Non Invasive, Multiscale 3D X-Ray Characterization of Porous Functional Composites and Membranes, with Resolution from MM to Sub 50 NM

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Abstract. We describe a novel x-ray computer tomography (CT) system for high contrast, non invasive 3D imaging of internal structures of functional ceramics, composites and polymeric membranes. System is capable of multi-length scale imaging from mm to sub 50 nm spatial resolutions and requires little or no sample preparation or staining. Relatively large samples with thickness from several mm to several microns may be imaged at high resolution. Examples using functional composites and membranes from SOFC (solid oxide fuel cell) and PEM (proton exchange membranes) fuel cell to derive direct information such as porosity and catalytic membrane degradation will be discussed. The key to the novel laboratory CT technology lies in utilizing proprietary x-ray optics with Fresnel Zone plates, and innovative high resolution, high contrast detectors.

1. Background
A variety of porous functional ceramics and membranes materials are actively being developed for energy conversion, microelectronics and biomedical applications. These includes fuel cell membranes and ceramic composites which can convert chemical energy directly into electrical energy without combustion, membranes that are responsive to their environment, breathable fabric that can neutralize biological and chemical agents. While conventional imaging tools such as optical microscopy, electron microscopy and AFM are adequate to visualize surface structures of these materials, it has been difficult to accurately characterize their internal 3D arrays, porosity and functionalities. To do that, destructive sample preparation through physical or chemical cross section must be performed. This approach can be tedious and introduces artifacts. Optical and confocal microscopy suffers from diffraction limits with spatial resolution no better than 200 nm. While electron microscopy can achieve spatial resolution in the nm scale, sample preparation can be very elaborate, including the need to be compatible with high vacuum and be electrically conductive. Moreover, conventional imaging modalities will not easily characterize functional and structural changes of materials and sensors in 3D at the multiscale level.
We describe a novel multiscale lab-based x-ray CT (computed tomography) system for rapid noninvasive 3D characterization of internal structures and porosity of advanced functional materials—from polymers, ceramics and composites to microelectronic sensors, with mm to sub 50 nm spatial resolution. Using x-ray lens and proprietary optics, the system is capable of imaging samples with dimensions from several cm to microns and at relatively large working distance, opening up the possibility to set up experimental fixtures for in situ characterization of degradation phenomena of materials under certain operating conditions. With phase contrast optics, low Z composite materials and polymers can be imaged with excellent contrast.

In this paper we will describe the use of the novel CT for non invasive 3D structural characterization using examples from two representative functional materials used in Fuel Cell technologies. The first illustration is porosity characterization of a ceramic composite from Solid Oxide Fuel cell (SOFC), a promising technology for power plants, while the next example shows the power of high contrast imaging to characterize polymer membrane degradation in Proton Exchange Membrane (PEM) Fuel cells. PEM is actively being research for automotive and portable power sources. Both materials are difficult to characterize in 3D with conventional imaging modalities such as optical, SEM (scanning electron microscopy) or TEM (transmission electron microscopy).

2. Method
By combining the novel MicroXCT™ [1] and nanoXCT™ [2,3] from Xradia Inc (Concord, CA), a laboratory based multiscale CT solution may be configured. For example, relatively large samples (such as 15 cm x 15 cm x few mm thick polymeric or composite panels) may be imaged at variable resolution, including the ability to zoom in on selected region of interest for tomography with high voxel resolution of 1 to 3 microns. At the other end of the spectrum, nanoscale imaging with resolution to 50 nm can be achieved with smaller sample sizes.

2.1. MicroCT system configuration
The schematic of the MicroXCT™ system configuration is depicted below (Figure 1).

![Figure 1. Schematic of the MicroXCT](image)

The MicroXCT™ uses a commercial microfocus x-ray source. The sample can be translated in x-y-z directions in a high resolution precision rotation stage. High resolution and high contrast capability is achieved with proprietary PhaseEnhanced™ x-ray imaging and detector optics- with effective detector pixel size < 1 micron.

Unlike other commercial 2D or 3D x-ray systems in the market, which uses geometric projection thereby limiting resolution to the spot size of its source, the novel microCT configuration does not require the use of small spot size x-ray source nor the need for the sample to be placed very close to the source to achieve high resolution imaging. High resolution and high contrast images of a number of polymeric and composite materials with relatively large sample dimensions and with thickness of several mm can be imaged to 1 to 3 micron resolution, at large working distance, several mm from the source.
2.2. nanoCT system configuration

X-ray imaging using conventional x-ray point projection with a submicron spot sized, transmission x-ray laboratory source is commercially available. However, the smallest spot size that can be generated by a commercial x-ray source is currently around 0.25 micron, hence spatial resolution is theoretically no better than 0.25 micron in 2D. However submicron 3D resolution has only been demonstrated for certain low Z materials provided sample diameter is < 1 mm and there is sufficient image contrast within the sample material. Coupled with the poor flux and spot drift when such x-ray tube is operating at this spot size, nanoscale x-ray imaging using this approach is not practical.

Compared to conventional point projection technique, the novel lens based nanoCT provides far superior spatial resolution (currently at 50 nm) and signal to noise, with 2 to 4x greater x-ray photons reaching the detector for imaging. This configuration is similar to the high resolution x-ray microscopes at synchrotron light sources which utilizes Fresnel zone-plates as objective lenses [4]. Fresnel zone plates (Figure 2) are diffractive optical elements which focus x-rays by means of diffraction.

![Zone Plate](image)

**Figure 2.** Fresnel Zone plates as focusing optics for x-rays. The Rayleigh resolution $\delta$ of a x-ray microscope is proportional to the outermost zone width $\Delta r_n$ of the zone plate: $\delta = 1.22 \Delta r_n$

![Schematic](image)

**Figure 3.** Schematic of sub-50 nm nanoXCT 3D X-ray microscope with specialized highly efficient reflective condenser, Fresnel Zone plate optics and high resolution imaging detector.

The Rayleigh resolution $\delta$ of a x-ray microscope is a function of the outermost zone width $\Delta r_n$ of the objective zone plate:

$$\delta = 1.22 \Delta r_n$$  \hspace{1cm} (1)

The resolution of the zone-plate based x-ray microscope is independent of x-ray source spot size and is ultimately limited by the outermost zone width of the zone plate (finer zones give higher resolution).

To compensate for the lack of flux from laboratory sources, for nanoscale imaging the novel nanoCT uses a very high-efficiency reflective capillary x-ray condenser lens matched to a numerical aperture (NA) of the Fresnel zone plate objective [Figure 4] [3]. This design is similar in concept to that of a transmission light microscope where glass refractive lenses are substituted with x-ray optics. Operating in the hard x-ray regime at 5.4 or 8.0 keV, the laboratory system can, for example, penetrate through as much as 100 microns of silicon (or equivalent), making it possible to obtain 3D images of the interiors of dense samples.
Contrast in transmission x-ray imaging is mainly based on absorption differences between different materials within the sample. For most composites, polymer or biomaterials, the x-ray attenuation length for these low Z materials can be very long, resulting in little x-ray absorption and therefore poor imaging contrast. To overcome this problem, the novel x-ray microscope can dramatically increase imaging contrast by operating in the Zernike phase contrast mode by means of a phase ring in its optics.

3. Results and Discussion

Examples of non invasive multiscale 3D characterization are illustrated with two representative functional materials from Fuel Cell technologies. The first example is porosity characterization of a ceramic composite from Solid Oxide Fuel cell (SOFC), a promising technology for power plants, while another example shows degradation of the polymeric catalytic membrane from Proton Exchange Membrane (PEM) Fuel cells under different test conditions. PEM is actively being research for automotive and portable power sources. Both materials are difficult to characterize in 3D with conventional imaging modalities such as optical, SEM or TEM.

3.1. Characterization of Functional Ceramics:

3.1.1. Porosity Studies in Ceramic composites of Solid Oxide Fuel Cell (SOFC)

A critical step in making SOFC more commercially viable for large scale generation of electricity in power plants is to improve the resistance of the electrode and electrolyte components to aging. The electrochemical reactions occur in a narrow zone along the three-phase boundary (TPB), where the electrode material, the solid electrolyte, and the gas are in contact. It is crucial to be able to non-destructively image these nano-porous structures in 3D to study the size, distribution, and connectivity of the pores and channels to model gas transport and ionic charge transport electrochemistry. As an example of the application of the novel nanoCT system, we show CT data of a fragment of a hollow tubular solid oxide fuel-cell (SOFC), with a solid YSZ electrolyte shell and a much thicker porous Ni-YSZ anode layer on the inside [Fig 5]. Raw projection data is shown in Figure 5 as it appears on the computer screen of the microscope. Data collection is fully automated with 5 min/projection exposure time in order to obtain data with a good signal to noise ratio. Since the electron density of the solid and porous material are very similar, the solid YSZ electrolyte appears darker on the left image because of the greater projected thickness the x-rays had to penetrate at this particular imaging angle.
A 2D radiograph of the sample incident shows evidence of pore structures within the sample (Figure 6a). As 2D data comprise several overlapping features, it is impossible to derive any quantitative porosity data. A major advantage of tomography is the ability to combine and mathematically reconstruct several such 2D projected images into a 3D virtual data set, where surface and buried information can be analyzed in different orthogonal planes through CT slices. Four CT slices in the depth direction from the rendered volume are shown in Figure 6(b-e). In particular, Figure 6(b) shows a CT section in anode layer, Figure 6(c) and (d) show the transition between the anode and electrolyte, and Figure 6(e) shows the electrolyte layer. Figure 6(f) shows a perspective of the rendered volume.

Furthermore, a 3D tomography data set can lend itself to further image analysis to derive important parameters such as porosity, open, connected and close pores, and the degree of tortuosity, which are critical for modeling electrochemistry, gas transport, electronic and ionic charge transfer [5].

While SEM can provide surface details in very high resolution to a few nm, it is not a practical imaging modality to derive porosity data in 3D especially for hard materials such as ceramics, since sample preparation to provide cross sections at the various depths and imaging planes are too tedious, time consuming and prone to artifacts. To calibrate for porosity of materials, the Mercury Intrusion
Porosity (MIP) is often used as the standard tool. While this technique is ubiquitous in the laboratory for such measurement, it does not give actual physical structure, the size of the pores at various depths, nor does it provide information on the degree of connected and close pores in the sample, which are readily available with the novel CT measurements. Validation of the novel CT data with that of the MIP for the above sample is shown in Figure 7.

3.1.2. Pore size distribution: Validation with Hg Intrusion Porosimeter

![Pore space results from nanoCT](image)

**Figure 7.** Pore size distribution profile comparing Mercury Intrusion Porosimeter (MIP) with novel nanoCT. However, CT results provide actual physical 3D and 2D structures & additional information such as the extent of pore connectivity [5]

The ability to non invasively characterize porosity and pore connectivity in 3D could provide critical validated data for simulation models used currently in the design of next generation SOFC micro and nano structures.

3.2. Characterization of Functional Polymeric Membranes

3.2.1. Degradation study in Proton Exchange Membrane (PEM) Fuel cell

The next example is the characterization of buried structures within functional polymeric membranes, which are also difficult to image with conventional imaging modalities such as visible or electron microscopy. Some advantages of using the novel CT for this class of functional materials includes: its non-invasive technique, it requires little or no sample preparation, does not require sample to be conductive and does not disturb the microstructure compared to TEM or SEM. Moreover, the novel CT instruments operate under ambient conditions rather than high vacuum, thus producing less morphological changes due to severe dehydration of the ionomer. X-rays generate much less sample beam damage for polymers compared to charged particles used in electron imaging techniques.

Proton exchange membrane (PEM) fuel cells offer great promise for direct conversion of hydrogen energy to electricity and are being currently developed for light transportation applications. A major requirement for this technology to be commercially viable is to improve the durability of these cells to at least 5000 operating hours with minimal degradation. Such durability benchmarks must be met under the conditions of transient power cycle operation, many start/stops, and over a range of vehicle operating temperatures (-40° to +40° C). Unfortunately the varying operating conditions have been shown to greatly exacerbate fuel cell degradation. Membrane degradation caused by Pt electrocatalyst sintering and consequent loss in active catalyst surface area and the corrosion of the supporting carbon are some of the key problems affect durability of the PEM fuel cells.

To better understand changes in the internal structure of fuel cell membrane electrode assemblies (MEAs) the novel CT is used to non invasively characterize the changes in morphologies across lengthscales, from micro to nanoscale and at high contrast [6].
3.2.2. Multilengthscale Characterization of PEM membrane degradation

3 MEAs (membrane electrode assembly) samples with dimensions of 22 mm x 22 mm were used for this study. They comprised 0.2 mg 20 wt% Pt supported on Vulcan XC-72 carbon (ETEK) anodes (GDL:E-Tek ELAT Version 2.0 w/double-sided MPLs) and cathodes (GDL:E-Tek ELAT Version 2.22 w/single-sided MPL) and Nafion 1135.

The 3 membranes are subjected to drive cycles with start stops and without stops until failure with one control (unused membrane). Results shown in Figures 8 and 9.

3.2.3. Results: microCT slices at 0.7 micron pixel resolution

Figure 8: MicroCT slices from 2 different planes. Images at the far right are CT slices from side and the first 3 images from the left are CT slices from top of the flat membrane

Membrane #1. Unused; sample electrode density is uniform; the interface is smooth

Membrane #2. Failed membrane: went through a drive cycle without stops until failure. Electrode interfaces rough with membrane thinning, significant C corrosion at cathode with Pt compaction

Membrane #3. Undergone drive cycle with start stops until failure: Cathode Electrode interface is rough and anode interface is smoother and more uniform density; C corrosion at cathode with Pt compaction
3.2.4. Results: Multiscale CT slices at 1 micron and 50 nm resolution

![Image](image.png)

**Figure 9**: Comparison of CT slices from MicroCT imaged at 0.7 micron pixel resolution (~1 micron spatial resolution), and the zoomed region for higher resolution imaging with nanoCT imaged at 25 nm pixel resolution (50 nm spatial resolution).

From both micro and nanoCT imaging, it is evident that transient operation of hydrogen fuel cells produced large redistributions of cathode catalyst and compaction of the cathode layer. The compaction of the cathode layer and thinning of membrane appears to be due to carbon loss, Pt migration and agglomeration, which are more readily apparent with the nanoCT images at 50 nm spatial resolution (Membrane #2 and 3). Nafion membrane texture also assumes a preferred orientation in the start-stop experiment (Membrane #3). Results were in agreement with earlier studies using TEM, XRF and XRD [7], with a TEM micrograph of Pt agglomeration shown below [Figure 10].

![Image](image.png)

**Figure 10**: TEM image of MEA showing Pt agglomeration after drive cycle testing
The set of preliminary results of such non-invasive CT imaging of relatively large samples at high resolution shows a lot of promise, as the study may be further extended to in situ characterization of intact PEM fuel cells for observing changes in the internal morphology of the cell under operating condition; or under controlled environmental conditions, such as freezing, heat and different humidity conditions which are encountered under normal vehicle operating environment.

4. Conclusions
Using representative examples of both hard and soft composite material, such as ceramic composites and polymeric catalyst membranes from Fuel cells as illustrations, we describe the potential applications and advantages of the novel multiscale CT system for rapid non-invasive structural and failure characterization of functional materials in 3D. As little or no sample preparation is required, it is envisioned that such a lab-based CT will find widespread adoption within the research community for a variety of advanced materials, biomaterials and sensors in the years to come.

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