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4D imaging of polymer electrolyte membrane fuel cell catalyst layers by soft X-ray spectro-tomography

Juan Wu[a], Lis G.A. Melo[a], Xiaohui Zhu[a], Marcia M. West[b], Viatcheslav Berejnov[c], Darija Susac[c], Juergen Stumper[c], Adam P. Hitchcock[a,*]

[a] Dept. of Chemistry & Chemical Biology, McMaster University, Hamilton, L8S 4M1, Canada
[b] Dept. of Pathology, McMaster University Hamilton, L8N 3Z5, Canada
[c] Automotive Fuel Cell Cooperation (AFCC) Corp., Burnaby, V5J 5J8, Canada

HIGHLIGHTS

- Soft X-ray tomography at multiple X-ray energies is used to map ionomer in PEM-FC.
- Compressed sensing processing allows valid reconstruction with ~15 tilt angles.
- Multi-set tomograms are used to guide dose reduction to get low damage measurements.
- Changes in 3D ionomer distribution occur due to radiation damage.
- Conditions to achieve low damage (< 5%) are identified and used for 4D imaging.

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ABSTRACT

4D imaging - the three-dimensional distributions of chemical species determined using multi-energy X-ray tomography - of cathode catalyst layers of polymer electrolyte membrane fuel cells (PEM-FC) has been measured by scanning transmission x-ray microscopy (STXM) spectro-tomography at the C 1s and F 1s edges. In order to monitor the effects of radiation damage on the composition and 3D structure of the perfluorosulfonic acid (PFSA) ionomer, the same volume was measured 3 times sequentially, with spectral characterization of that same volume at several time points during the measurements. The changes in the average F 1s spectrum of the ionomer in the cathode as the measurements progressed gave insights into the degree of chemical modification, fluorine mass loss, and changes in the 3D distributions of ionomer that accompanied the spectro-tomographic measurement. The PFSA ionomer-in-cathode is modified both chemically and physically by radiation damage. The 3D volume decreases anisotropically. By reducing the incident flux, partial defocusing (50 nm spot size), limiting the number of tilt angles to 14, and using compressed sensing reconstruction, we show it is possible to reproducibly measure the 3D structure of ionomer in PEM-FC cathodes at ambient temperature while causing minimal radiation damage.

1. Introduction

Quantitative imaging of the chemical components of polymer electrolyte membrane fuel cell (PEM FC) electrodes is needed to analyze catalyst layer (CL) fabrication quality and failure modes [1]. The 3D distribution of the components in CLs determines porosity and thus permeability for fuels and products; electrochemical effectiveness, and thermo-mechanical properties. Analytical electron microscopy and X-ray microscopy both have the spatial resolution and chemical sensitivity to provide useful analytical information about CL components. However, the electron and X-ray beams cause radiation damage [2–4] in soft materials such as biological materials [5] and polymers [4,6,7] and is a major limitation in analytical microscopes which use ionizing radiation. Radiation damage brings into question the reliability of the quantitation, especially for the perfluorosulfonic acid (PFSA) ionomer component which is extremely radiation sensitive [8–10]. The electron beam in Transmission Electron Microscopy (TEM) and the photon beam in X-ray microscopy (XRM) both inject energy into the sample and cause radiation damage, the severity of which depends on the sample and method used [2,3]. Changes to the chemical composition, structure

* Corresponding author.
E-mail address: aph@mcmaster.ca (A.P. Hitchcock).

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and spatial distributions caused by radiation damage can limit effective spatial resolution and definitely limit analytical accuracy. In order to obtain meaningful analytical results, it is important to understand how the analytical spectral signal changes both qualitatively and quantitatively, and to characterize the physical and chemical changes that occur.

This study focuses on the PEMFC cathode catalyst layer, which is composed of graphitic carbon support particles decorated with Pt catalyst, and the ionomer proton conductor, perfluorosulfonic acid (PFSA). The spatial distribution of catalyst particles and ionomer in a PEM-FC cathode affects the efficiency of the fuel cell device since the oxygen reduction reaction (ORR) at the cathode is the rate limiting process. For the ORR to occur, protons must be transported along a continuous pathway of PFSA from the membrane/cathode boundary to all of the ORR catalyst sites throughout the cathode. Since the reaction only happens at the interface of PFSA, catalyst particles, conductive carbon support, and with access via a porous network to O_2 reactant and product water removal, it is important to accurately measure the distribution of PFSA and pores, not only in 2D [11–16], but also in 3D [17–20].

Hard X-ray tomography in the laboratory [21,22] and at synchrotrons [23] is well-developed, and has been used for 3D characterization of the gas diffusion layer (GDL) [24] as well as tracking liquid water transport in model PEM-FC structures [25,26]. The microstructure of the solid phase of PEMFC electrodes [22] and changes in PEM-FC membranes following transient operation [26] have also been studied by X-ray computed tomography. However, the lab and most synchrotron hard X-ray methods do not provide chemical analysis and have a spatial resolution of ~1 μm at best. Saida et al. [27] have used full field X-ray microscopy, and spectro-laminography at the Pt L_3 edge, to characterize the oxidation state of the Pt catalyst in fresh and degraded PEM-FC MEAs, with a spatial resolution of 1.5 μm (x,y) and 5 μm (z). Very recently, Matsui et al. [28] have reported *operando* spectro-tomography at the Pt L_3 edge, thereby providing 3D chemical maps of Pt in the catalyst layer before and after *in situ* accelerated degradation testing (total of 20,000 cycles). Again the spatial resolution was a few μm. In both cases [27,28] complete Pt L_3 spectra were acquired. These are outstanding measurements which provide important chemical state information on the Pt catalyst but little or no information on the morphology and chemical state of the low-Z support, ionomer and membrane components of the membrane.

Soft X-ray tomography has higher spatial resolution (~30 nm [29]) than hard X-ray tomography and excellent analytical capability if tomograms at multiple photon energies are measured. 3D density based imaging using full field transmission soft X-ray microscopes is well developed [30]. However it has not been applied to PEM-FC to our knowledge, and does not provide spectroscopy in most implementations. Soft X-ray STXM tomography using multiple photon energies for direct 3D chemical mapping, was pioneered by Johansson et al. [31–35]. A comprehensive review of soft X-ray STXM spectro-tomography, which includes results on PEM-FC and related materials, was published recently [36].

Soft X-ray STXM [37–40] has been demonstrated to be a useful method for quantitative chemically sensitive imaging of the PEM-FC cathode catalyst layer, and in particular, for giving accurate 2D projection maps of the ionomer in PEM-FC cathodes with negligible radiation damage [10–16,40]. Over the last few years, our group has been working to extend STXM characterization of cathode catalyst layers to 4D imaging which involves multi-photon energy tomography, or imaging in four dimensions (x, y, z, E). 4D imaging measures the spatial distribution of each chemical species of a heterogeneous sample in 3D. Prior to this study, STXM tilt-series spectro-tomography at the C 1s and F 1s edges was applied to two types of pristine catalyst coated membranes (CCM), demonstrating that the ionomer in the cathode could be visualized in 3D [19]. However, the 3D spatial resolution was somewhat less than the 2D spatial resolution, and the morphology and ionomer amount was significantly modified by the large radiation doses used in those studies [19]. The doses used in that early work were large – many 100's of MGy - because the same volume was measured repeatedly at multiple photon energies and multiple tilt angles, using maximum usable incident flux.

The objective of the research reported in this paper is to find ways of performing room temperature STXM spectro-tomography with significantly reduced dose so as to perform 4D imaging of the PFSA ionomer in a real PEM-FC cathode sample without extensive fluorine mass loss, without modification to the ionomer distribution, and without changes to the local chemical structure of the PFSA. To guide the operational changes that have allowed us to achieve this goal, we have developed a multi-set tomography method which tracks the mass loss, chemical transformation, and 3D structural reorganization of PFSA in PEM-FC cathodes during tomography. A major improvement was the use of a new reconstruction method called compressed sensing [41]. By combining compressed sensing tomographic reconstruction, reducing the number of tilt angles, and a 50-fold reduction in incident flux, we show that it is possible to measure meaningful, quantitative 3D ionomer-in-cathode distributions of real PEM-FC samples using STXM spectro-tomography at ambient temperature.

2. Materials and methods

2.1. Samples

Several different fuel cell PEM-FC catalyst coated membrane (CCM) samples were used in this study. Table 1 summarizes their compositions and properties. The CCMs were cut into small rectangular pieces and embedded in an amine epoxy resin (called TTE for short), prepared by mixing trimethylolpropane triglycidyl ether and 4,4′-methylenebis(2-methylcyclohexylamine) in a 1:1 wt ratio and cured at 70 °C overnight [42]. The embedded samples were microtomed at room temperature using a DiATOME™ diamond knife with a Leica Ultracut UCT to generate sections with nominal thicknesses between 100 and 300 nm. The sections were transferred from the surface of a water bath to formvar coated 100-mesh Cu TEM grids, which were then used for STXM studies.

There are size constraints in the STXM chamber which are important for tomography measurements [36]. The distance from the sample to the order sorting aperture (OSA), which is the first optical element upstream from the sample, is only 250 μm when measuring at

Table 1
Properties of the MEA samples examined in this work.

Sample label	source	Membrane	C_support	Ionomer	I/C[a]	Pt load (mg/cm^2)[a]	Cathode fabrication method
MEA "C" 2071 TMP	Gore	ePTFE micro-reinforced; Gore-Select, 18 μm	Gore LSAC	Gore		0.4	Slot-die coating
MEA "A"	AFCC	Continuous; NRE-211, 25 μm, 1100EW	LSAC	Nafion 117	1.44	0.25	Mayer bar coating
MEA "B"	AFCC	Continuous; NRE-211, 25 μm, 1100EW	LSAC	Nafion 115	0.57	0.25	Mayer bar coating
MEA 11 GDE	Ballard	Continuous; NRE-211, 25 μm, 1100EW	LSAC	Nafion 117	1.07	0.6–0.7	Screen print

[a] Target values, defined from ink composition.