

X-Ray Microscopy for Hierarchical Multi-Scale Materials

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Introduction

Many materials made by nature and in the laboratory exhibit structure on multiple length scales. The multi-scale structure of these "hierarchical materials" plays an important role in bulk materials properties, as well as in processes that occur from the nanoscale to the mesoscale. Bone, wood, and leaves are well-known examples of hierarchical structures in nature (Figure 1). Taking a cue from nature, hierarchical materials development has tried to exploit these structures at various scales to realize enhanced materials properties. For example, the "lotus effect" is an example of superhydrophobicity where an extremely water-repellent surface arises from the hierarchically textured leaf surface and chemistry. The effect is created from the leaf surface, which has micrometer-scale papillae on epidermal cells and nanometer-scale hair-like features from the superimposed epicuticular wax layer. Artificial "self-cleaning", that is, superhydrophobic or even superoleophobic glass surfaces have been inspired by the lotus leaf. For example, a fluorinated bilayer coating is used on Corning's Gorilla® glass, which consists of silica microspheres of two different sizes formed using a self-assembly process. This has been characterized in 2D by ZEISS field emission scanning electron microscopy (FE-SEM) technology [1].

The design and fabrication of hierarchical structures presents many challenges for theory, computational design, synthesis, and characterization—all at multiple length scales and in three dimensions. For example, multi-scale materials modeling aims to create a continuum model appropriate to a given length scale, which integrates information from finer scales for inputs into the next-scale up. This requires improvement of fundamental "ball and stick" models to more sophisticated morphologies [2, 3]. Fabricating nature-inspired structures is also challenging. Hierarchical structured porous materials for energy conversion and storage applications use bottom-up biotemplating approaches that are difficult to scale to manufacturing processes [4]. Bridging the gap by linking the top-down design and bottom-up assembly approaches in a vast parameter space requires methods to map and characterize structures in three spatial dimensions and as a function of time.

X-ray microscopy (XRM) is a rapidly emerging technique to non-destructively image and quantify microstructure in 3D across a variety of length scales from tens of nanometers to millimeters. It has been used to study a wide spectrum of materials from carbonate rocks to murine brains, including a variety of hierarchical structured materials [5–8]. This article reviews the basic principles of XRM at various length scales and focuses on a handful of recent scientific studies on hierarchical, porous materials from the user community.

X-Ray Microscopy

XRM provides non-destructive three-dimensional (3D) and four-dimensional (4D) imaging capabilities for specimens across a range of length scales, from nanometers to millimeters. Recent developments initiated at synchrotron beamlines have yielded a number of X-ray optical elements that have driven improvements in resolution and contrast for laboratory-based (non-synchrotron) systems to levels previously unachievable with conventional projection-based X-ray computed tomography (CT) instrumentation [9]. Furthermore, the non-destructive imaging capabilities of high-resolution XRM provide unique opportunities to study samples in their native environments (*in situ*) and to quantify how their microstructures evolve in 3D and over time (4D) [10–12]. These combined characteristics have motivated increased correlative characterization alongside conventional central microscopy laboratory resources, including scanning electron microscopy (SEM), focused ion beam SEM (FIB/SEM), transmission electron microscopy (TEM), and light microscopy. Specifically, we point to XRM as a required guidepost in a several correlative microscopy workflows. By examining materials in 3D at multiple resolutions and identifying regions of interest for closer inspection with complementary 2D or 3D modalities (for example, light, electron, and ion microscopies with associated analytical facilities), a more complete picture of a specimen or experiment emerges. By simplifying the way in which we find and analyze volumes of interest, the ability to cross-correlate information from multiple resolutions and multiple modalities becomes highly desirable.

Since the most recent review of XRM in *Microscopy Today* last year [5], 2013 saw significant improvements in leading laboratory-XRM technology, in both contrast and throughput. Nanoscale XRM (ZEISS Xradia 810 Ultra) has been extended to lower energies (5.4 keV), which has enabled contrast (and throughput) improvements of up to an order of magnitude for a variety of materials, most typically of medium- and low-atomic number materials. This has enabled a rapid benefit in acquisition time for nanoscale 3D XRM datasets, now making 4D experiments a

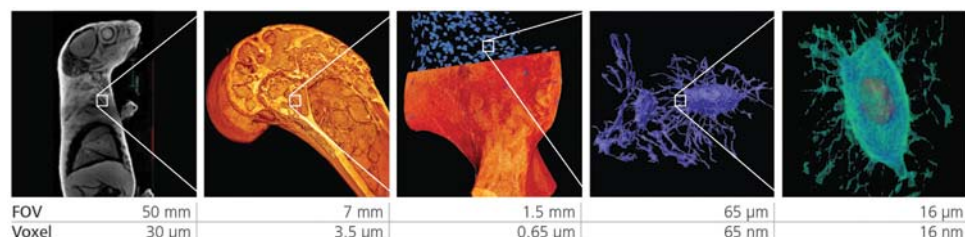
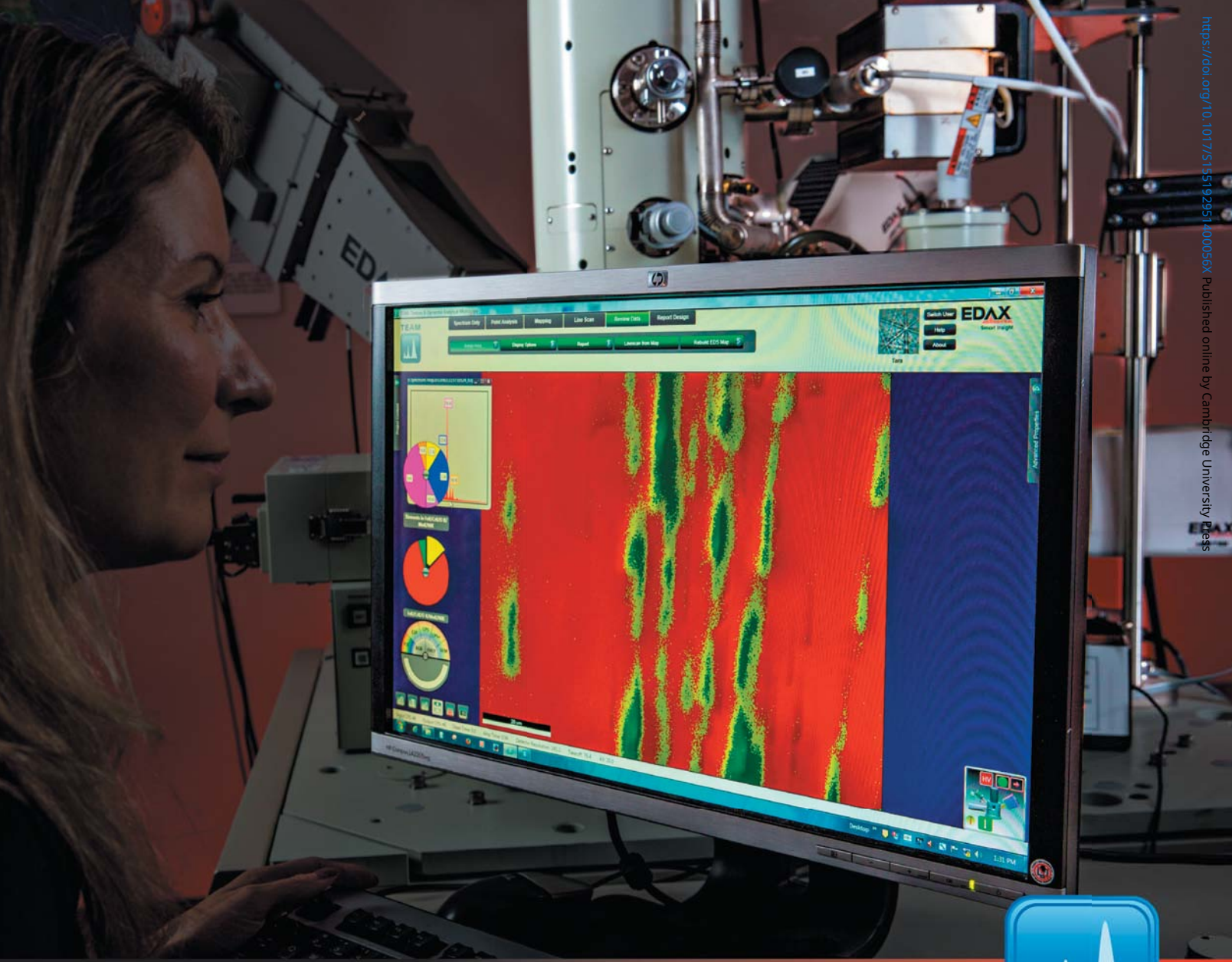


Figure 1: Images of hierarchical structure in bone were collected using multi-scale X-ray microscopes (ZEISS Xradia Versa and Ultra). 3D rendered datasets collected a range from a FOV of 50 mm (30 μm voxel) to 16 μm (16 nm voxel).



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reality on practical timescales. Sub-micrometer XRM (ZEISS Xradia 520 Versa) continues to evolve and has extended the contrast space by creating an efficient acquisition and analysis infrastructure to obtain and explore datasets acquired at different energies—Dual energy CT and Dual Scan Contrast Visualizer (DSCoVer) [13]. The ability to provide high contrast (tunable absorption and phase contrast) for samples of low- Z materials has opened up a number of important new pathways for biomedical and basic biology research, including developmental biology, soft and hard tissues, agriculture-related nanotoxicity, and bio-engineered materials, including 3D scaffold materials and macroporous ordered templates.

Ordered Macroporous Monoliths

Colloidal crystals have a structure of 3D periodic lattices, which are assembled from monodisperse spherical colloidal particles. Because of their unique structures, colloidal crystals have been used as templates for making porous materials with highly ordered porous structures for applications such as reversible CO₂ capture and bicontinuous cathodes [14, 15]. Templating methods are still being developed, but the resulting 3D ordered macroporous (3DOM) structure ideally consists of close-packed crystals of sub-micrometer spheres, whose long-ranged ordered structure is replicated in a 3D solid matrix with ordered pores. The 3DOM structure can be imaged using the commonly used 2D electron microscopy techniques. However, it is a challenge to assess in 3D the sub-surface quality of the macroporous structure, particularly the interconnection of pores. In a recent study by the Matyjaszewski lab, XRM was used to characterize the 3D structure of porous polymers formed by colloidal crystal templating and to evaluate the influence of two different infiltration methods (capillary and vacuum filtration) on the porosity of the affording materials [14].

Nanoscale XRM (ZEISS Xradia 800 Ultra) revealed that for the sample prepared through infiltration by vacuum filtration, the sub-surface structure was a non-homogeneous mixture of successfully templated and non-templated regions (Figure 2). In contrast, the sample prepared by milder capillary forces resulted in a more continuous and homogeneous ordered pore structure with fewer non-templated regions and better interconnection of the pores in the products. SEM was also used to characterize the 3DOM polymers, and the results were in good agreement with those obtained by XRM. However, the morphology observed by SEM was from the sample surfaces: no internal structure could be seen. XRM was advantageous for the characterization of both the external and internal structures of 3DOM materials and their distribution in three dimensions.

Scaffolds

Often challenging, bottom-up assembly is another approach to synthesizing hierarchical porous polymer materials for applications such as catalyst supports and biomedical scaffolds. Recently, Sai and co-workers at Cornell University developed a synthetic method using well-established concepts of macro-scale spinodal decomposition and nanoscale block copolymer self-assembly, as reported in *Science* [16]. The developed preparation method, dubbed SIM²PLE, is a “one-pot” approach that combines facile preparation with a high degree and choice of ordering within the macroporous structure. Having solved a difficult synthesis challenge, Sai et al. used XRM (ZEISS Xradia 520 Versa) in combination with SEM, small-angle X-ray scattering (SAXS), and TEM for quantitative pore-structure characterization. Using electron microscopy techniques and SAXS, nanopore size and assigned symmetry were determined, respectively. However, as evidenced by SEM, the macropores were non-periodic and broadly distributed in size, making pore measurements difficult

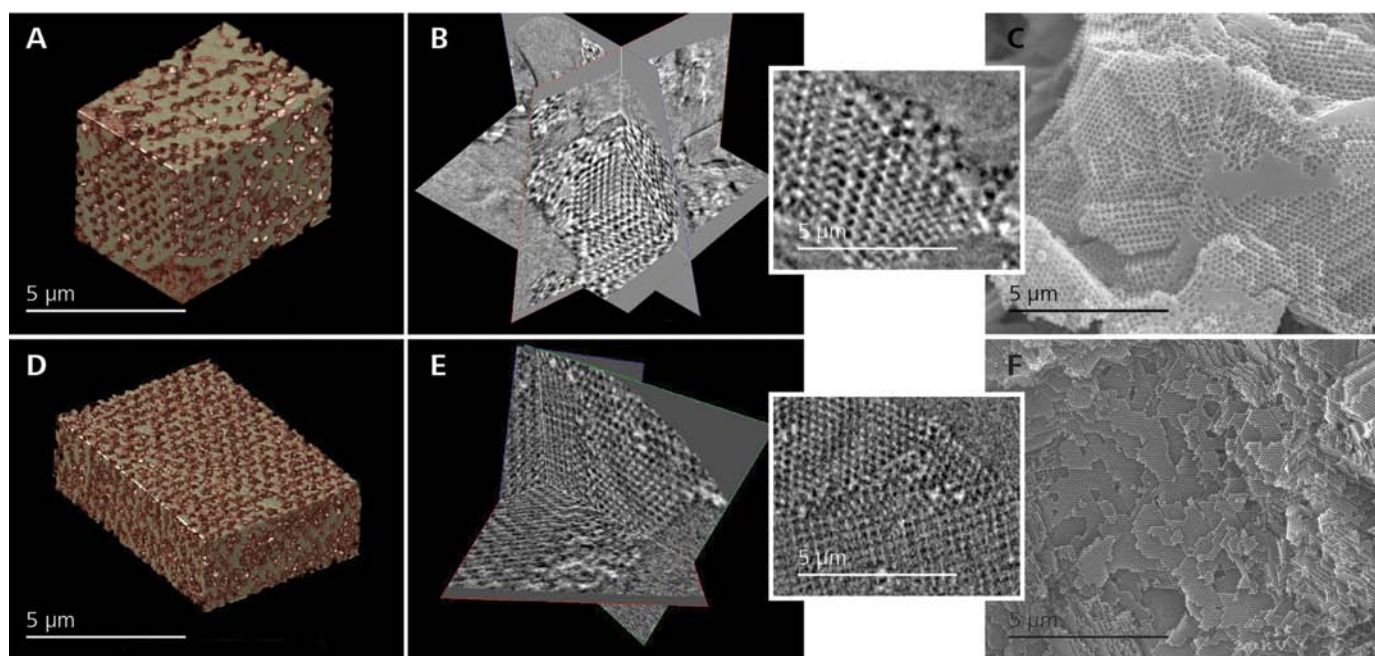


Figure 2: 3D ordered macroporous (3DOM) polymers prepared by vacuum filtration (A–C) and by capillary force (D–F): (A, D) 3D XRM renderings showing surface structure, (B, E) XRM virtual slices through imaged 3D volume (insets are the enlarged images of selected areas), and (C, F) SEM images of surfaces. Image courtesy of H. He and K. Matyjaszewski of Carnegie Mellon University.

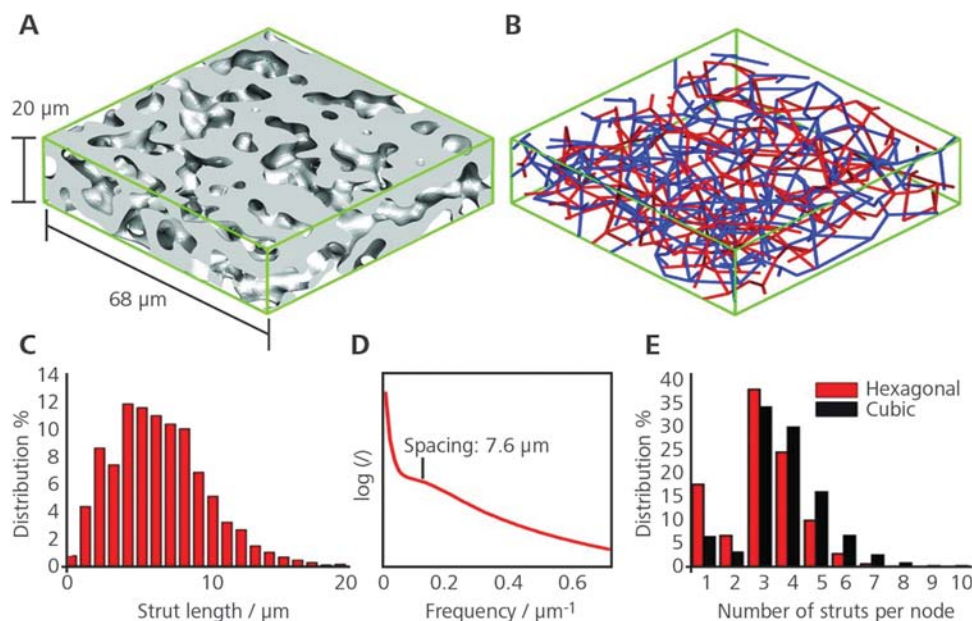


Figure 3: Macrostructure XRM characterization and quantitative analysis of scaffold. A 3D tomographic reconstruction of the hexagonal mesostructure of a hierarchical porous polymer scaffold material from block copolymers using ZEISS Xradia 520 Versa XRM. (A) Isosurface visualization. (B) Skeletal networks for (A) of the polymeric (blue) and the porous (red) regions. (C) Node-to-node distance distribution of the porous network from a 136 mm cubic region. (D) Radial distribution function of the 3D FFT volumetric data from (C). (E) Population distribution of struts per node for (C) (red columns), as well as an identically generated network of a sample cast at 100°C with cubic mesostructure (black columns). From [16], reprinted with permission from AAAS.

solely by SEM. 3D tomographic reconstructions from data collected non-destructively via XRM provided visualization of relatively large volumes of $\sim 1\text{ mm}^3$, including visualization of the skeletal networks for the polymer and pores (Figure 3). Beyond volumetric visualization, the XRM dataset provided quantitative analysis of the skeletal network to determine the range of distribution of feature sizes from the node-to-node distance distribution to the number of struts per node for various symmetries. XRM enabled 3D volume visualization and quantitative network analysis to correlate to complementary electron microscopy structure characterization.

Hierarchically-Porous Membrane Materials

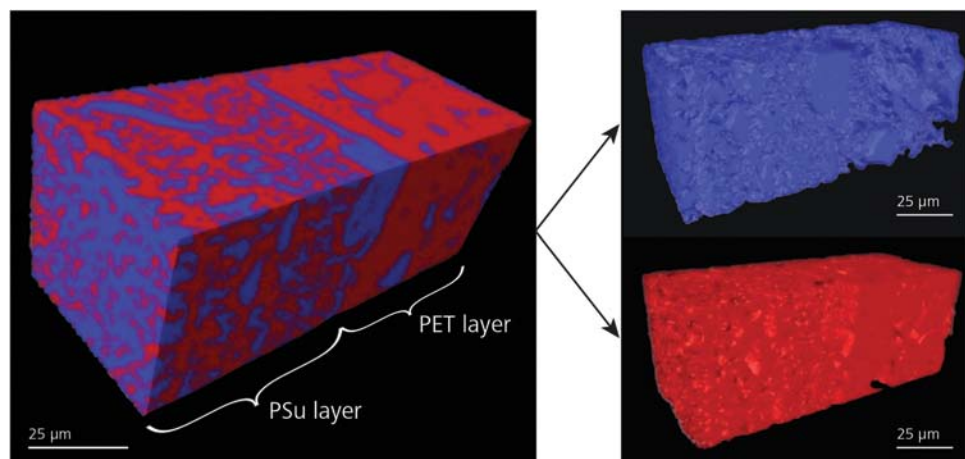
Engineered osmosis (EO) is a method of water desalination (via forward osmosis) and power production (via pressure-retarded osmosis) using porous polymeric membranes. The commercialization of this technology is currently limited by internal concentration polarization (ICP), which is difficult to characterize due to a poor understanding of the structure-property relationships of the membranes and the general difficulty in characterizing porous polymer structures [17]. In a study published by Manickam et al. [18], the XRM technique was applied to characterize the structural differences between two EO membranes traditionally used for reverse osmosis (Figure 4). XRM affords the capability of visualizing and modeling the pore structures in these membranes using phase contrast imaging techniques, down to the 50 nm resolution regime [9, 18]. Applying micrometer-scale XRM (Xradia MicroXCT-200), the porosity distributions were obtained as a function of depth from the surface of the sample. This provided a quantitative depiction of the interface between multiple layers in the hierarchically porous thin-film composite structure, which was used to calculate the

structural metrics, such as porosity, tortuosity, and support layer thickness, important for modeling transport phenomena. Nanoscale XRM (ZEISS Xradia 800 Ultra) was subsequently used for further refinement of the pore models, which enabled calculation of the structural parameter, S , relating the porosity, tortuosity, and thickness.

These results were compared to experimental flux measurements performed using mercury intrusion porosimetry (MIP) and revealed a large discrepancy between the MIP and XRM results. This discrepancy was reported to represent errors in the MIP method, introduced by incomplete wetting during forward osmosis flux testing of the hydrophobic polysulfone layer. The multi-scale XRM results, therefore, were reported to give a new perspective on mass transport and suggested a need for revisiting the traditional characterization methodologies for mass transport in porous polymer thin-film composites [18]. Furthermore, XRM can be used to assess structural anisotropy to incorporate anisotropy into the structural parameter. This has not been incorporated with any membrane transport model primarily because obtaining such structural information has been unavailable until now. The multi-scale XRM technique can be used to provide insight into the structure-property relationships of these anisotropic materials to better design membranes for engineered osmosis.

Porous Energy Materials

Researchers in Professor Shawn Litster's laboratory at Carnegie Mellon University have explored the distribution of pores within Polymer Electrolyte Fuel Cell (PEFC) materials [19–21]. Fuel cells are complicated systems. Efficient energy conversion in porous electrodes depends on a combination of factors, such as the electrochemical reaction kinetics, the electrode architecture, and the transport phenomena. For this reason, direct quantification of the 3D electrode architecture to evaluate different electrode formulations and to obtain morphological inputs for modeling is very important. Morphological analysis using nanoscale XRM (Zeiss Xradia 800 Ultra) has explored the 3D structure of the PEFC electrode, which consists of a carbon support with platinum catalyst bound by Nafion polymer electrolyte, to elucidate the distribution of the nanoscale pore structure that dictates the performance of such cells and to input these structure characterizations into various predictive models. For example, the PEFC electrode agglomerate model typically assumes a single, representative agglomerate diameter, whereas in reality there is a distribution of agglomerate sizes. By incorporating an agglomerate diameter distribution determined by XRM (Figure 5, left), the diameter distribution causes the agglomerate model predictions to differ by as much as 70% when compared to reasonable single agglomerate diameter choices [19].



laboratory to extend characterization to 3D and measure multiple length scales. The technique is useful across a wide spectrum of sample types and can characterize samples in their native environments (*in situ*). The 3D XRM method also can non-destructively follow the evolution of a microstructure in response to environmental conditions or stressors, providing characterization over time (4D). After XRM characterization, the 3D information can be used to navigate and correlate to the next smaller length scale, typically via SEM, FIB/SEM or TEM analysis. The incorporation of multi-scale XRM 3D geometry data with EM-level information into computational models provides a synergistic pathway for the design, fabrication, and understanding of hierarchical structures.

Figure 4: Surface renderings of 3D XRM datasets of hierarchically-porous membrane materials. The complete structure of the membrane, where blue regions denote pore space and red regions denote the polymer matrix. These images can be deconvoluted in pore phase and polymer matrix as shown by the images on the right. Reprinted from [18] with permission from Elsevier.

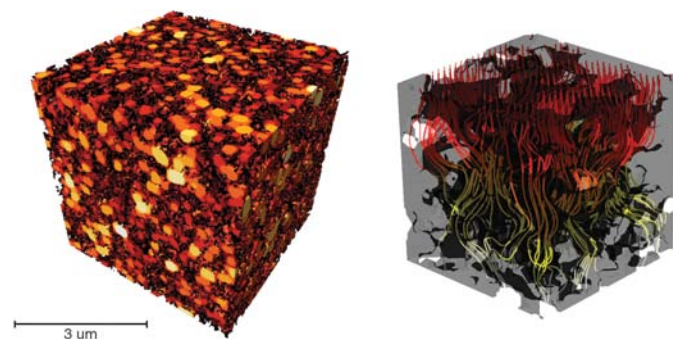


Figure 5: (Left) PEFC electrode, where the solid phase is colored by the local agglomerate diameter, which is an important length for considering the resistance for oxygen transport to the Pt catalyst within the composite solid phase [19]. (Right) Gas diffusion stream lines through a PEFC electrode. Diffusion stream lines are colored by the concentration. The local pore size dependent diffusion coefficient was used in this modeling work [21]. Images courtesy of Prof. Shawn Litster, Pratiti Mandal, and Arjun Kumar, Carnegie Mellon University.

Additionally, there is great interest in PEFC research to reduce the amount of the costly platinum catalyst by reducing transport resistances in the electrochemical cell and improve overall cell performance. Structural XRM characterization was combined with gas diffusion simulation analysis to determine transport properties such as effective diffusivity [21]. XRM provided the true 3D geometry input necessary to properly capture diffusivity anisotropy in PEFCs and other properties that require an accurate portrayal of the 3D structure (Figure 5, right). The ability of XRM to non-destructively measure electrode microstructures lends itself naturally to *in situ*, 4D, and *in operando* experiments to study structural changes of the device even in packaged cells [22].

Conclusion

XRM is a rapidly emerging technique to tomographically image and quantify sub-surface microstructure in 3D across a variety of length scales from tens of nm to mm. This is ideal for characterization of hierarchical, porous materials with good contrast, even for low-Z materials. XRM is a complementary non-destructive imaging technique for the general microscopy

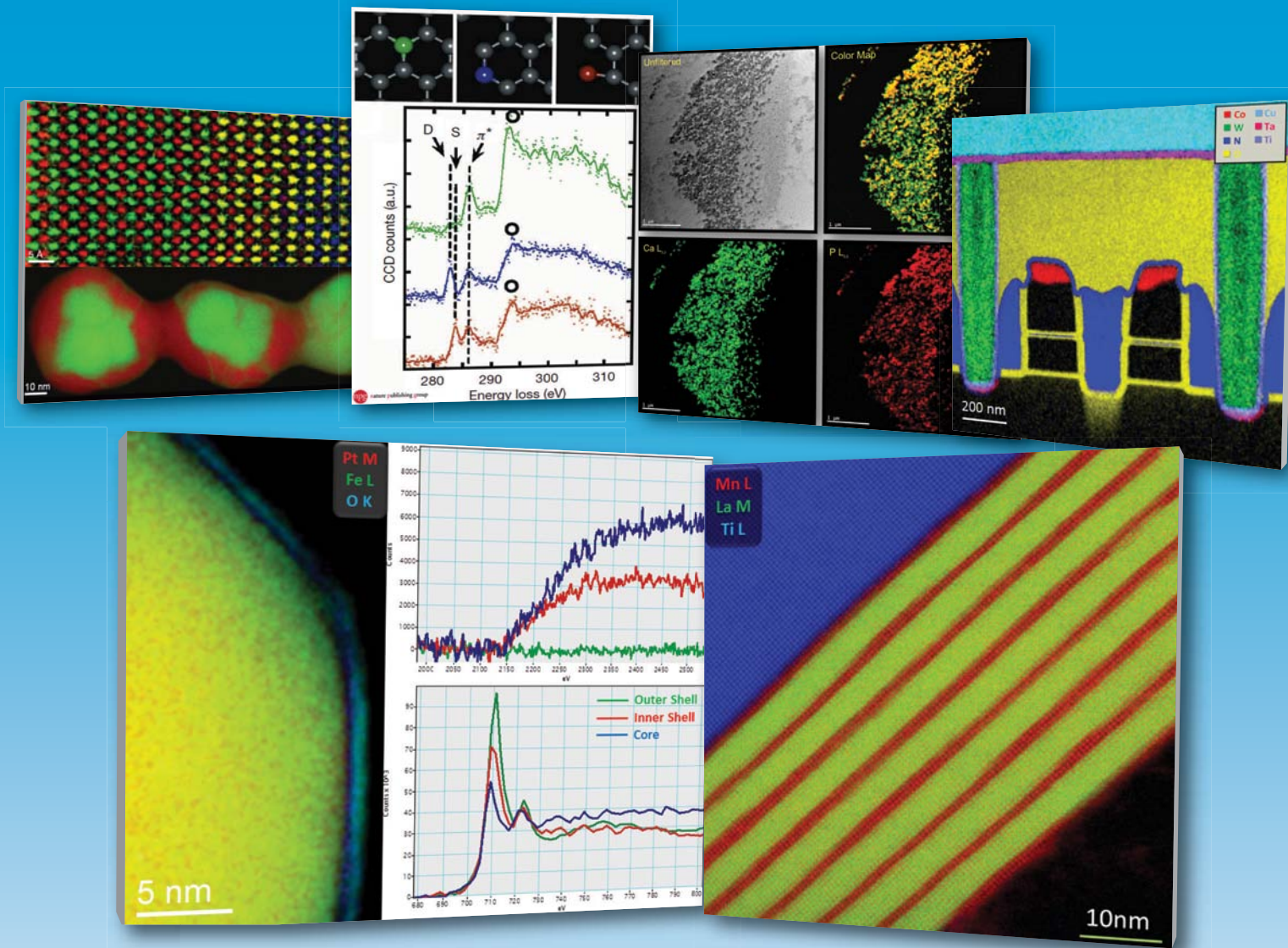
References

- [1] J Liu and A Baca, *Materials Today* 15 (2012) 287.
- [2] P Ball, *MRS Bulletin* 38 (2013) 873–85.
- [3] U.S. Department of Energy, Basic Energy Sciences Advisory Subcommittee on Mesoscale Science, "From Quanta to the Continuum: Opportunities for Mesoscale Science," September 2012.
- [4] Y Li, ZY Fu, and BL Siu, *Advanced Functional Materials* (2012) 4634–67.
- [5] AP Merkle and J Gelb, *Microscopy Today* March (2013) 10–15.
- [6] OP Popova et al., *Science* 342 (2013) 1069–73.
- [7] Y Zhang et al., *Advanced Functional Materials* (Nov. 26, 2013) doi: 10.1002/adfm.201302957.
- [8] X Jin et al., *Advanced Functional Materials*, doi:10.1002/adfm.201304184.
- [9] A Tkachuk et al., *Kristallogr* 222 (2007) 650–55.
- [10] M Andrew, B Bijeljic, and MJ Blunt, *Geophysical Research Letters* 40(15) (2013) 3915–18.
- [11] BM Patterson, K Henderson, and Z Smith, *J Mater Sci* 48(5) (2013) 1986–96.
- [12] SP Ho et al., *Biomaterials* 31(25) (2010) 6635–46.
- [13] RA Ketcham and C Koeberl, *Geosphere* 9(5) (2013) 1336–47.
- [14] H He et al., *Advanced Functional Materials* 23(37) (2013) 4720–28.
- [15] H Zhang, X Yu, and PV Braun, *Nature Nanotechnology* 6(5) (2011) 277–81.
- [16] H Sai et al., *Science* (341) (6145) (2013) 530–34.
- [17] SS Manickam, and JR McCutcheon, *Journal of Membrane Science* 407–408 (2012) 108–15.
- [18] SS Manickam, J Gelb, and JR McCutcheon, *Journal of Membrane Science* 454 (2013) 549–54.
- [19] WK Epting, J Gelb, and S Litster, *Advanced Functional Materials* 22(3) (2012) 555–60.
- [20] WK Epting and S Litster, *International Journal of Hydrogen Energy* 37(10) (2012) 8505–11.
- [21] S Litster et al., *Fuel Cells* 13 (2013) 935–45.
- [22] DS Eastwood et al., *Advanced Energy Materials* 4(4) (2014) doi:10.1002/aenm.201470016.

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Top Images, left to right:

- (Top) Colored elemental map showing Sr $L_{2,3}$ -edges (green), Ti $L_{2,3}$ -edges (red), La $M_{4,5}$ -edges (yellow), and Mn $L_{2,3}$ -edges (blue). Data captured using a Gatan Enfinium™ER. Sample courtesy of Prof. David Smith, Arizona State University.
- (Bottom) RGB composite EELS SI image of Au/Pd nanoparticle; Au $M_{4,5}$ -edges at 2206 eV in green and Pd $L_{2,3}$ -edges at 3173 eV in red. Data captured using a Gatan GIF Quantum™ER. Sample courtesy Dr. Jianfang Wang of The Chinese University of Hong Kong.
- ELNES of individual atoms in graphene. Different states of atomic coordination are illustrated at top. ELNES of carbon K (1s) spectra shown on bottom. Green, blue and red spectra correspond to the normal sp² carbon atom, a double-coordinated atom and a single coordinated atom, respectively. Data captured using a Gatan Quantum™ER Low-Voltage Special. Data courtesy of K. Suenaga and M. Koshino (AIST, Tsukuba, Japan). Figure 1 from: K. Suenaga et al. "Atom-by-Atom spectroscopy analysis at graphene edge"; Nature 468, 1088 (2010). Permission to use Figure 1 granted by K. Suenaga and Nature Publishing Group. Copyright © 2010, rights managed by Nature Publishing Group.
- Unfiltered, conventional TEM image and elemental maps of a capillary blood vessel captured using a Gatan GIF Quantum™ER. The Ca and P elemental maps were extracted from an EFTEM-SI dataset acquired using Gatan's DigitalMicrograph™ software. EFTEM-SI is capable of revealing relative concentrations below 1% as shown in the P elemental map. Sample courtesy of Dr. Wenlang Lin, Mayo Clinic.
- Color composite EELS composition map from data acquired using a GIF Quantum™ERS system on a 300 kV probe corrected STEM with 1.0 nA beam current. The EELS data was acquired at 4.1 ms/pixel with a 20 mR convergence angle and 42 mR collection angle. The 200 x 200 pixel map took under 3 minutes to acquire (164 s). The black areas are Si, which has been omitted for clarity. TEM facilities courtesy FELMI and TU Graz, Austria.

Bottom Images, left to right:

- (Left) Colored elemental map based on Pt M-edge (red), Fe L-edge (green), and O K-edge (blue) intensities. Data captured using a Gatan GIF Quantum™ERS and 300 kV probe corrected STEM with 180 pA beam and 5 ms exposure.
- (Right) Extracted Pt $M_{4,5}$ edges (upper) and Fe $L_{2,3}$ edges (lower) from the thin outer shell (green), low density inner shell (red) and core (blue). Despite the sub-nm proximity of the outer shell to the core, no Pt is detected. The Fe-L2/L3 ratio and peak position vary significantly with the Fe chemistry of the layer. Sample and TEM facilities courtesy McMaster University, Canada.
- Colored 1k x 1k elemental map of LaMnO₃ / SrMnO₃ superlattices grown on SrTiO₃ (Mn - Red, La-green, Ti L-blue). Data was acquired on an Enfinium™ (JHV special) coupled to a 100 kV NION UltraSTEM. Image courtesy Mundy, Adamo, Schlom & Muller, Cornell University. (Results published in Monkman & Adamo, et al, Nature Materials, vol 11, 2012).



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