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Short communication

Composition analysis of a polymer electrolyte membrane fuel cell microporous layer using scanning transmission X-ray microscopy and near edge X-ray absorption fine structure analysis



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Novel application of scanning transmission X-ray microscopy to microporous laver. Spatial mapping of microporous layer
- carbon and PTFE distributions. • Visualisation of PTFE agglomerations in the microporous layer of PEM fuel
- cell. Identification of PTFE mesostructure
- in the microporous layer.

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ABSTRACT

The novel application of scanning transmission X-ray microscopy (STXM) to the microporous layer (MPL) of a polymer electrolyte membrane fuel cell is investigated. A spatially resolved chemical component distribution map is obtained for the MPL of a commercially available SGL 25 BC sample. This is achieved with near edge X-ray absorption fine structure spectroscopic analysis. Prior to analysis the sample is embedded in non-reactive epoxy and ultra-microtomed to a thickness of 100 nm. Polytetrafluoroethylene (PTFE), carbon particle agglomerates, and supporting epoxy resin distributions are identified and reconstructed for a scanning area of $6 \,\mu m \times 6 \,\mu m$. It is observed that the spatial distribution of PTFE is strongly correlated to the carbon particle agglomerations. Additionally, agglomerate structures of PTFE are identified, possibly indicating the presence of a unique mesostructure in the MPL. STXM analysis is presented as a useful technique for the investigation of chemical species distributions in the MPL.

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1. Introduction

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The microporous layer (MPL) significantly influences polymer electrolyte membrane fuel cell performance by improving water management and reducing contact resistance between the catalyst layer and the carbon fiber gas diffusion layer [1-3]. This is achieved by its hydrophobic treatment with polytetrafluoroethylene (PTFE)

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and characteristic nanoporous structure. The primary components of the MPL are amorphous carbon particles (typically Vulcan XC-72 or Acetylene black [1]) and PTFE, which acts as both a binder and hydrophobic agent. Traditionally, the material composition and distribution of the MPL components are assumed to be homogeneous. New insight is needed at high resolution to characterize the MPL structure and composition.

Understanding the chemical composition and distribution of the MPL is valuable for manufacturers and researchers interested in fuel cell modelling. Botelho and Bazylak [4] and Zamel et al. [5] assumed a uniform value of thermal conductivity for the solid phase of the MPL. Heat transfer modelling could be advanced to include material specific thermal conductivities resulting in improved predictions of thermal behavior. This can also be extended to investigations of electrical conductivity.

Hitchcock et al. have applied scanning transmission X-ray microscopy (STXM) to fuel cell material characterization [6–13]. It is a radiographic spectromicroscopic analysis technique capable of providing spatial distribution maps of chemical species and bonding environments when combined with near edge X-ray absorption fine structure (NEXAFS) spectroscopy [14–18]. Hitchcock et al. provided a comprehensive review of STXM [19], and NEXAFS has been extensively discussed in the literature [17,20–22]. This technique utilizes the discrete changes to mass absorption coefficients of materials in the soft X-ray energy range (<2500 eV), and is particularly well-suited to the investigation of polymers and carbon based structures, achieving spatial resolutions of up to 30 nm [21]. Accordingly, STXM enables the differentiation between unique components, such as carbon particle agglomerates and PTFE, in the MPL structure.

Herein, we report the initial findings from an investigation of an MPL using STXM to understand the spatial distribution of individual components. Chemical maps of the carbon particles, PTFE, and binding epoxy distributions were obtained.

2. Methodology

2.1. Sample preparation

The MPL of a commercially available SGL 25 BC sample was investigated using STXM analysis coupled with NEXAFS. Sample preparation requirements for STXM analysis are detailed by Susac et al. [12,13]. 1×3 mm pre-sectioned samples were set overnight under vacuum in non-reactive epoxy resin (trimethylolpropane triglycidyl ether and 4,4'-methylenebis-(2methylcyclohexylamine)) [23] for structural support. Throughplane cross-sectional slices approximately 100 nm-thick were then obtained using an ultra-microtome (Leica Biosystems). For imaging of carbon components at the C 1s edge, the lowest energy range used in this study, samples must be less than 150 nm thick in the beam direction [21]. Microtomed slices were mounted onto 100-mesh 3.0 mm Formvar-coated copper TEM grids. Aside from the procedure above, no special treatment or modifications were applied to the sample.

2.2. STXM analysis

The measurements in this study were performed on the Soft Xray SpectroMicroscopy Beamline (SM-10ID-1) [24] at the Canadian Light Source (CLS). Incident monochromatic X-rays were filtered using a Titanium filter to remove small contributions of the secondorder light in the C K-edge and focused by a 35 nm Fresnel zone plate to a 40 nm spot on the sample. The spatial resolution achieved by STXM was assumed to be suitable for this investigation based on the comparison of the 40 nm pixel resolution and the expected size of individual carbon particles (on the order of 50 nm diameter) in the MPL [25]. A sample region of $6 \times 6 \,\mu m$ was selected and rasterscanned to form a transmission image at each photon energy step. For the scan size of 6 \times 6 μm , with a spatial resolution of 40 nm and a step size of 40 nm, the resolution of the image is 150×150 pixels. An interior portion of the MPL in the through-plane direction was chosen as the scan area. This scan area was deliberately chosen for its inclusion of a void region (without any sample material) for the incident light (I_0) measurement, which was necessary to convert the transmission data into absorption data [26]. STXM image stack (sequence) scans were performed across the C 1s, O 1s, and F 1s edges. The C 1s edge was scanned from 280 to 320 eV in 0.15 eV increments in the NEXAFS peak regions with a dwell time of 1 ms and a spatial step size (for the raster-scan) of 40 nm. The O 1s and F 1s absorption edges were scanned with the same dwell time and spatial step size from 525 to 560 eV in 0.2 eV increments and 680 to 740 eV in 0.3 eV increments in the NEXAFS peak regions, respectively.

X-ray transmission through the sample was measured using STXM. Resulting transmission images were converted to a linear optical density (OD) scale, which was used to quantitatively identify the content of particular chemical species using the Beer-Lambert law [18],

$$OD = -\ln\left(\frac{I}{I_0}\right) = \mu\rho d. \tag{1}$$

In this equation, *I* is the transmitted X-ray intensity through the material, I_0 is the un-attenuated incident X-ray intensity, μ is the mass absorption coefficient, ρ is the material density, and *d* is the X-ray path length through the sample. The mass absorption coefficient is a function of the attenuating species at a particular location (pixel) in the scanned sample region. When material constituents are known, composition at each pixel can be determined by fitting the absorption profile (based on reference spectra) of each individual component to match the observed absorption across all energy levels.

Ideally, the reference spectra used to identify the primary chemical species in the sample are characterized using pure samples of the known components; carbon particles, PTFE, and epoxy (TTE) in this case. However, due to the proprietary nature of the MPL sample composition and limited beamtime availability, internally defined reference spectra were used for differentiating these major constituents. The spectra were identified in the C 1s and F 1s image stacks and manually selected from discrete, and relatively pure, regions in the scan area. Selections were confirmed by Principal Component Analysis (PCA). Fig. 1 shows NEXAFS spectroscopic features of the three distinct components at the C 1s K-edge and F 1s K-edge. Reference spectra extraction from image stacks and all subsequent analysis was performed using aXis2000 software [27]. Absorption peaks at 285.1 and 292.1 eV indicated the presence of graphitic and amorphous carbon structures, respectively. PTFE is characterized by strong absorption near 292 eV, 295 eV [28,29] and absorption peaks in the F 1s edge, but the peak at 285.1 eV was not indicative of the presence of PTFE. Rather, the weak 285.1 eV peak indicated a minor presence of carbon particles in the selected PTFE reference region.

3. Results & discussion

Fig. 2 presents the spatially resolved distributions of carbon particles, PTFE, and epoxy (TTE). These distributions were obtained by fitting the spectroscopic features of the C 1s and F 1s combined image stack at each scanned pixel with the internally identified reference spectra Fig. 1 using singular value decomposition [30]. A

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