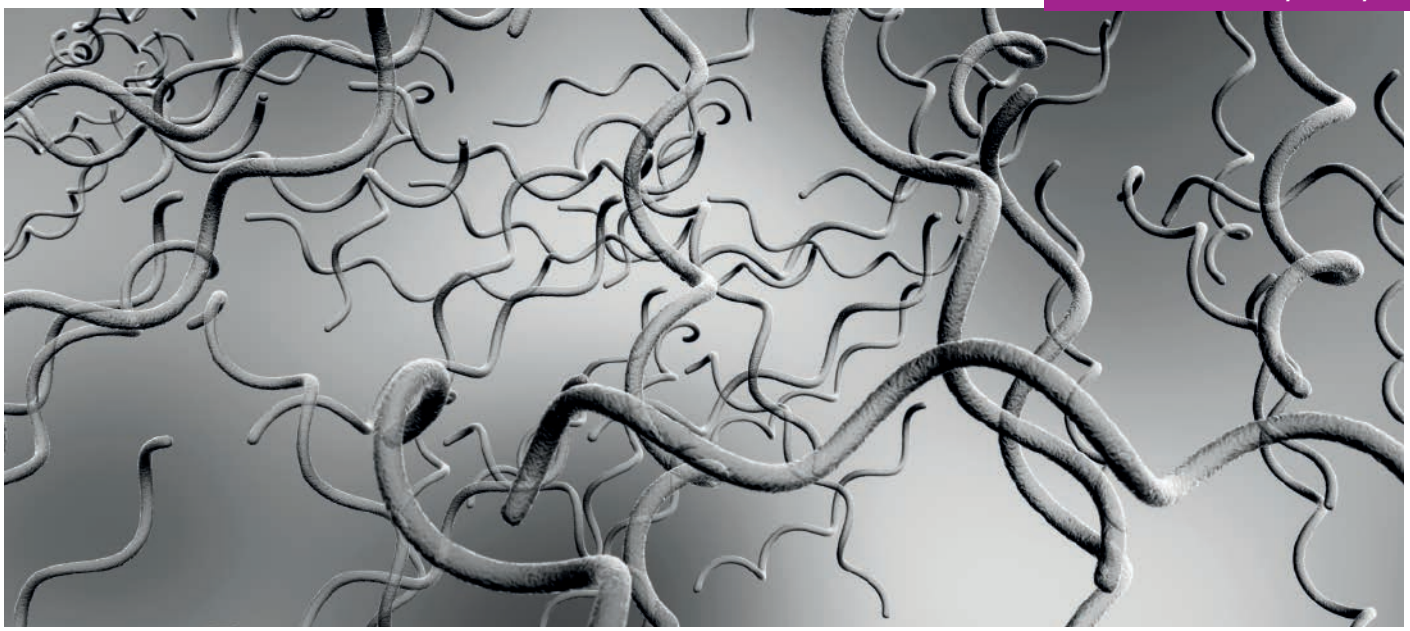

Advances in Soft X-Ray Spectromicroscopy

Fuel Cells and Biomagnetism

Adam Hitchcock

Synchrotron based soft X-ray scanning transmission X-ray microscopy (STXM) provides spectra and quantitative 2D and 3D chemical mapping at a spatial resolution better than 30 nm. Recently the resolution has been pushed below 5 nm by implementing ptychographic coherent diffraction imaging in STXM platforms. These methods are presented and illustrated with examples of chemically specific imaging in 2D and 3D of (1) proton conducting ionomer in fuel cells, and (2) magnetotactic bacteria.

Introduction

Synchrotron based soft X-ray scanning transmission X-ray microscopy (STXM) was developed in the 1990s and is now implemented at over 20 light sources around the world [1]. STXM provides quantitative 2D and 3D mapping of chemical species with a routine spatial resolution better than 30 nm, limited by the Fresnel zone plate lens used to focus monochromatic X-rays. Coherent diffraction imaging (CDI) has been shown to provide spatial resolution beyond the limitations of X-ray focusing lenses. In the ptychography implementation of CDI, coherent scattering images are recorded at an array of overlapping spots. The requirement of identical phase and amplitude in the overlapping regions provides the basis for robust and efficient algorithms to reconstruct real space images from sets of diffraction images. Recently, ptychography has been implemented in soft X-ray STXMs at the Advanced Light Source (ALS, Berkeley, CA, USA). Soft X-ray ptychography is now a routine chemical imaging method with better than 5 nm spatial resolution [2,3]. Here examples from two scientific applications illustrate current STXM and ptychography performance.

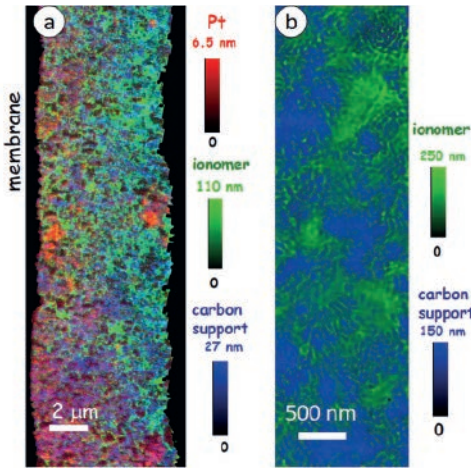

Fig. 1: (a) Color coded composite of Pt (red), carbon support (blue) and perfluorosulfonate ionomer (green) in anode of an automotive polymer electrolyte membrane fuel cell (PEM-FC) derived from a C 1s image sequence measured by STXM. (b) Color coded composite of carbon support (blue) and perfluorosulfonate ionomer (green) in the cathode of a PEM-FC measured by 2-energy F 1s spectro-ptychography [12]. Color intensity scales are quantitative thickness in nm.

Polymer electrolyte membrane fuel cells (PEM-FC) are an attractive replacement of automotive internal combustion engines since they have similar range and refueling times, in contrast to battery electric vehicles [4]. An important aspect is the mission-critical proton conducting ionomer in the cathode, which is very difficult to image using electron microscopy techniques due to its extreme radiation sensitivity. We have developed practical STXM and ptychography methods for quantitative imaging of ionomer in PEM-FC. These results help optimize cathode layer formulations and processing to improve performance and reliability [5,6].

Magnetotactic bacteria (MTB) biomineralize chains of high-quality magnetite single crystals which provide an internal compass which orients cells along the earth's magnetic field [7]. This, in combination with oxygen chemotaxis, allows MTB to find their preferred habitat, the oxic-anoxic boundary. Fe L-edge spectroscopy and X-ray magnetic circular dichroism of MTB measured by STXM [8] and ptychography [3] are being used to study MTB. This is the simplest, well characterized biomineralization system [9]. It is being study by many disciplines.

Material & Methods

Membrane electrode assemblies from fuel cell stacks, provided by the Automotive Fuel Cell Co-operation Corporation (AFCC), were prepared as ~250 nm thin cross-sections by

ultramicrotomy. *M. blakemorei strain MV-1* cells were cultured anaerobically [9], deposited on TEM grids and washed to remove culture salts. For both systems, images, and image sequences were measured using standard procedures [1]: STXM data was measured using microscopes at the ALS and CLS and was processed using aXis2000 [14]. Ptychography data was measured using the Nanosurveyor I system on ALS beamline 5.3.2.1 and reconstructed using SHARP [10]. Tomography data sets were reconstructed using compressed sensing in Mantis [11, 15].

Results & Discussion

Figure 1 presents quantitative 2D mapping of ionomer and other components in a PEM-FC electrode by STXM and ptychography. The STXM mapping (fig. 1a) shows there are continuous pathways of ionomer (green) across the width of the electrode. Ptychography (fig. 1b), which has much higher spatial resolution, was accomplished with only 2 photon energies, a 100 nm spot size, and 20 ms acquisition time per diffraction image, resulting in negligible radiation dose [12]. However, it is the 3D chemical structure, in particular the continuity of both the ionomer and porosity, that control performance and thus are the ultimate analytical target. Progress is being made on using spectro-ptycho-tomography to get higher spatial resolution 3D mapping of PEM-FC cathodes [12]. Figure 2 presents visualizations of a compressed sensing reconstruction of a ptychography tomography data set of a PEM-FC cathode. Images at two photon energies, one below, the other above the F 1s edge, were measured at 14 angles. Quantitative amounts of ionomer and carbon support were derived from the 2-energy spectroscopic information contained in the spectro-ptycho-tomo data. The z-direction data range is limited by sample thickness which is less than 300 nm due to finite penetration of soft X-rays. Even so, with the higher spatial resolution of ptychography (~16 nm), there is clear chemical differentiation in the z-direction (figs. 2b, 2c). All 3D ptycho-tomography studies to date have required doses which generate unacceptable levels of radiation damage [12]. The recently opened ALS COSMIC beamline, dedicated to ptychography, has much higher coherent flux than the bend magnet beamline used for the spectro-ptycho-tomo measurements reported here. Higher coherent flux provides more intense coherent scattering. This, along with improved soft X-ray cameras, give hope that

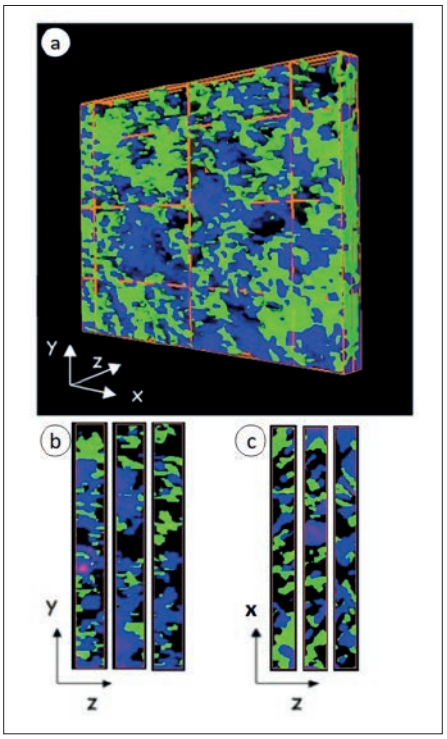

Fig. 2: (a) Perspective view of 3D chemical structure of a PEM-FC cathode derived from a 14 tilt angle, 2-energy (684, 694 eV) spectro-ptycho-tomography measurement on a microtomed sample. Carbon support is blue, ionomer is green. The slab has dimensions of 4 μm x 4 μm x 250 nm. (b) cuts in the y-z plane from 3 x positions. (c) cuts in the x-z plane from 3 y positions [12].

3D chemical imaging of radiation sensitive ionomer can be performed by ptychography with acceptable damage.

Figure 3a presents an image of a single cell of *M. blakemorei strain MV-1*, recorded by spectro-ptychography [3]. Figure 3b presents the Fe L_3 spectra of 4 regions: (A, dark green) a gap in the magnetosome chain; (B, light green) a low density magnetosome which is a precursor; (C, red) an immature magnetosome, and (D, blue) a mature magnetosome. The latter exhibits the spectrum of high quality, single crystal magnetite. The spectra of the immature magnetosome (C), and the precursor (B) are different, in particular, having more intensity around 708 eV, which can arise either from a fully Fe(III) structure like hematite, or from an Fe(II) state. The gap region (A) is similar to a pure Fe(II) species. The changes in the spectra of the different morphologies show the potential of STXM and ptychography to give insights into mechanisms of mag-

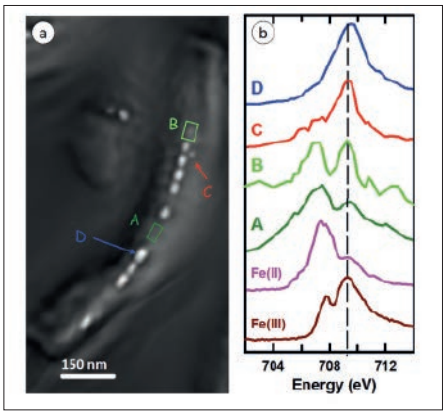

Fig. 3: a) Average of 76 ptychography absorption images from 700 to 732 eV of a single M. blakemorei strain MV-1 magnetotactic bacterial cell. Four regions, labeled A, B, C, and D, are identified. (b) Fe L_3 spectra from a gap in the magnetosome chain (region A), a precursor-like region (B), an immature magnetosome (C), and a mature magnetosome (D). The spectra of $FeCl_2$ $0.4H_2O$ [Fe(II)] and $FeCl_3$ $0.6H_2O$ [Fe(III)] are also plotted [3]. The line indicates the peak of the dominant line in magnetite.

netosome biomineralization. Recently we have developed methods to prepare *Magnetospirillum magneticum* AMB-1 samples at well-defined times in the process of conversion of a culture from fully Fe-depleted, in which magnetosomes are not generated, to a culture where, after 2 days, most cells display a well-developed chain of magnetosomes. This time course study is providing new insights into magnetosome chain biomineralization [13].

Acknowledgements
Research performed using the ambient-STXM on BL 10ID1 at the Canadian Light Source and STXMs on beamlines 5.3.2.1, 5.3.2.2 and 11.0.2 at the Advanced Light Source. CLS is funded by CFI while ALS is funded by DoE BES. We thank Marcia West for excellent microtomy, and the beamline staff at CLS and ALS for their support. Research supported by AFCC, NSERC and the Catalyst Research for Polymer Electrolyte Fuel Cells (CaRPE-FC, Canada) network.

Contact
Prof. Dr. Adam Hitchcock
Department of Chemistry & Chemical Biology
McMaster University
Hamilton, ON, Canada
aph@mcmaster.ca
http://unicorn.mcmaster.ca