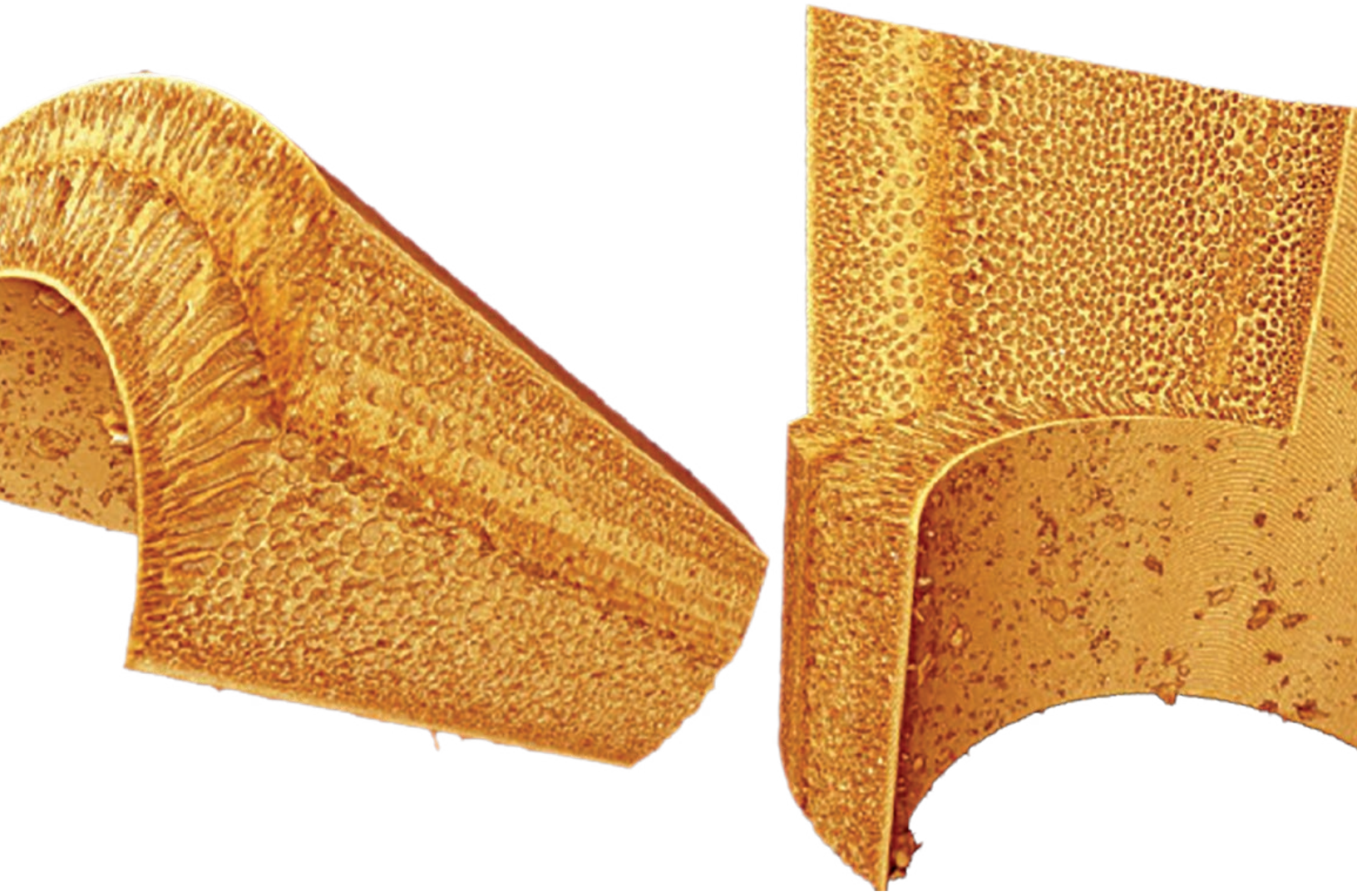
Application Note



Non-destructive 3D Analysis of Engineered Porous Media

ZEISS Xradia Multi-lengthscale 3D X-ray Microscopes

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Numerous modern engineering challenges involve the design and control of porous structures over a range of length scales. Applications for such engineered porous materials cover a broad spectrum, ranging from biological scaffolds to electrochemical devices to membranes and heat exchangers. Although the applications vary, these types of materials often display a common theme: an intimate link between porous microstructure and material performance. This link can be found, for example, in the detailed liquid or gas transport through an interconnected pore network, or in the physical response of a porous material to a compressive or tensile force. Frequently the material performance can be quite sensitive to its discrete, complex pore structure thereby motivating the need to investigate and understand the morphology of these materials in 3D at the appropriate pore scale. Zeiss 3D XRM microscopes offer a flexible solution for multi-scale imaging and visualization for a wide variety of these engineered porous media.

The common goal for many porous media applications is gaining a detailed understanding of how the 3D pore networks impact material or device performance. Traditionally, however, the direct experimental observation of the size, distribution, connectedness, isotropy, or even anisotropy of such volumetric networks has presented a challenge as these phenomena are inherently 3D and highly irregular. The latest developments in 3D X-ray microscopy (XRM) from ZEISS have emerged as a powerful tool and one possible solution for the characterization of porous materials over a range of length scales. By incorporating synchrotron-influenced components and architecture, ZEISS XRM provide non-destructive tomographic 3D imaging for a wide variety of material types and applications, enabling unique and new opportunities to probe internal porous microstructures not previously accessible using established methods. High resolution X-ray tomography can differentiate solid and pore phases, and enable measurement of common microstructural properties such as porosity, specific surface area, pore tortuosity, etc. Adjustable magnification capabilities of ZEISS XRM enable multi-scale 3D imaging ranging from fine-scale detailed surface morphology up to large regions of interest to obtain representative volume elements (RVE) that connect the pore-level microstructure with the device-level performance. Furthermore, XRM data sets play a valuable role by serving as 3D modeling domains, providing realistic simulation structures for identifying either physical limitations or enhancements (so-called emergent properties) brought about by the discrete porous microstructure.

Qualitative and Quantitative Pore Structure Analysis

By probing the internal structure of a sample, X-ray tomography can nondestructively provide valuable quantitative pore-scale parameters critical to understanding material function. Metrics such as porosity, pore size distribution, tortuosity, and specific surface area are obtainable from 3D XRM data and can frequently serve as valuable inputs to higher level performance models. Furthermore, one can determine if there are spatial variations in pore locations, the connectedness (or isolation) of pore networks, or if there is an anisotropic orientation of certain pore or solid features. For example, Figure 1a displays the complex cracked and porous structure of a commercial catalyst monolith, examined with the Xradia Versa (Novak, 2013). From the 3D rendered volume, the cracks in the ceramic are observed to extend well beyond the surface into the interior of the catalyst layer. Virtual cross sections may be used to view the interior of the solid structure at any arbitrary orientation and location to gain more detail of how the cracks vary with depth. The geometry of the cracks and pores impacts diffusive transport of the reactive gases as well as the mechanical integrity of the entire catalyst structure. In Fig. 1b, a surface rendering of a metallic foam with 44.7 micron voxels is depicted (Iasiello, 2014). Similar to the catalyst material,

evaluation of the foam's topology and pore structure can help elucidate connections between micro-scale features and performance. Voxel counting methods were used to measure foam porosity of 89.4% and specific surface area of 1116 m^{-1}.
A ray-shooting method was implemented to determine the size distribution of solid and pore phases, with the resulting solid phase distribution depicted in Fig. 1c. The distribution reveals a concentration of effective diameters in the 0.5-1.0 mm range, indicative of the typical strut thickness. The longer dimensions measured by the ray shooting method (>1.0 mm) correspond to those rays that have propagated down the strut, effectively providing a measure of strut length. These values help provide characteristic length scales for transport phenomena both through the foam structure and at the solid-pore interface.

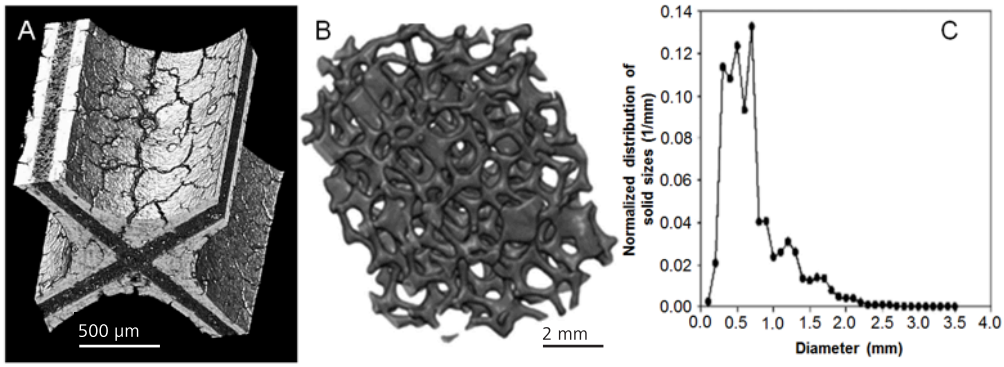

Figure 1: a) 3D rendering of a commercial catalytic monolith obtained with ZEISS Xradia Versa (2.18 micron voxels). Cracks extending from the catalyst surface, as well as interior voids, are easily observed. Novak, 2013, reprinted with permission from Elsevier. b) Surface rendering of the porous structure of an aluminum foam (44.7 micron voxels) used in heat exchanger applications. c) Solid foam size distribution measured by performing a ray shooting routine on the structure shown in (b). Iasiello, 2014, reprinted with permission from ASME.

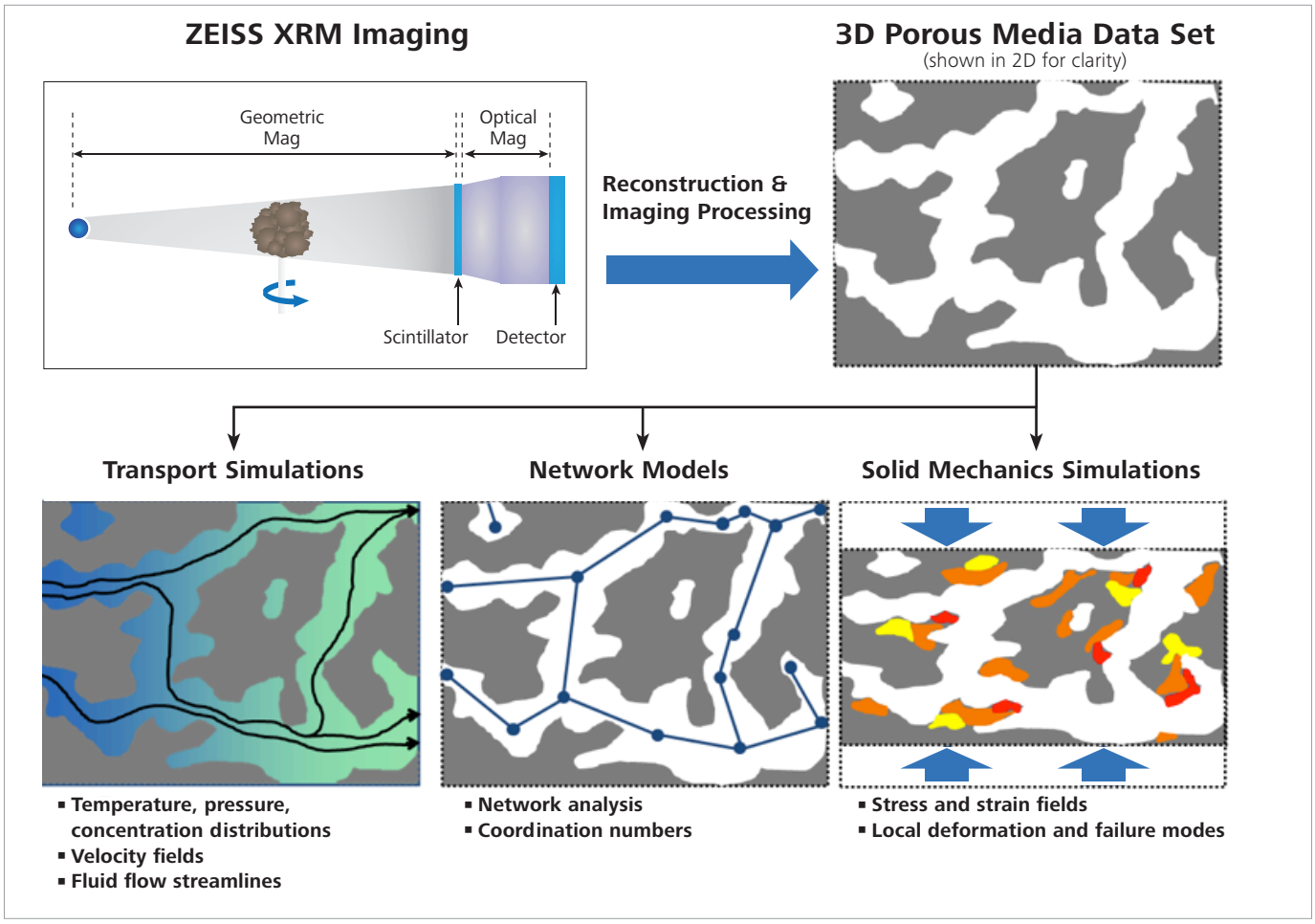

Figure 2: Utility of 3D tomographic imaging of porous media for generation of realistic modeling domains. ZEISS XRM imaging creates a 3D dataset, although 2D images are shown here for clarity. 3D data can be exported from the ZEISS Xradia software and subsequently used by the researcher as a domain for modeling of transport processes, network analysis, and solid mechanics simulations.

Creation of 3D Simulation Domains

In addition to measuring pore-scale structural parameters, the 3D datasets produced by XRM can also be leveraged directly as modeling domains, empowering computer simulations by providing results conformal to the true porous structure. This approach has been demonstrated for such applications as heat exchangers, lithium ion battery and fuel cell electrodes, and catalyst supports, and is demonstrated schematically in Figure 2. Results of conformal modeling can provide information spanning a range of length scales, including the quantification of: i) microstructure-induced bulk transport coefficients, such as gas diffusion coefficients or thermal diffusivity, which explain the macroscale behavior of the material as a function of the complex microscale structure, and ii) local field information, such as temperature, concentration, or displacement fields which can identify local constrictions or "hot spots" in the microstructure. Knowledge of localized information can be used to help guide design by suggesting what types of local geometries, and therefore what types of fabrication conditions, should be sought or avoided.

As a specific example, simulated gas diffusion through a region of a polymer electrolyte fuel cell (PEFC) electrode is shown in Figure 3. This data was acquired with ZEISS Xradia Ultra in Zernike phase contrast mode at 50 nm spatial resolution. To evaluate electrode performance, the local solid agglomerate and pore sizes were first determined in 3D using a morphological opening algorithm. The local pore size was then used to introduce a size-dependence on the local gas diffusion coefficient based on Knudsen effects within nanometer-scale channels. The spatially varying diffusion behavior was then input to gas transport simulations to reveal streamlines of the most prevalent transport pathways, localized constrictions in the microstructure, and the gas concentration distribution. An overall, "effective" diffusion coefficient of gas through the entire porous medium was also determined.

Nondestructive 4D Imaging

Due to its nondestructive operation, X-ray tomography is able to examine porous materials *in situ*, or "4D" through operation or time, creating new understanding of how porous media react, evolve, and degrade over the lifespan of the material. The architecture of ZEISS X-ray microscopes is particularly amenable to the incorporation of *in situ* stages and test cells due to a unique capability to maintain high resolution even at high source-sample working distance. This resolution at a

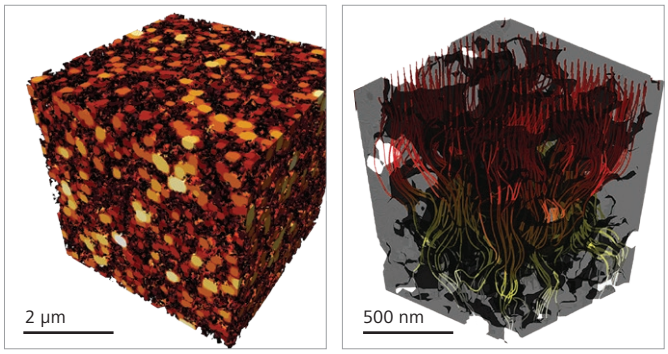

Figure 3: A porous PEFC catalyst layer structure, imaged with ZEISS Xradia Ultra in Zernike phase contrast mode. Catalyst agglomerate structures can be visualized and quantified in 3D, with brighter colors indicating larger agglomerate particles. A sub-region of the total sample was then used to simulate gas diffusion through the pore network, depicted by streamlines indicating the flow direction and colored by the local gas concentration. Sample courtesy of Shawn Litster, Carnegie Mellon University.

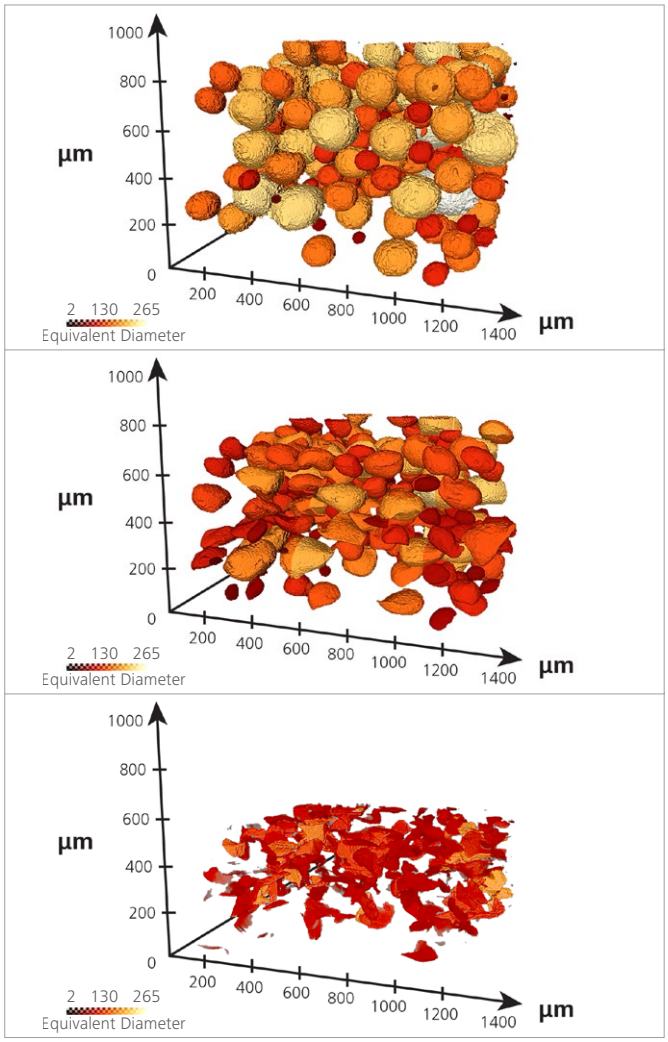

Figure 4: In situ *observation of silicone foam compression. Internal void regions, shown in this rendering and colored by size, can be seen to deform and decrease in total volume during the compression process.*
Sample courtesy of Brian Patterson, Los Alamos National Laboratory

distance (RaaD) feature is a result of a combined geometric and optical magnification system, reducing the dependence on pure geometric magnification that is a defining limitation of traditional laboratory microCT instruments. For Zeiss XRM porous media applications, this facilitates a number of possible studies such as imaging the deformation of the material under mechanical load, evolution of the structure in response to a factor such as heat or time, or visualization of fluid flow through a pore network.

Figure 4 depicts the evolution of discrete internal void structures of a porous silicone foam during mechanical compression of 0, 20, and 40%, as measured with the ZEISS Xradia Versa and a voxel size of five microns. By observing material deformation *in situ*, it becomes possible to not only quantitatively evaluate mechanical properties such as the elastic modulus and the Poisson ratio, but to also correlate these properties with direct observations of how the material microstructure deforms at the pore scale.

ZEISS X-ray microscopes provide internal structural information critical to the evaluation of modern porous materials as well as the design of next generation materials and devices. Although the applications vary, these types of materials often display a common theme: an intimate link between porous microstructure and performance. XRM datasets can provide qualitative and quantitative pore network analysis as well as 3D simulation domains for conformal modeling of realistic structures. The ability to visualize structures in 3D with good contrast and resolution even down to 50nm, particularly under operating conditions or elapsed time (4D), can help quickly determine why certain structures, synthesis methods, or operating conditions fail and why others succeed. This can help to bypass some of the empiricism and interpretation that can be associated with less direct structural characterization tools, expediting the iterative design process for the researcher and saving time in the design of future porous materials.

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