# Probing nanoscale membrane degradation in fuel cells through electron tomography

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## ARTICLE INFO

## ABSTRACT

The physical integrity of perfluorosulfonic acid (PFSA) ionomer membranes for fuel cell application depends on their internal morphology and distribution of hydrophilic and hydrophobic phases. Here, contrast enhanced transmission electron microscope-tomography (TEM-t) of pristine and degraded PFSA ionomer membranes is carried out to explore the effects of degradation in operating fuel cells. Nanoscale 3-D image reconstruction followed by Marker-based Watershed segmentation is used to identify weak phase boundaries in the tomograms and thereby reveal the hydrophilic and hydrophobic phase distributions in the membrane. The pristine membrane exhibits a randomly interconnected hydrophilic phase with a scaffolding hydrophobic phase, as expected from morphological theory. The degraded membrane subjected to combined chemical/mechanical degradation is found to have similar overall morphology while containing thinner ionomer bundles and reduced hydrophilic volume fraction with smaller hydrophilic pores in regions with elevated chemical degradation. Numerical analysis of the phase-segmented tomograms enables detailed quantification of the structural properties, as reported herein, which is not possible with 2-D approaches and therefore contributes important new information for nanoscale analysis of fuel cell membranes.

## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are recognized as a clean power source for stationary and mobile applications [1]. In a $H_2$/air PEFC, hydrogen is electrochemically oxidized to protons, which diffuse through a solid polymer electrolyte and are consumed in the oxygen reduction reaction at the cathode to produce water and heat (Fig. 1(a)) [2]. The most widely employed solid electrolyte for PEFC application is the perfluorosulfonic acid (PFSA) ionomer membrane. It consists of poly-tetrafluoroethylene (PTFE) backbone and fluorinated-ether side chains terminating with sulfonic acid groups, forming a biphasic structure of hydrophilic ionic nanochannels and hydrophobic fluorocarbon regions, which provide high proton conduction and mechanical durability, respectively [3]. The morphological, physical, sorption, and transport properties of PFSA ionomer membranes have been thoroughly characterized [4]. A wide range of structural descriptions concerning the phase-separated PFSA ionomer morphology have been reported to date [2]. Descriptions based on indirect imaging through scattering experiments have revealed distinctive microstructures that relates to high proton conductivity [5–7]. Interpretation of scattering data relies on matching with computed scattering patterns. Debate

continues on the shape and structure of the ion-rich clusters and fluorocarbon phases in the absence of direct imaging methods. Direct imaging techniques, such as conventional transmission electron microscopy (TEM), provide interpretable 2-D images of the phase-separated PFSA ionomer structure with an incorporated contrast-enhancing staining agent [8,9]. While the TEM technique provides qualitative information on the morphology of thin slices of membrane in the form of 2-D images, quantification of the internal structure, volume fraction, distribution, shape, and size of the hydrophilic and hydrophobic phases is difficult. Volumetric, 3-D imaging analyses are warranted.

Through recent advancements in TEM-tomography (TEM-t) [10,11], image analysis has become more precise. In this evolving field of research, the 3-D ionomer distribution in an electrode and its coverage on Pt/C electrocatalyst particles has been investigated with the aid of staining agents [12,13]. Recently, a 3-D morphological investigation on a hydrated, as-cast ionomer thin film (~ 100 nm thick) carried out using cryo-electron tomography [14] revealed a networked, channel-type hydrophilic phase. Though these studies provided critical insight regarding the morphology of thin PFSA ionomer films, the 3-D morphology of *in situ* degraded PFSA ionomer membranes is of particular interest for fuel cell engineers and polymer chemists developing
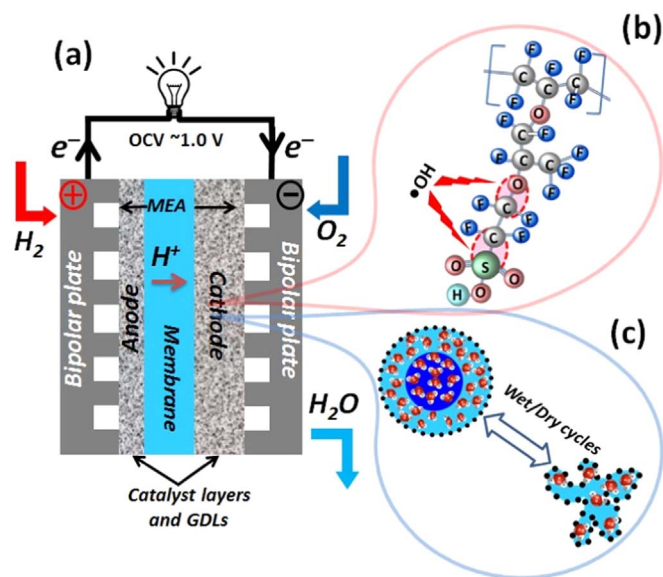
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**Fig. 1.** Schematics of (a) polymer electrolyte fuel cell, (b) vulnerable sites in the membrane ionomer structure that experience hydroxyl radical attack, and (c) hydrophilic domains in the membrane that experience humidity cycling during fuel cell operation.

advanced membrane materials combating chemical (Fig. 1(b)) and mechanical (Fig. 1(c)) stress. Although information on the 3-D morphology of Nafion as an *ultra-thin film* is available in the literature [14], a baseline morphology of bulk Nafion-type membrane is necessary in order to make a reasonable comparison with membranes extracted from PEFCs, especially since PFSA ionomer as a bulk membrane and as a thin film show disparate nanostructures and structure-dependent properties [15–18]. The objective of the present work, therefore, is to obtain a complete 3-D reconstruction of the nanoscale morphology of *in situ* degraded PFSA ionomer membrane and compare with its pristine state, which is achieved using TEM-tomography. Using the reconstructed morphological structures of degraded membrane, detailed results regarding volume fractions and distributions of the hydrophilic and hydrophobic phases are compared with an appropriately established baseline morphology for pristine ionomer membrane.

## 2. Experimental

For the purpose of contrast enhancement in TEM-t imaging, the protons in a pristine Dupont Nafion NR-211 PFSA ionomer membrane were exchanged with $Pb^{2+}$ ions by soaking in a saturated solution of lead acetate for about 48 h. The membrane was then washed, dried at room temperature, embedded in Araldite 502 epoxy, and sliced into 70–90 nm sections using a Leica UC6 ultramicrotome instrument equipped with a glass knife. The slices were then collected onto Cu grids with the membrane cross section exposed to the electron beam. For *in situ* degradation, gas diffusion electrodes (GDEs) were fabricated by coating a micro-porous layer made of polytetrafluoroethylene (PTFE) and carbon black on a non-woven carbon paper gas diffusion layer substrate followed by coating a catalyst layer consisting of carbon-supported platinum catalyst and PFSA ionomer solution. Research scale membrane electrode assemblies (MEAs) were prepared by hot pressing the cathode and anode GDEs with PFSA ionomer membranes. Five MEAs were assembled into a fuel cell stack with graphitic bipolar plates and co-flow parallel straight channels and subjected to combined chemical/mechanical degradation using the cyclic open circuit voltage accelerated stress test (COCV AST). The COCV AST consisted of an open circuit voltage (OCV) phase under high temperature low relative humidity conditions to induce chemical membrane degradation followed by a series of wet/dry cycles in an inert $N_2$ atmosphere to induce mechanical membrane degradation. The chemical and mechanical

portions of the test were applied in an alternating pattern until membrane failure was reached, as identified by a critical hydrogen leak rate ( > 10 sccm) across the membrane, which in this case occurred after 13 cycles. Further information on the COCV AST, including a wide range of diagnostic data, is available elsewhere [19]. In the end-of-life MEA selected for this research, the membrane ionomer mass was reduced by ~ 46 wt% accompanied by ~50% thinning, as estimated by thermogravimetric analysis and cross-sectional scanning electron microscopy, respectively. The proton conductivity of the membrane calculated from *in situ* measured high frequency resistance data was found to decrease linearly with degradation. The degraded membrane attracted more water in the formed cavities as a result of physical damage such as cracks and pinholes [20]. The degraded membrane specimen, extracted from the MEA by carefully removing the diffusion media on each side, was subjected to the same staining and microtoming procedure as for the pristine membrane in preparation for TEM-t imaging. The specimen was taken from the inlet region of the MEA which normally experiences the highest level of degradation.

A transmission electron microscope (Osiris Tecnai) from FEI Inc. was used to measure tilt series images of the membrane samples. A single-tilt tomography sample holder was used. The 3-D Explorer software from FEI was used to obtain tilt series images between − 52° and + 56° incident electron beam angles using a 1° step for the pristine membrane. The tilt range was kept between − 70° and + 70° using a 2° step for the degraded membrane. The images were recorded at an accelerating voltage of 200 keV with a Gatan Ultrascan 1000XP-P 2k x 2k pixel CCD camera. The post processing of the obtained tilt series images was carried out using Inspect-3D software to align and adjust the shift in the axis of rotation. The parallel image stack was imported to Amira 6.0 visualization software from FEI. The hydrophilic and hydrophobic domains were identified based on the difference in contrast exhibited by the strong electron scattering Pb ion exchanged ion-rich regions and the weak scattering PTFE regions, respectively. A smoothing filter was applied to the grayscale image series for image de-noising. Marker-based Watershed (MW) segmentation was used to segment hydrophilic and hydrophobic phases for surface reconstruction. This method uses marker seed pixels as catchment basins instead of local minima, thus successfully identifying weak boundaries in the tomographic slices [21]. MW segmentation produces closed and adjacent contours of the image, thus avoiding severe oversegmentation which may occur with other segmentation methods. The thresholding technique was used to positively identify the explicit regions of the hydrophilic and hydrophobic phases and the corresponding marker seeds were created. A gradient image of both phases was computed which was used to construct the boundary surface of both phases. Once the hydrophilic and hydrophobic phases were reconstructed, the data sets were exported to a binary grid of hydrophilic and hydrophobic solid cells and used for further analysis using numerical algorithms developed in our group [22,23].

## 3. Results and discussion

### 3.1. 2-D morphology

Representative bright-field 2-D TEM images of the nanoscale structure of the pristine and degraded PFSA ionomer membranes are presented at 88,000x (Fig. 2(a),(b)) and 440,000x (Fig. 2(c),(d)) magnifications. These images were selected based on a comprehensive survey of each specimen which indicated homogenously distributed features across the membrane thickness. The pristine membrane exhibits homogeneously distributed dark hydrophilic and bright hydrophobic phases (Fig. 2(a),(c)). The membrane subjected to combined chemical/mechanical degradation, in contrast, has enlarged hydrophilic domains as evidence of a global degradation effect [9] as well as locally-elevated degradation characterized by small regions embedded within the bulk degraded region with depleted hydrophilic domains,