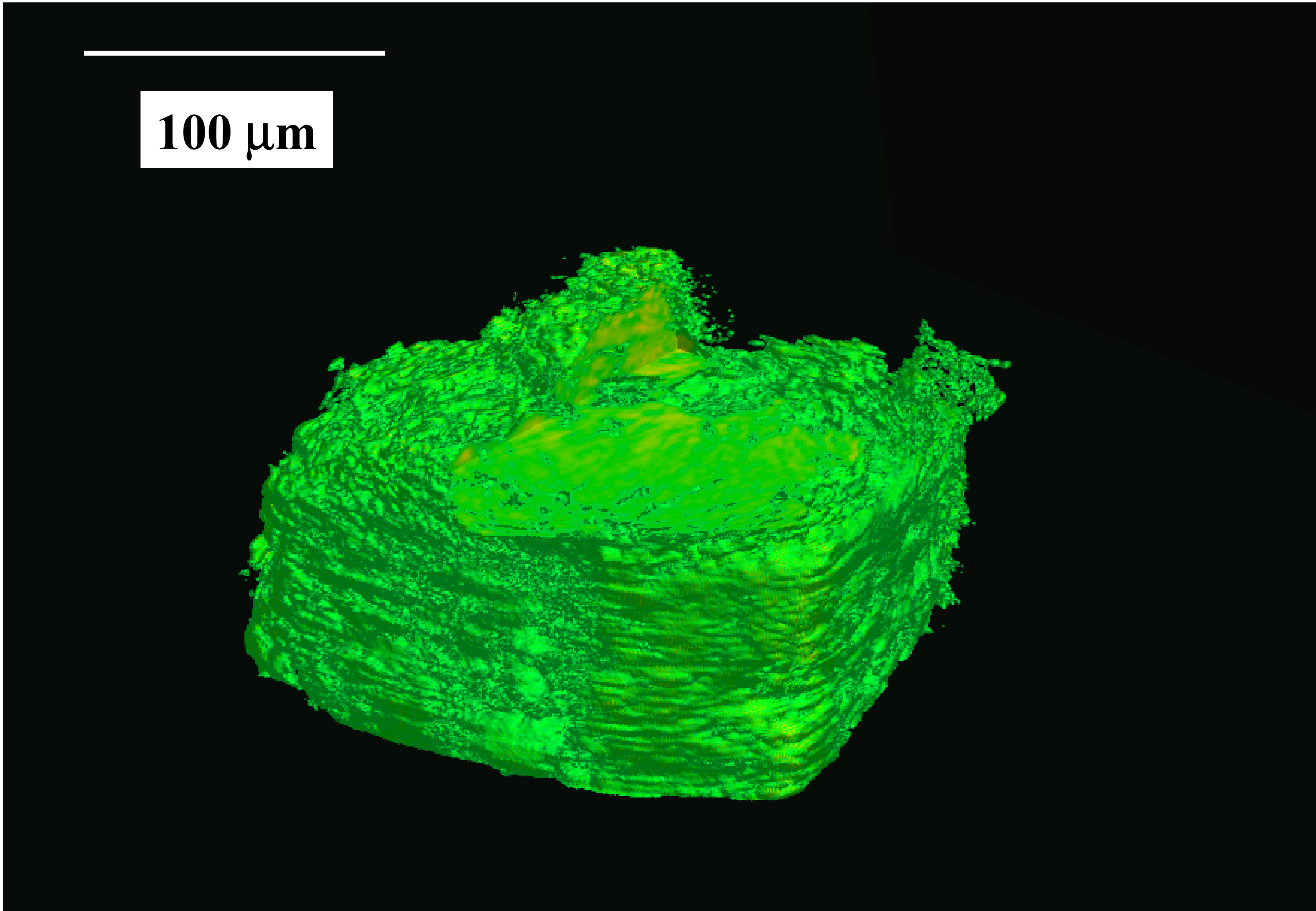
Raw Data Set	1.6 (6.4) GB (2000 by 2000 pixels)
Normalized	2.8 (11.2) GB
Reconstructed	3.9 (15.9) GB
Total	8.3 (33.5) GB

SRICAT Collaborator: Francesco DeCarlo

Tomographic Image Reconstruction and Visualization.

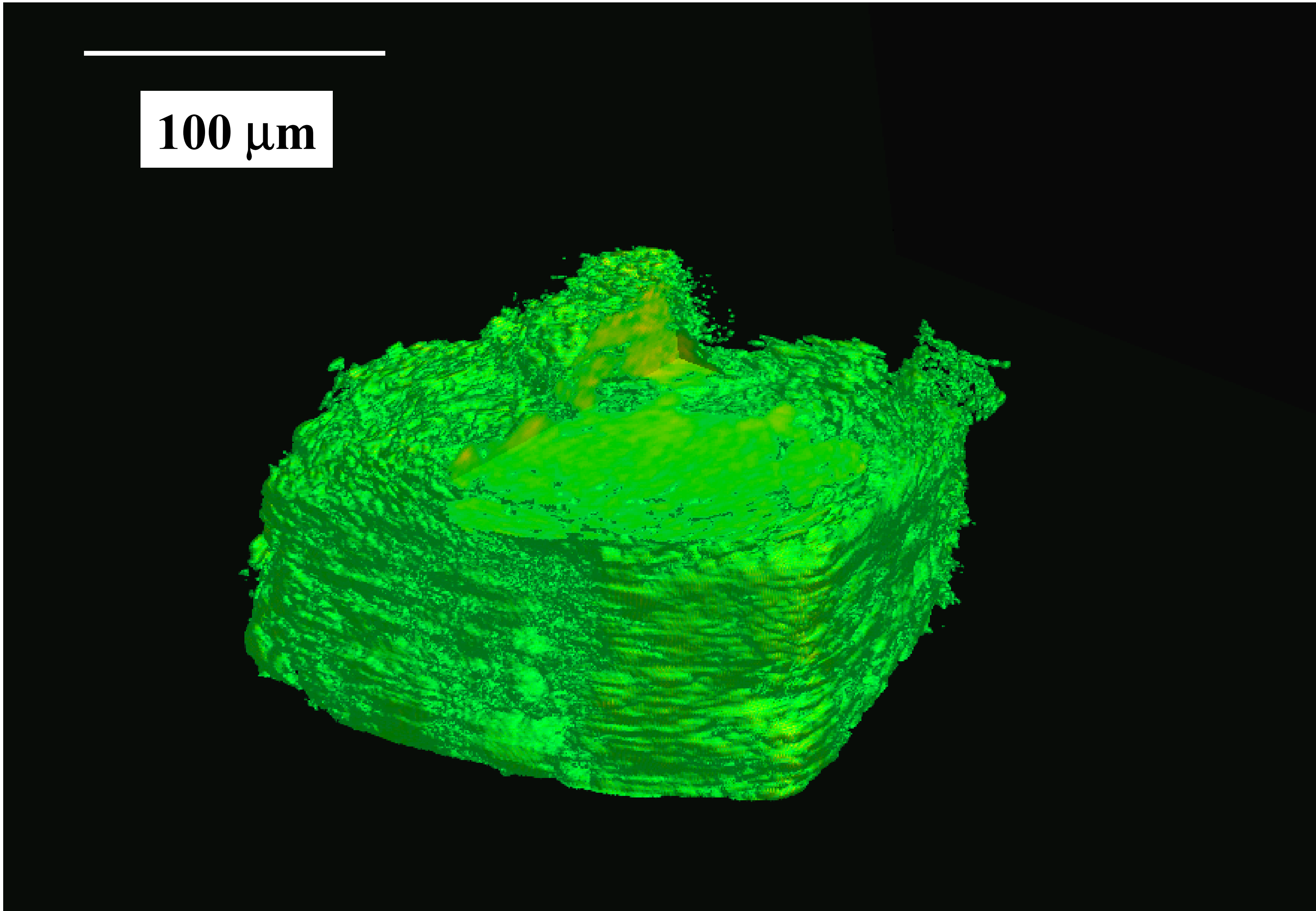


Porous Cathode, LSM



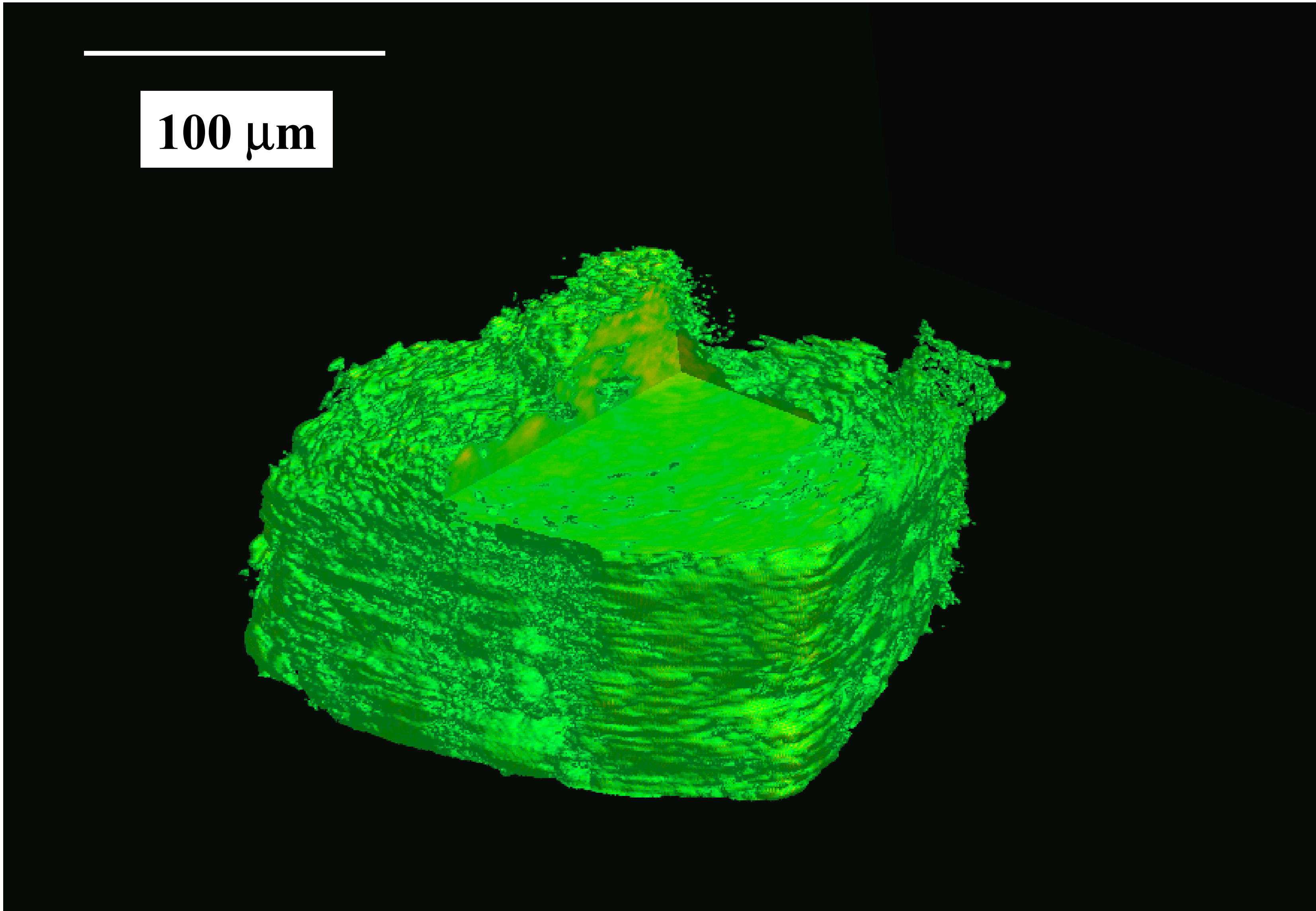
TOP

Porous Cathode, LSM



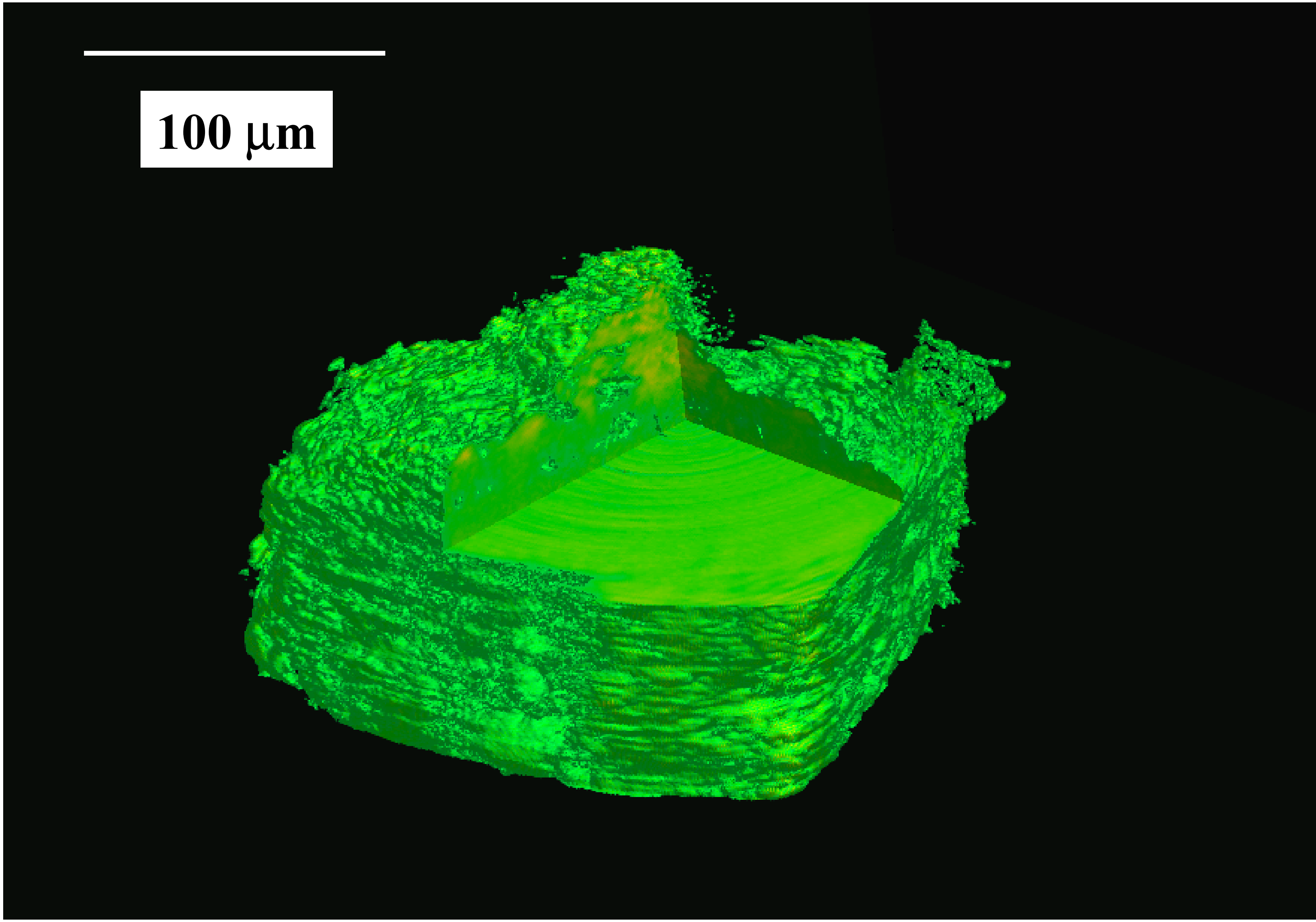
MIDDLE

Porous Cathode, LSM



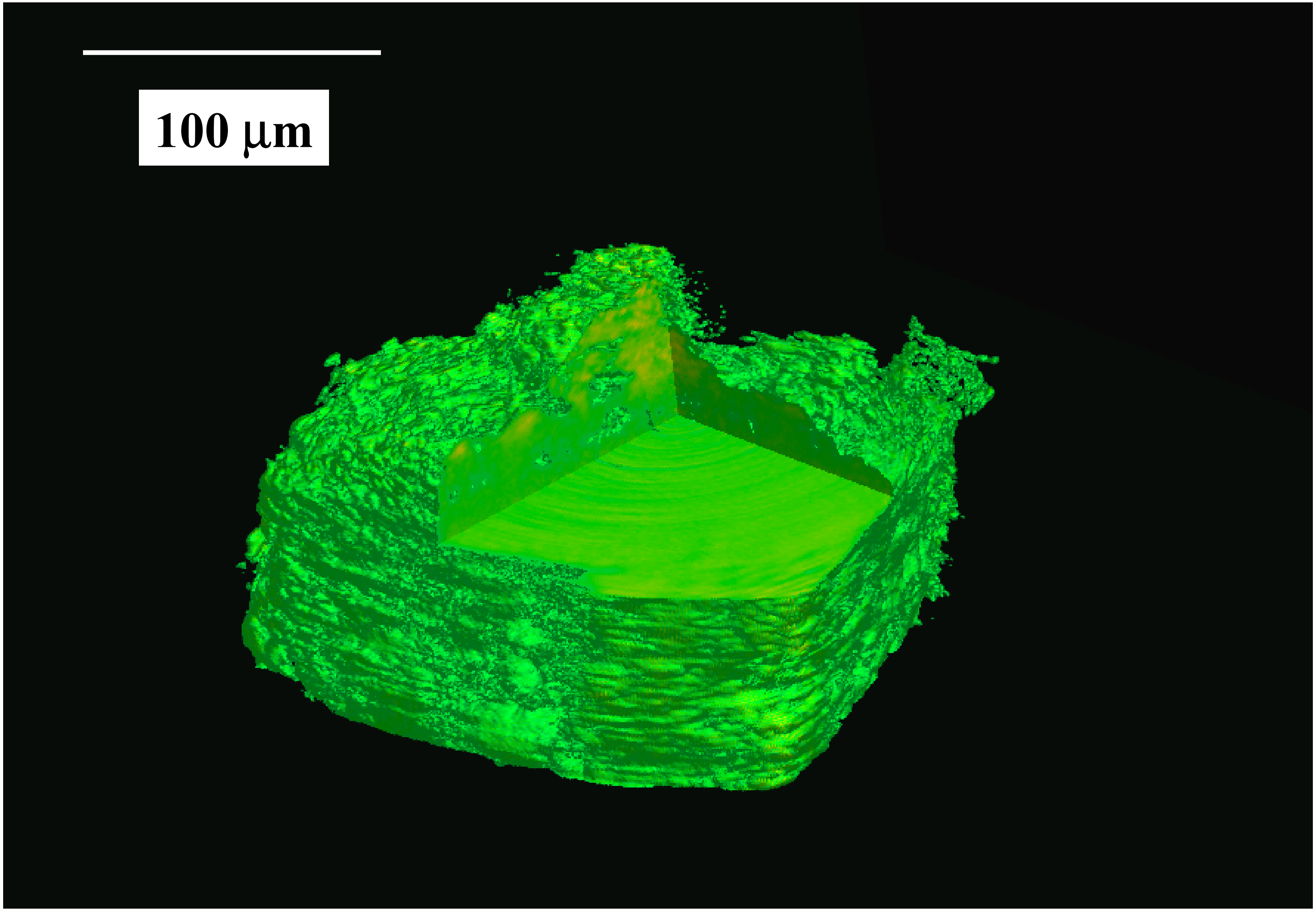
BOTTOM

Dense Electrolyte, YSZ



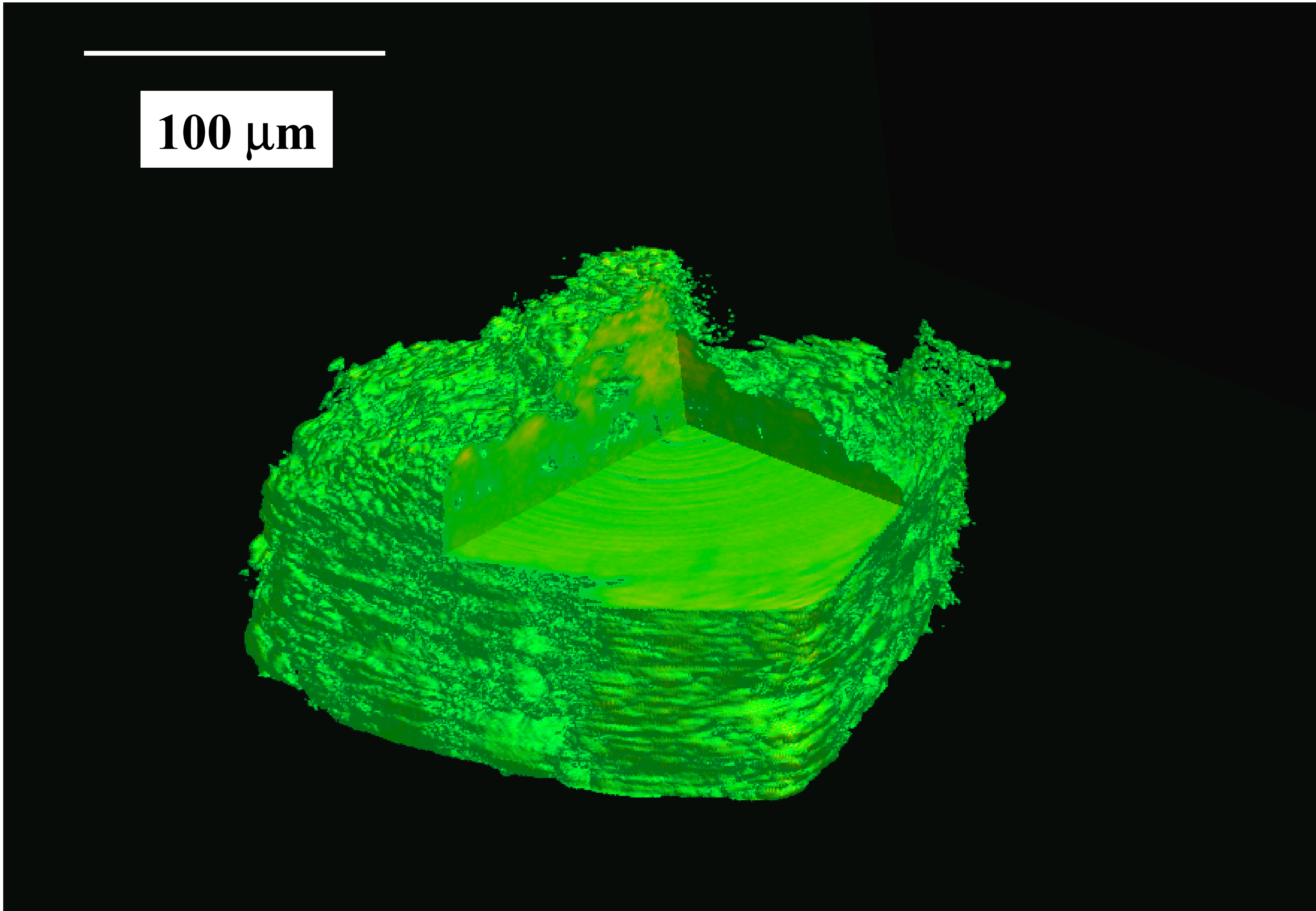
TOP

Dense Electrolyte, YSZ



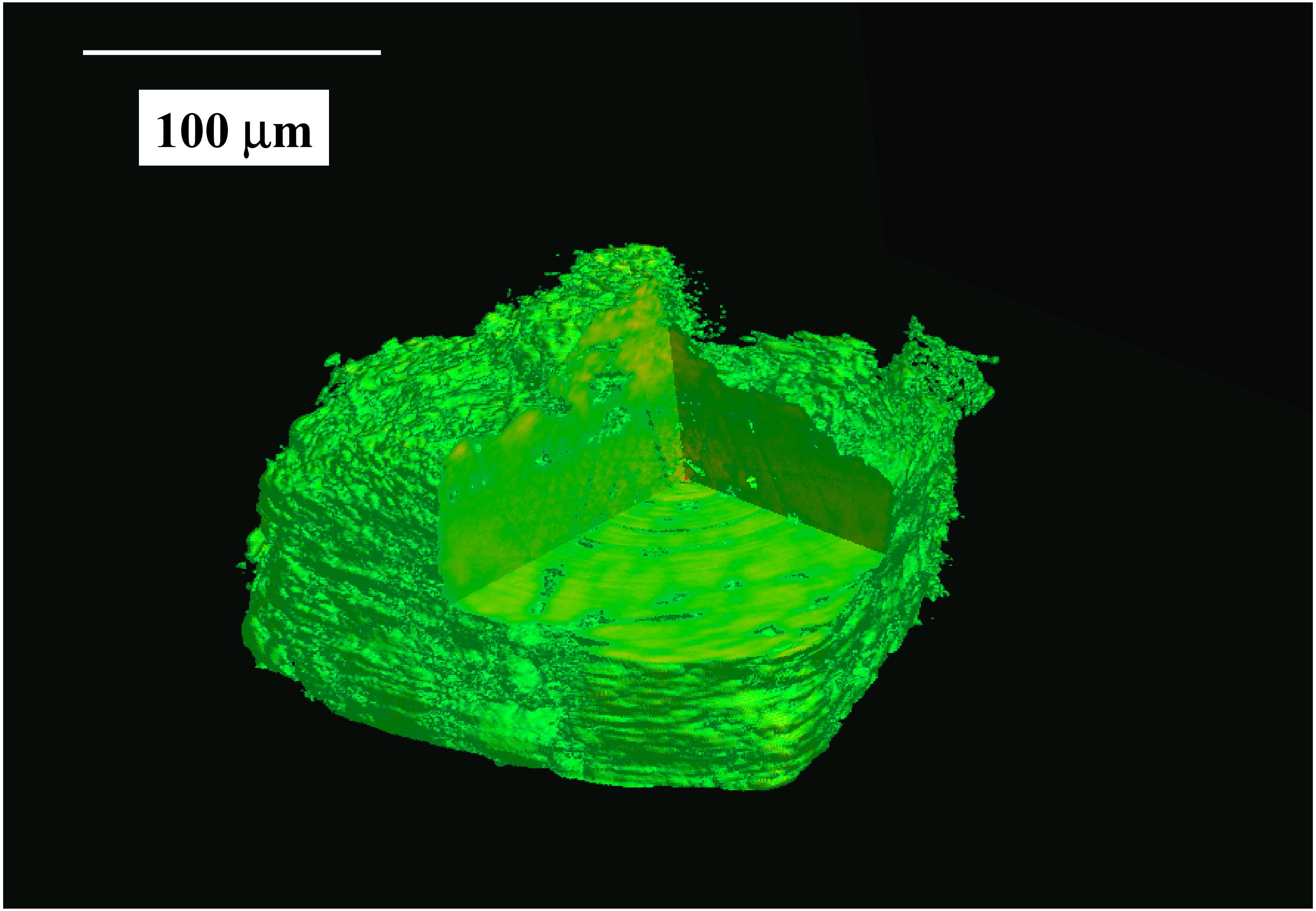
MIDDLE

Dense Electrolyte, YSZ



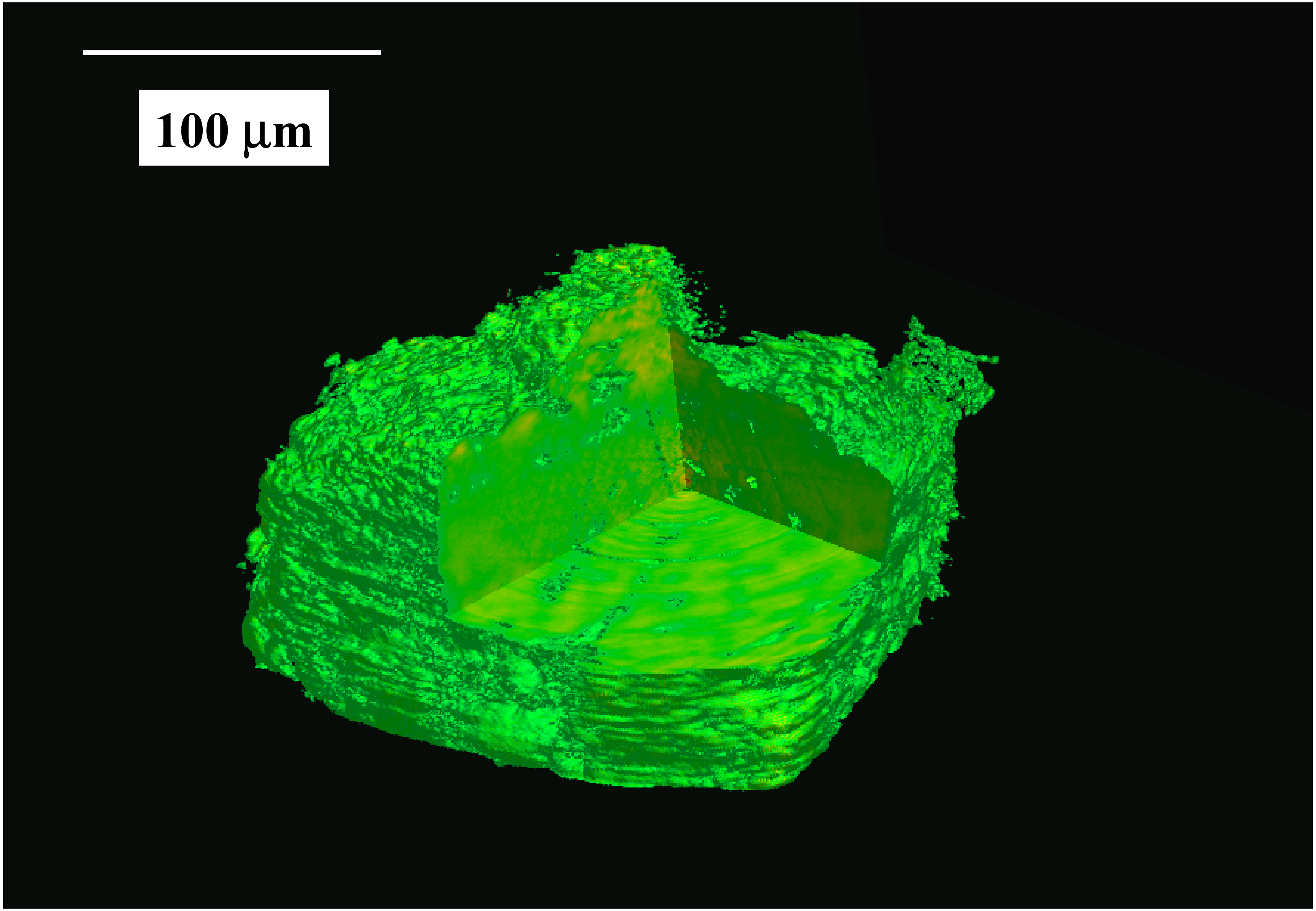
BOTTOM

Porous Anode, Ni (YSZ)



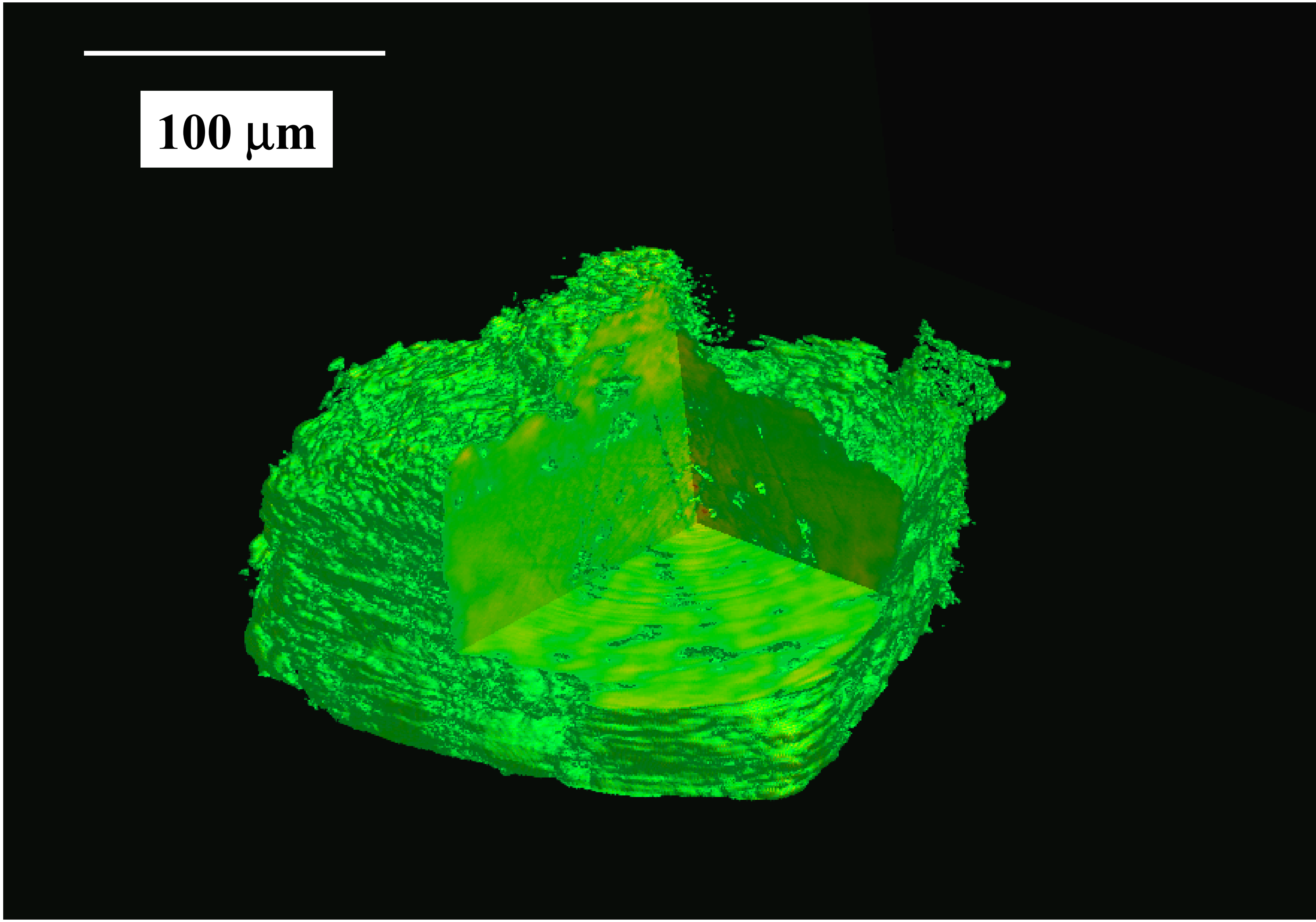
TOP

Porous Anode, Ni (YSZ)



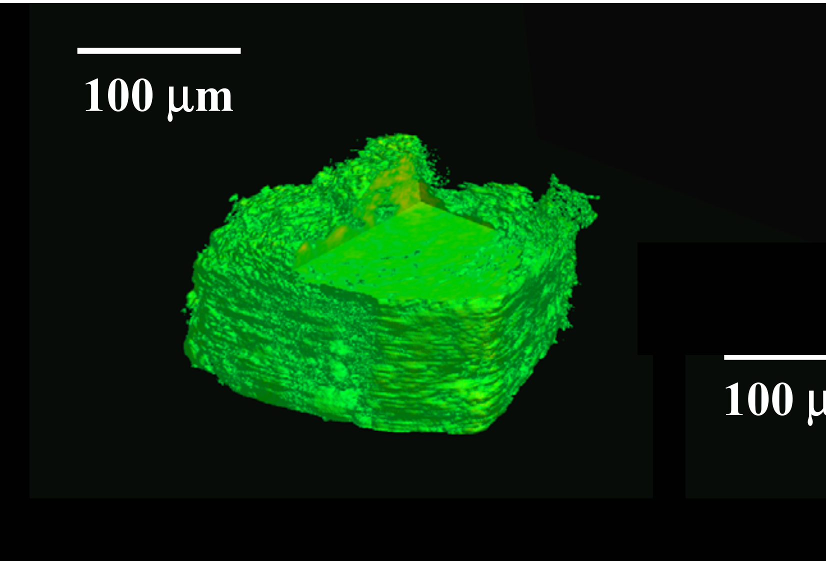
MIDDLE

Porous Anode, Ni (YSZ)

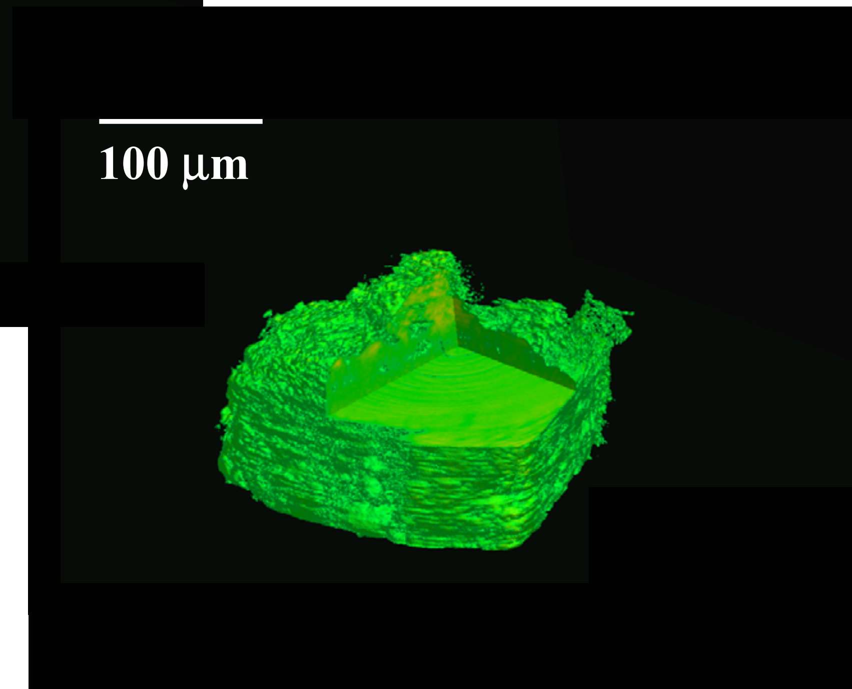


BOTTOM

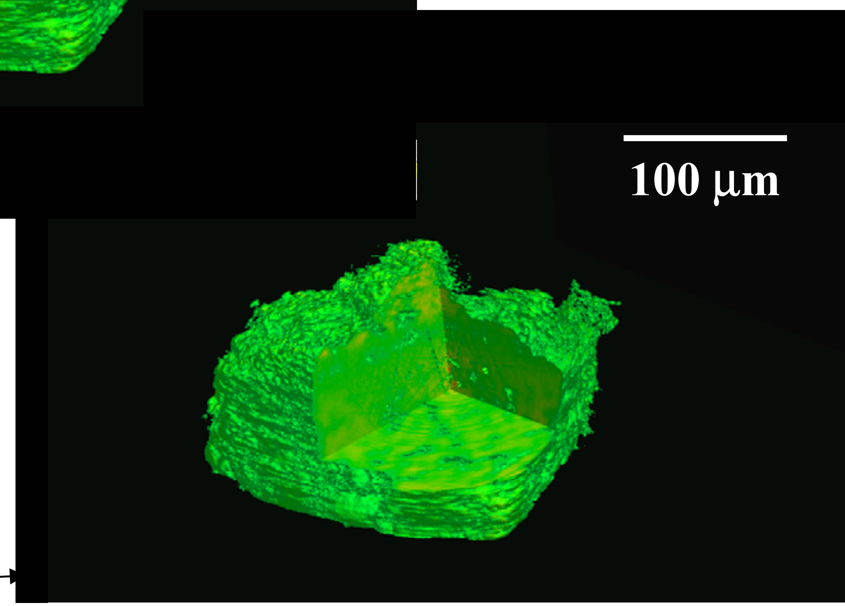
Tomography Resolution:
~1 to 2 μm



Slices in LSM
Cathode:
Porous Layer



YSZ Electrolyte:
Dense Layer



Slices in Ni(YSZ)
Anode:
Porous Layer

USAXS and HESAXS:

- Void volume fractions, surface areas, and sub-μm size distributions have been obtained in the LSM cathode and Ni/YSZ cermet anode layers. Non-spherical void shapes can also be modeled as needed.
- HESAXS development shows promise for obtaining a sufficiently fine beam size to study the YSZ electrolyte layer alone.

XMT of undisturbed microstructure:

- Void morphologies in all 3 layers of a SOFC section have been spatially resolved and distinguished using a single x-ray energy.
- Voids greater than ~ 1 μm have been visualized in 3D including the void inter-connectivity.

What next?

- Quantitative void microstructures will be characterized in all SOFC layers as overlap in *feature* resolution for SAXS (few nm to few μm) and XMT (1 μm and above) is increased and finer beam sizes are defined for HESAXS.
- Quantitative microstructure data will be input for processing and property prediction using microstructure computer models. For extreme void shapes, SAXS will determine fine opening dimensions controlling transport properties.

Acknowledgments:

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